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DETERMINATION OF ASCORBIC ACID IN THE PRESENCE OF EPINEPHRINE AT Pt ELECTRODE MODIFIED WITH POLY(3-METHYLTHIOPHENE)

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Poly(3-methylthiophene) film has been prepared by using repetitive CV technique on Pt disk electrode in acetonitrile. The obtained Pt/P3MT modified electrode was used for ascorbic acid CV-determination in the presence of epinephrine in 0.5 M sulphuric acid. The anodic peak potential for ascorbic acid oxidation was in the range from 0.44 V to 0.41 V, anticipated in comparison to that resulting at Pt bare electrode (0.51 V --- 0.55 V). A separation between the ascorbic acid and epinephrine anodic peaks were obtained. The anodic peak currents depend linearly (with correlation coefficients of 0.997) on ascorbic acid concentration in the concentration interval studied.

INTRODUCTION

Ascorbic acid (AA) is an important biologically active compound in body fluids and, also, an important interfering compound in electrochemical detection of many neurotransmitters; so it is necessary to understand its electrochemistry in order to quantify its content. Its electrochemistry is rather a problem due to the irreversibility of the electrode reaction (for example in contrast with epinephrine which displays reversible behaviour [1]) as well as the major drawback of the fouling of the electrode surface. Therefore, the improvement of the behaviour of the electrodes, as concerning the sensitivity and selectivity, towards the ascorbic acid oxidation is a continuous interesting preoccupation of research. In order to determine the ascorbic acid, a very promising way is not to reactivate the electrode surface but to eliminate the passivation.[2] To realize this purpose a deliberate modification of the electrode surface with an organic conducting polymer could be chosen. Among these organic conducting polymers, thiophene derivatives have been studied. [3] The P3MT coating of the electrode [4-7] is relatively easy to obtain, the P3MT film being also very stable and offering a very good resistance to fouling, because the P3MT operates differently in comparison with the bare electrodes hindering the accumulation of reaction product to the electrodic interface - this is the core of oxidation of ascorbic acid at usual bare electrodes like Pt. In addition to this, the P3MT film could avoid the partial overlapping of the similarly sized anodic peaks which is involved on usual bare electrodes. In this way the selectivity of the chemically modified electrode enhances in comparison with the bare electrodes. Chemically modified electrodes with P3MT films were used to study the electrochemical oxidation of neurotransmitters [8,9] or to eliminate the fouling of the electrode surface [1] or for its electronic properties [10] or for determining aminoacids. [11,12] One of the main advantages of the conducting polymers is that the conduction and interfacial electron transfer can occur in relatively wide potential windows and, on another hand, they can be obtained in a suitable oxidation state because they can provide more active sites, depending upon the electrode potential. The formed polymers tend to exist in "p-doped" state or doped state (the polymer being positively charged) and their electrochemical reduction leads, for instance in the

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polythiophenes case, to "n-doped" state or undoped state. In both states, the conducting polymer is very conductive. [13] It is also possible to control the thickness of the polymer films as a function of the overall charge passed through the working electrode.

EXPERIMENTAL

Apparatus: The preparation of P3MT film by electropolymerization of the monomer was performed by using a potentiostat/galvanostat Autolab 30 (Ecochemie). A 10-mL electrochemical cell (Metrohm) was used together with a Pt disk as working electrode, Ag/AgCl in saturated KCl solution as reference electrode and a Pt disk as counter-electrode. All the electrode potentials quoted in this paper refer to this reference electrode.
Chemicals: All electrolyte solutions were prepared in acetonitrile (Carlo Erba) (LC degree) used without further purification. All other reagents: 3-methylthiophene (Merck), $TBAPF_6$ (Merck), ascorbic acid (Merck), epinephrine (Fluka) and sulphuric acid (Sigma-Aldrich) were also used without further purification and they all were analytical reagent grade.

Preparation of Pt/P3MT modified electrode

The bare Pt electrode was polished to a mirror finish using 0.3 and 0.05 μm alumina slurry; then it was rinsed with twice distilled water, cleaned by ultrasonication (5 min) in twice distilled water and finally dried in air.

The Pt/P3MT modified electrode was prepared by potentiodynamic procedure using the multi-cycling of the electrode potential (15 scans) by cyclic voltammetry (CV) technique, at a scan rate of 50 mV/s, in the potential range from 0.0 V to +1.7 V, in a freshly prepared solution containing 0.05 M 3MT as monomer and 0.1 M $TBAPF_6$ as indifferent electrolyte in acetonitrile. After its electrochemical synthesis, the modified electrode was washed in acetonitrile and then dried in air. Then, the Pt/P3MT modified electrode was used to study its response in a solution containing different concentrations of ascorbic acid in an electrolyte solution containing 0.5 mM epinephrine and 0.5 M sulphuric acid the CV technique.

All measurements were carried out at room temperature. All solutions were deaerated by dry nitrogen stream for 5 min before every experiment and a nitrogen atmosphere was maintained above the solution during experiment (a slight nitrogen pressure being maintained during the experiment).

RESULTS AND DISCUSSION

The organic conducting polymer was grown by multi-cycling (15 scans) the electrode potential between 0.0 V and 1.7 V at a scan rate of 50 mV/s, from a solution consisting of 0.05 M 3MT and 0.1 M $TBAPF_6$ in acetonitrile. As one can see in Fig. 1, upon sequential cycles, there were a gradual increase in the current intensity (either cathodic or anodic), indicