

VOLTAMMETRIC DETERMINATION OF DOPAMINE AT PEDOT-PRUSSIAN BLUE COMPOSITE MODIFIED ELECTRODES

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Poly(3,4-ethylenedioxythiophene) conducting polymer films doped with Prussian Blue (PB, iron (III) hexacyanoferrate (II)) has been prepared by a two steps method. In a first step, the PEDOT coating was electrogenerated in the presence of ferricyanide ions. Then, the modified electrode was cycled in aqueous solution containing Fe^{3+} ions. The in-situ formation of PB inside the PEDOT matrix has been demonstrated by using cyclic voltammetry. The electrochemical oxidation of dopamine at the modified electrode has been studied in phosphate buffer aqueous solution. The composite coating showed a high electrocatalytic effect towards the dopamine oxidation in the presence of ascorbic acid. Linear dependence of the anodic peak current from differential pulse voltammetry over the dopamine concentration ranging from 4×10^{-5} to 1×10^{-3} M was obtained.

INTRODUCTION

The modified electrodes are one of the most rapidly growing and advancing areas of electroanalytical chemistry. Many studies have been devoted to electrodes modified with conductive films of polymers, such as polyaniline, polypyrrole and polythiophene, due to their interesting electrochromic and conducting properties.¹⁻³ Recently, conducting polymers doped with various anions have been extensively studied due to their improved electrocatalytic, electroreleasing and electrochromic properties. For instance, it is possible to prepare polyaniline films containing ferricyanide, which exhibits potentiometric response to ferricyanide ions.⁴ The incorporation of various ions in conducting polymer films, aiming to produce robust and highly conducting coatings capable of fast electron transfer during redox reactions, is based on the electrostatic stabilization and attraction between the positively charged polymer backbone and the negatively charged doping ions. Different procedures for the preparation of inorganic-organic hybrid material coatings

containing conducting polymers and cyanometallates have been reported. The hybrid materials can be prepared in two geometries, one consisting of an inorganic inner layer and an organic outer layer, and the opposite one where the inorganic films is deposited on top of the conducting organic layer. Polypyrrole⁵, polyaniline^{6,7}, thiophene derivatives⁸⁻¹⁰ were used as organic modifiers, while the inorganic modifier was Prussian Blue (PB, iron (III) hexacyanoferrate (II)). PB has attracted a great attention due to the electrocatalytic properties. However, the stability of PB in neutral aqueous solution is not satisfactory due to the decomposition with iron (III) hydroxide formation.¹¹ This lack of PB stability in neutral solution has underpinned new strategies for the preparation of conducting polymers doped with inorganic redox materials. Among conducting polymers, poly(3,4-ethylenedioxythiophene) (PEDOT) has been the subject of several studies because of its excellent stability and conducting properties. Moreover, PEDOT coatings can be prepared by electrochemical polymerisation in aqueous solution, which allows the direct incorporation of water soluble anions,

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like ferricyanide. Recently, a PEDOT coating doped with ferricyanide has been reported.¹² First, the PEDOT coating has been electrogenerated in aqueous solution and then the polymer film was doped with ferricyanide ions. The composite film was used for the electrochemical determination of dopamine. Dopamine (DA) is an important neurotransmitter in the mammalian central nervous system, which can cause Parkinson's disease and other similar diseases.¹³ The determination of DA is complicated by the coexistence of many interfering compounds, such as ascorbic acid.¹⁴ Thus, selectivity and sensitivity are important in the development of new analytical methodologies for DA quantification. The use of electrodes modified with inorganic redox mediator and/or conducting polymers is very promising.¹⁵

In this work, the in-situ formation of PB inside a PEDOT matrix is presented. The hybrid inorganic-organic coating has been prepared by a two steps method. Firstly, the PEDOT film was electrogenerated by potentiodynamic polymerisation in aqueous solution in the presence of ferricyanide ions. Then, the ferricyanide doped film was transferred in Fe^{3+} ions containing aqueous solution where the electrode potential was cycled from 0.6 to -0.4 V. During the potential cycling PB is formed inside the PEDOT matrix.

The resulting composite modified electrode was investigated in neutral aqueous solutions by using cyclic voltammetry and electrochemical quartz crystal microbalance. The electrocatalytic activity of the composite coating towards the dopamine oxidation has been also investigated.

EXPERIMENTAL

All chemicals: FeCl_3 (Merck), $\text{K}_3[\text{Fe}(\text{CN})_6]$ (Merck), HCl (Merck), KCl (Carlo Erba), KClO_4 (Merck) and 3,4-ethylenedioxythiophene (EDOT, Aldrich) were used without any further purification. De-ionised water was always used to prepare aqueous solutions. The electrochemical experiments were carried out with an Autolab PGSTAT 20 potentiostat/galvanostat (Ecochemie) coupled to a PC running the GPES software, using a single-compartment, three-electrode cell, at room temperature. As working electrode was used a 3-mm diameter Pt disk electrode (Metrohm). A saturated silver-silver chloride electrode was the reference electrode, and a platinum wire (Metrohm) was the auxiliary electrode. A Pt inlaid disk ultramicroelectrode with diameter of 25 μm was also used as working electrode. Before each electrochemical test, the surface of the working electrode was polished subsequently with 1 and 0.3 μm alumina powder to a mirror finish, and rinsed with deionised water. All the solution used for the electrochemical measurements were bubbled with Ar for 10 minutes and an Ar flow was maintained over the solutions during the experiments.

Deposition procedure of PEDOT-PB composite films

The composite film has been prepared by forming the PB film directly into the PEDOT matrix by using a two step method. First, the PEDOT film has been electrogenerated starting from an aqueous solution containing 0.01 M EDOT, and 0.1 M $\text{K}_3[\text{Fe}(\text{CN})_6]$ as supporting electrolyte. In this way a PEDOT film doped with ferricyanide ions, denominated as PEDOT-FeCN, is obtained. Then, the modified electrode was immersed in 5×10^{-3} M 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 V s^{-1} for 5 successive scans. During the potential cycling the in-situ formation of PB layer takes place. A similar preparation procedure has been used for the preparation of the modified ultramicroelectrode, except that the number of scans was 3 in the first step, and 5 for the second one, respectively. After the formation of the composite PEDOT-PB coating, the modified electrode was rinsed with doubly distilled water and then immersed in the transfer solution, where it has been characterised by using cyclic voltammetry and differential pulse voltammetry.

RESULTS AND DISCUSSION

Preparation of PEDOT-PB hybrid coating on conventional-size and ultramicroelectrodes

Fig. 1 shows the cyclic voltammograms recorded during the electropolymerisation of EDOT in the presence of ferricyanide ions.

The shape of the cyclic voltammograms indicates that the current increases cycle after cycle, evidencing the formation of a film on the electrode. The electropolymerisation process is less visible considering only the current, since the signal of the redox couple $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ present at higher concentration covers those of the monomer oxidation and of the polymer p-doping. During the very first scan, we can observe that the current starts increasing at $\sim +0.84 \text{ V}$, indicating the beginning of deposition process of PEDOT on the electrode. The deposition process takes place until +0.8 V is reached in the backward scan. Only in this small potential range (+0.85 \rightarrow +1.0 \rightarrow +0.85 V) the electrodeposition process takes place, as can be seen from Fig. 1. After the preparation of ferricyanide-doped PEDOT coating, the modified electrode was transferred into an aqueous solution containing 5 mM FeCl_3 , and 0.01 M HCl, where the electrode potential was cycled from 0.6 to -0.4 V, at a sweep rate of 50 mV/s. Fig. 2 reports the cyclic voltammograms and the frequency change during potential cycling. Due to the presence of Fe^{3+} ions into the solution, the reduction of these ions takes place at the polymer/solution interface and the resulted Fe^{2+} ions are reacting with ferricyanide present inside the PEDOT matrix. As

a result of this reaction, the formation of PB is expected during the potential cycling. During the potential cycling towards negative potential values, one can observe two reduction peaks situated at ca. +0.2 and 0.05 V, respectively. The first cathodic

peak is associated with the reduction of 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 iron II ions with ferrocyanide anions.

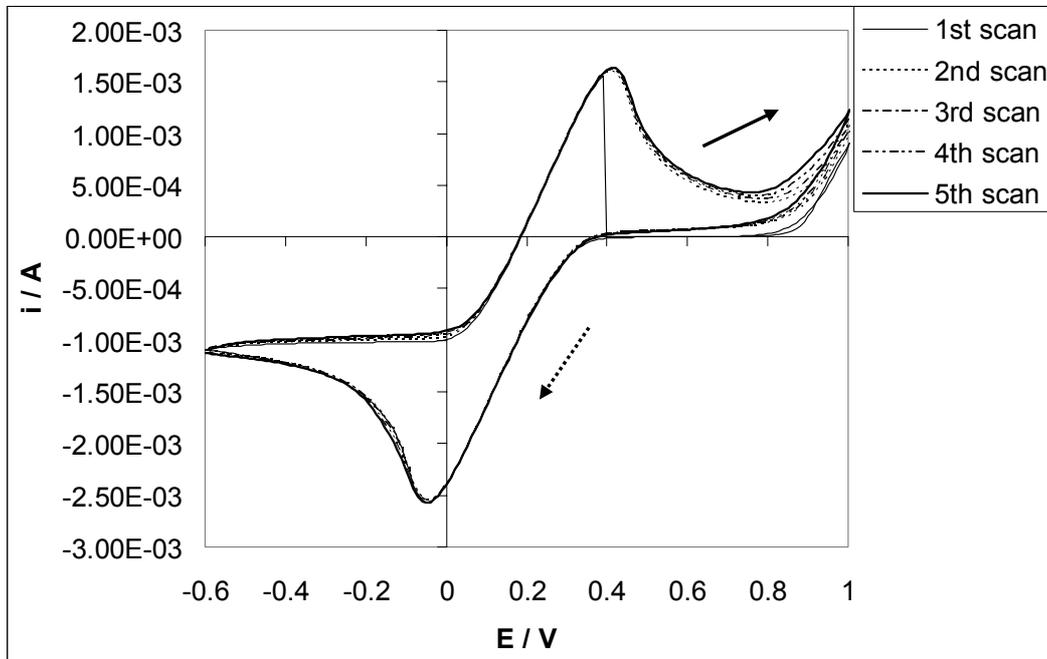


Fig. 1 – Cyclic voltammograms recorded during the electrochemical polymerisation of EDOT at Pt electrode in aqueous solution containing 0.01 M EDOT and 0.1 M $\text{K}_3\text{Fe}(\text{CN})_6$. Potential scan rate: 50 mV/s. The first 5 scans are represented.

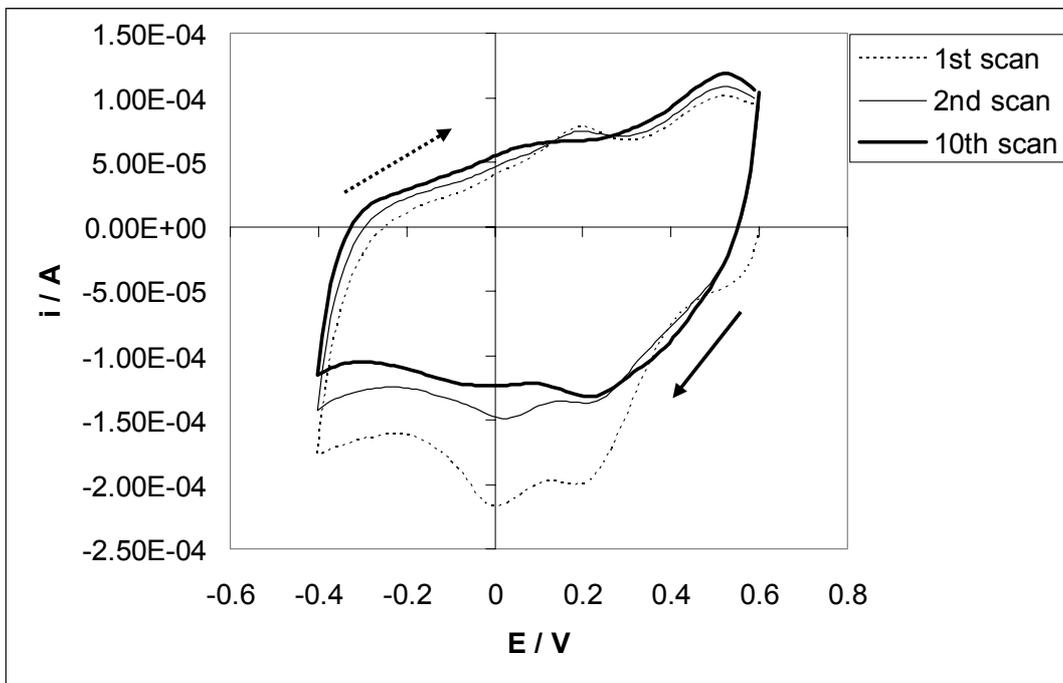


Fig. 2 – Cyclic voltammograms recorded at a Pt/PEDOT-FeCN modified electrode during the in-situ formation of PB layer in a solution containing 5 mM FeCl_3 and 0.01 M HCl. Potential scan rate: 50 mV/s. The 1st, 2nd, and 10th scans are depicted.

After the formation of PB inside the PEDOT matrix, the composite modified electrode was immersed in aqueous solution containing 0.1 M KClO_4 , where it has been investigated by CV and EQCM. Fig. 3 reports the cyclic voltammograms recorded during the potential cycling in the range from 0.6 to -0.4 V at a scan rate of 50 mV/s. The composite modified electrode displays a redox wave with a value for the anodic peak potential (E_{pa}) of 0.2 V and a corresponding cathodic peak potential (E_{pc}) of 0.1 V, respectively. This wave should be ascribed to the redox process associated with the PB/ES redox system.

The same preparation procedure has been used for the deposition of PEDOT-PB composite coating onto ultramicroelectrode. Fig. 4 shows the cyclic voltammograms recorded at Pt disk ultramicroelectrode, with diameter of 25 μm , in aqueous solution containing 0.01 M EDOT and 0.1 M $\text{K}_3\text{Fe}(\text{CN})_6$, in the potential range from +0.4 to +1.0 and reversed back to (-0.6) V, at a scan rate of 50 mV/s. The electropolymerisation of EDOT takes place in the potential range from +0.85 to +1.0 V and back to +0.85 V on the reverse scan.

The current increases cycle after cycle in this potential range attesting the formation of a PEDOT layer onto ultramicroelectrode surface. The redox

wave of the ferricyanide/ferrocyanide couple is observed at a half-wave potential value of ca. +0.3 V.

The electrochemical polymerisation process is more evident than in the case of the conventional-size electrode. This behaviour is due to the special features characteristics to ultramicroelectrodes. After the deposition of the ferricyanide-doped PEDOT film, the modified electrode was immersed in aqueous solution containing Fe^{3+} ions and the electrode potential was scanned from +0.6 to (-0.4) V, at a scan rate of 50 mV/s, for 5 successive cyclic scans. The same mechanism for PB in-situ formation inside the PEDOT matrix as for the conventional-size electrode takes place. However, the shape of the cyclic voltammograms is characteristic for ultramicroelectrodes, that is only one wave is observed for both processes, i.e. de-doping of PEDOT and reduction of ferricyanide ions (see Fig. 5).

The resulted PEDOT-PB composite modified ultramicroelectrode was transferred in aqueous solution containing phosphate buffer of pH = 7.2, and the electrode potential was scanned from +0.6 to (-0.3) V, at a scan rate of 50 mV/s. The modified electrode displays a redox wave characterised by an anodic peak potential of +0.2 V and a cathodic peak potential of ca. +0.15 V, as it can be seen from Fig. 6.

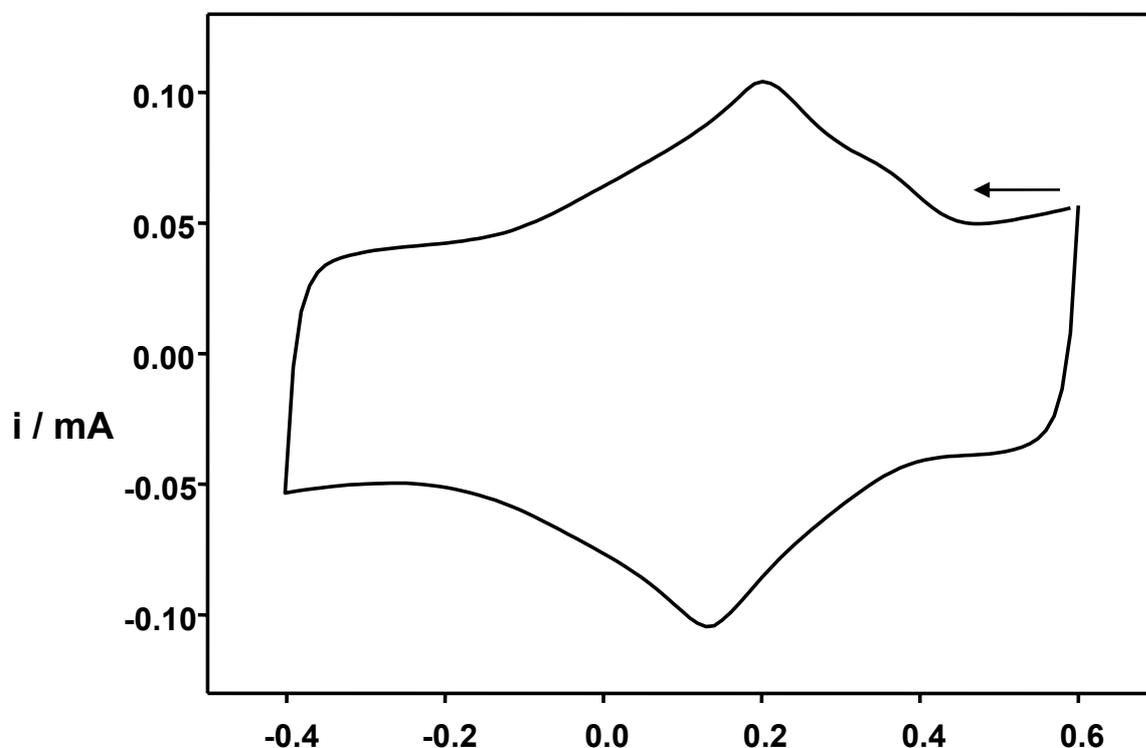


Fig. 3 – Cyclic voltammogram recorded at a Pt/PEDOT-PB composite modified electrode in a solution containing 0.1 M KClO_4 . Potential scan rate: 50 mV/s.

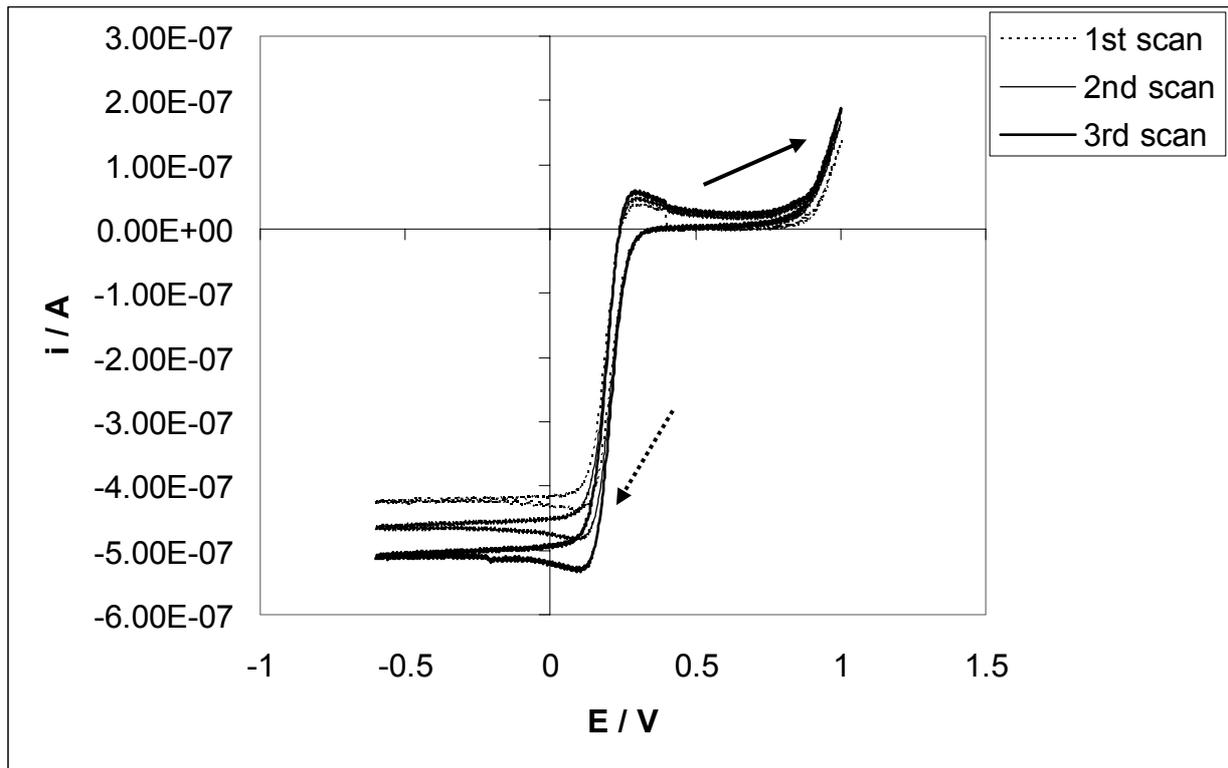


Fig. 4 – Cyclic voltammograms recorded during the electrochemical polymerisation of EDOT at Pt ultramicroelectrode in aqueous solution containing 0.01 M EDOT and 0.1 M $K_3Fe(CN)_6$. Potential scan rate: 50 mV/s. The first 3 scans are depicted.

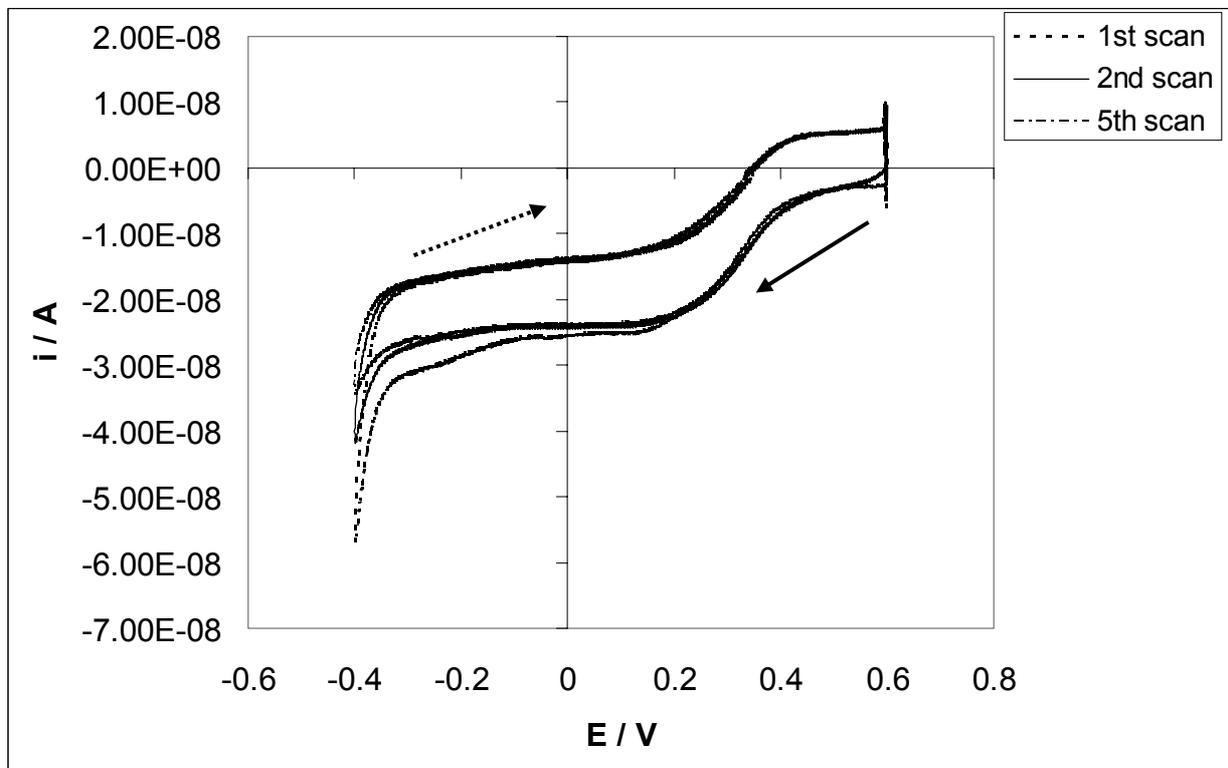


Fig. 5 – Cyclic voltammograms recorded at a Pt/PEDOT-PB composite modified ultramicroelectrode in a solution containing 0.1 M $KClO_4$. Potential scan rate: 50 mV/s. The 1st, 2nd and 5th scans are depicted.

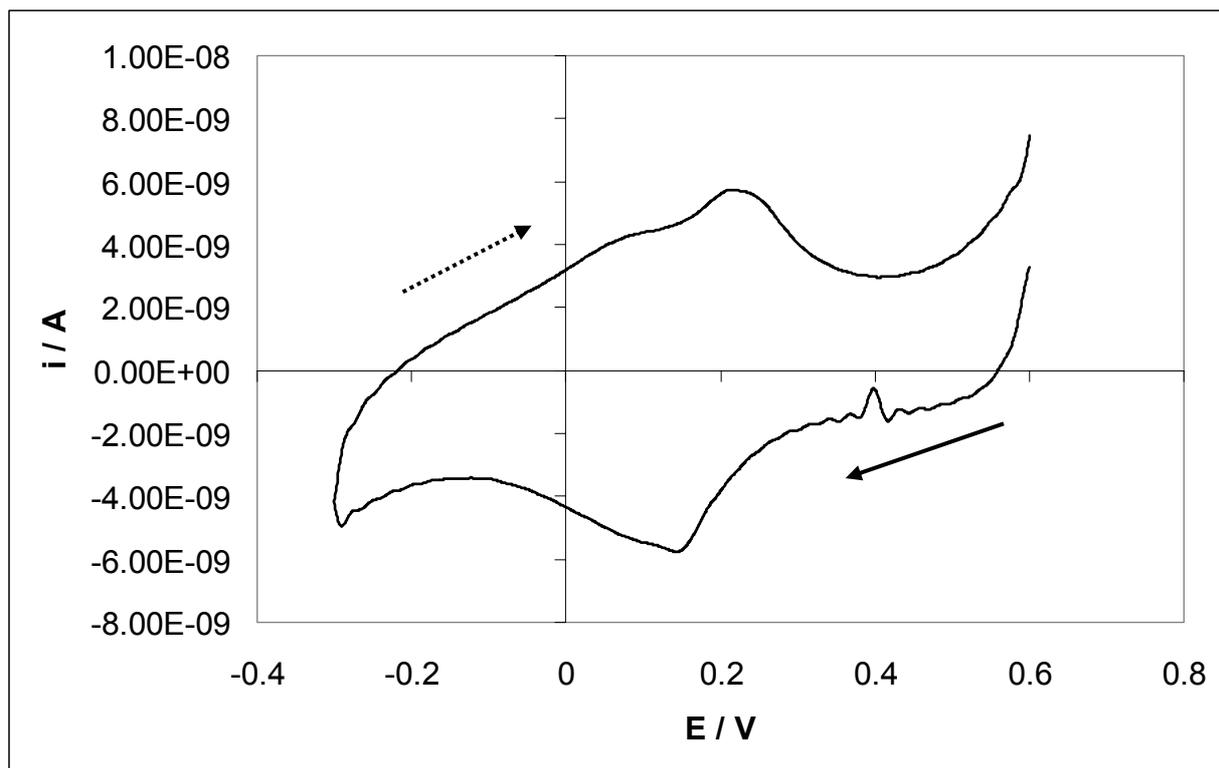


Fig. 6 – Cyclic voltammogram recorded at a Pt/PEDOT-PB composite modified ultramicroelectrode in a solution containing 0.1 M KClO_4 . Potential scan rate: 50 mV/s.

The shape of the voltammograms is similar to that recorded at conventional-size modified electrode, attesting the usefulness of the preparation procedure to produce stable and electroactive composite coatings.

Voltammetric determination of DA at Pt/PEDOT-PB composite modified electrodes

The voltammetric determination of DA at Pt/PEDOT-PB composite modified electrode has been carried out in buffered aqueous solution at pH = 7.2 by using differential pulse voltammetry. The both forward and backward traces differential pulse voltammograms of Pt/PEDOT-PB composite modified electrode recorded in phosphate buffer solution are depicted in Fig. 7. Two well defined redox peaks can be observed at ca. 0.08 V on the forward trace and 0.09 V on the backward trace, respectively. These peaks are associated with the PB/ES system.

After the investigation of the Pt/PEDOT-PB composite modified electrode in aqueous buffer solution, the electrochemical oxidation of dopamine at this modified electrode was studied by using differential pulse voltammetry. The oxidation of DA occurs at a potential value of ca.

0.17 V, which is less positive than that observed at bare Pt electrode. From test at different DA concentrations ranging from 1×10^{-5} M to 1×10^{-4} M it can be observed that there is a linear increase of the anodic current, according to the equation: $I_{pa} (\mu\text{A}) = 0.1522 \text{ DA } (\mu\text{M}) - 1.024$, with a correlation coefficient of $r^2 = 0.9953$. These results indicated that the PEDOT-PB composite coating exerts an electrocatalytic effect on DA oxidation.

This behaviour clearly demonstrates that the composite modified electrode exhibit a linear response for low DA concentrations, which allows its use for DA electrochemical detection. It is well known that ascorbic acid (AA) interferes in the electrochemical determination of DA in real sample. Due to the contemporary presence of both species, the anodic oxidation wave of AA overlaps over that of DA. The separation of these waves can be achieved by using tailored modified electrode surfaces. To this purpose, the electrochemical oxidation of both species present contemporary in the solution has been investigated. Fig. 8 displays the differential pulse voltammograms recorded at Pt/PEDOT-PB composite modified electrode for the electrochemical oxidation of AA in the presence of 1×10^{-4} M DA.

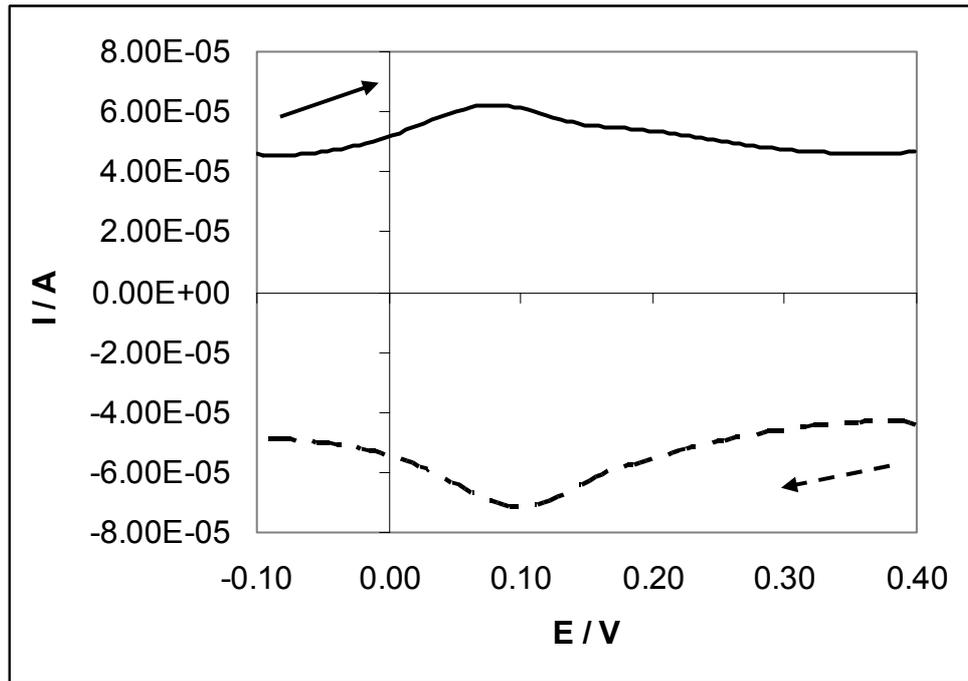


Fig. 7 – Differential pulse voltammograms recorded at Pt/PEDOT-PB composite modified electrode in 0.1 M phosphate buffer solution of pH 7.2. Pulse amplitude: 50 mV; pulse step: 5 mV; pulse width: 0.15s.

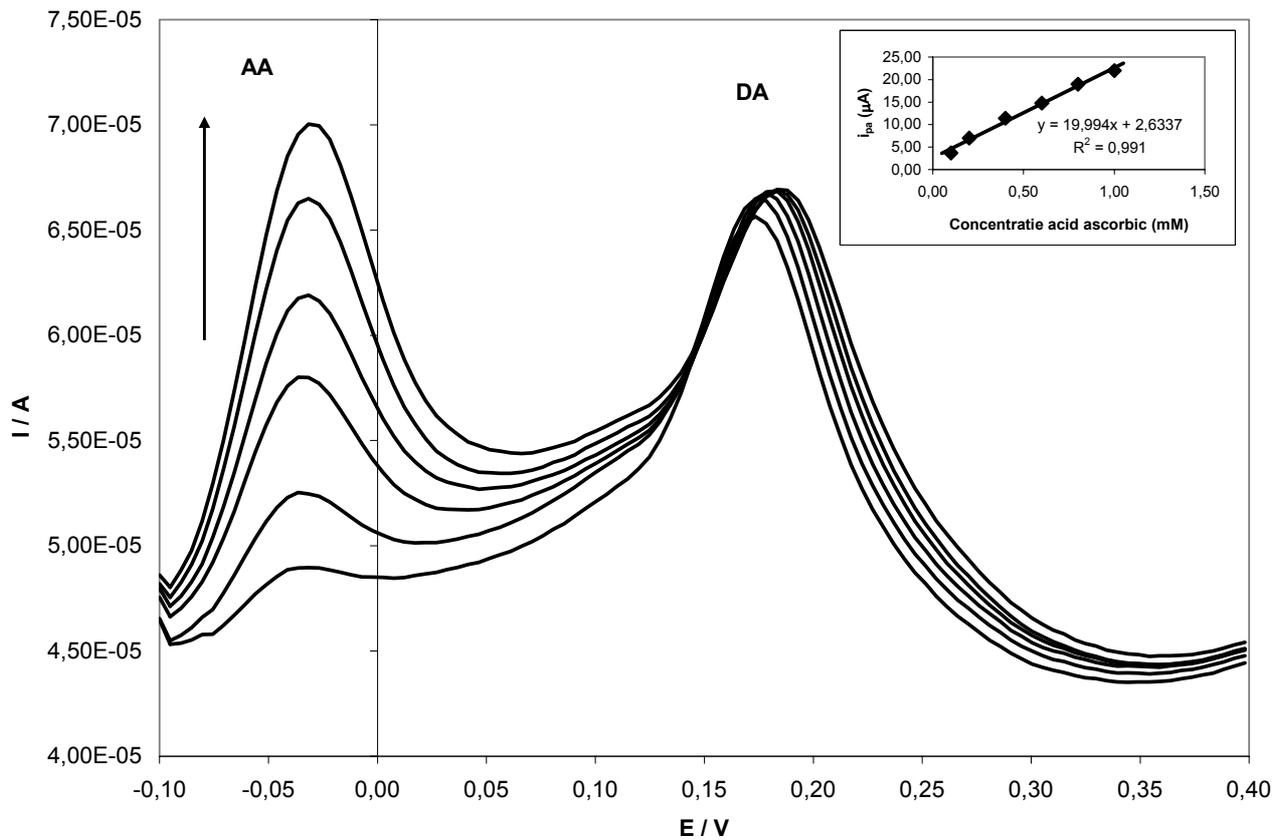


Fig. 8 – Differential pulse voltammograms recorded at Pt/PEDOT-PB composite modified electrode in 0.1 M phosphate buffer solution of pH 7.2 and 1×10^{-4} M DA, in presence of different AA concentrations ranging from 1×10^{-4} M to 1×10^{-3} M. Inset: the dependence of the anodic peak current for the oxidation of AA at Pt/PEDOT-PB composite modified electrode in the presence of 1×10^{-4} M DA.

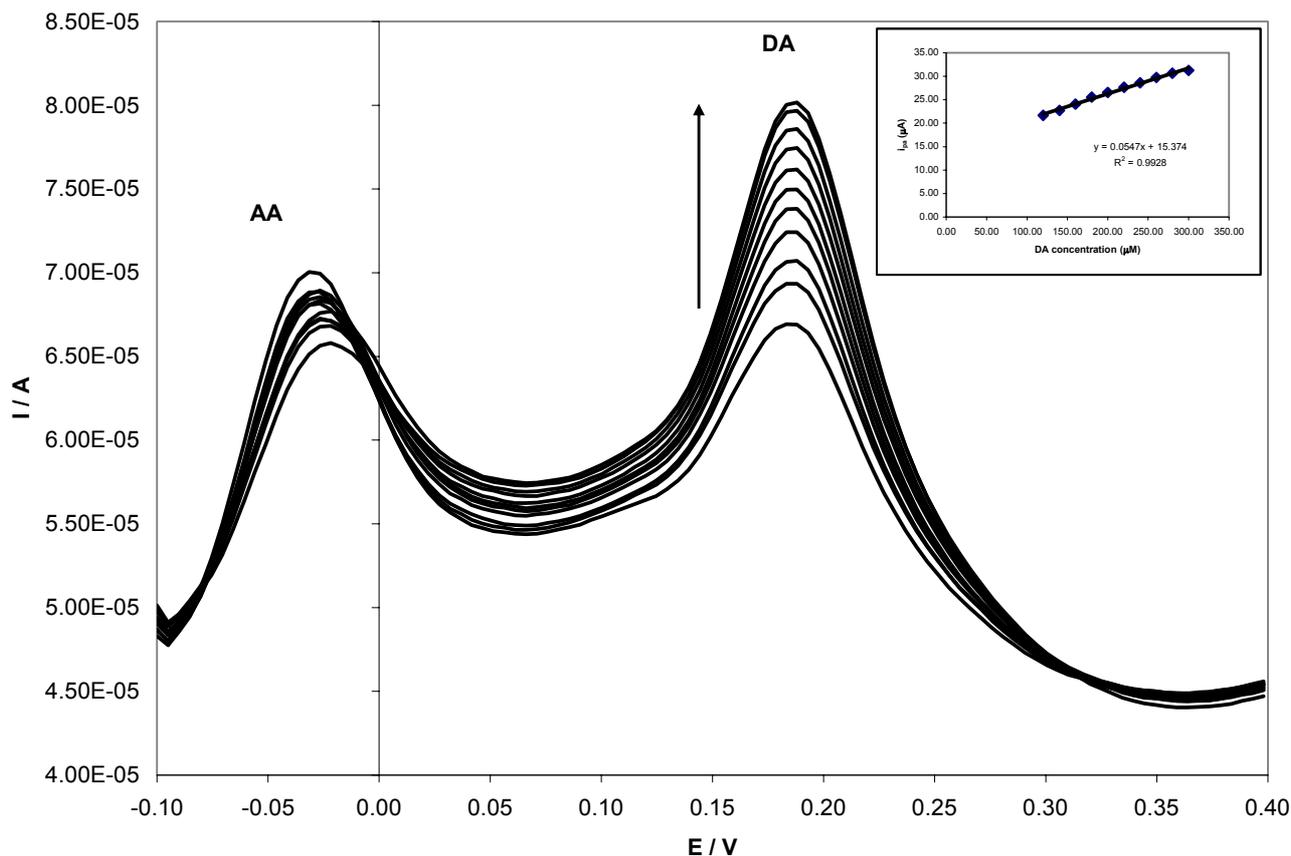


Fig. 9 – Differential pulse voltammograms recorded at Pt/PEDOT-PB composite modified electrode in 0.1 M phosphate buffer solution of pH 7.2 and 1×10^{-3} M AA, in presence of different DA concentrations ranging from 1.2×10^{-4} M to 3×10^{-4} M. Inset: dependence of anodic peak current on DA concentration at Pt/PEDOT-PB composite modified electrode in the presence of 1×10^{-3} M AA.

It can be seen that the AA oxidation produces an anodic wave at ca. -0.03 V, which is shifted towards negative potential values with about 200 mV than the DA anodic oxidation peak. This result shows that the composite coating exhibit an excellent electrocatalytic activity and selectivity towards the oxidation of AA and DA in the same sample. Moreover, the anodic peak potential for AA oxidation increases linearly with the concentration over the range from 1×10^{-4} to 1×10^{-3} M according to the equation: $I_{pa} (\mu A) = 19.994 AA (mM) + 2.6337$, with a correlation coefficient of $r^2 = 0.991$.

Similar tests have been performed at different DA concentrations in the presence of a large excess of AA. From Fig. 9 it can be observed that the anodic peak potential of DA oxidation increases linearly over the concentration range from 1.2×10^{-4} M to 3×10^{-4} M, even in the presence of 1×10^{-3} M AA. The appropriate regression equation was: $I_{pa} (\mu A) = 0.0547 DA (\mu M) + 15.374$, with a correlation coefficient of $r^2 = 0.9928$. A detection limit (S/N = 3) of 100 μM has been also obtained. It is worth to note that the

electrochemical sensor exhibited a linear response towards DA oxidation only for a limited DA concentration range due to the presence of a higher AA concentration than in the case of AA determination in the presence of DA (see Fig. 8). That is, the presence of AA strongly influences the DA voltammetric determination.

The modified ultramicroelectrode has been also used for the electrochemical determination of dopamine in the presence of ascorbic acid. The oxidation of dopamine occurs at a potential value of ca. +0.18 V, similar to the value recorded for a conventional-size electrode. The anodic peak current increases with the dopamine concentration. A linear range of the anodic current on the dopamine concentrations ranging from 4×10^{-5} to 1×10^{-3} M, in the presence of 1 mM ascorbic acid, has been obtained. The electrochemical sensor based on modified ultramicroelectrode showed a linear response for DA over a wide concentration range than in the case of the conventional-size modified electrode. A detection limit of 40 μM for the voltammetric determination of dopamine at the modified ultramicroelectrode, in the presence of an

excess of ascorbic acid, was obtained. These results clearly demonstrate that the PEDOT-PB composite coating exhibit excellent electrocatalytic effect towards the dopamine oxidation.

These new electrochemical sensors, as can be seen from our results, may be used for the simultaneously determination of both dopamine and ascorbic acid with low detection limits.

CONCLUSIONS

The good stability of the composite 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 composite coating has proved a high electrocatalytic effect towards the dopamine oxidation in the presence of ascorbic acid. The peaks of both species are separated by a difference of about 200 mV, which allows the simultaneous determination of these analytes. A linear response over a wide range of dopamine concentrations ranging from 4×10^{-5} to 1×10^{-3} M has been obtained. Detection limits of 100 μ M and 40 μ M for conventional-size electrode and ultramicroelectrode, respectively, were obtained.

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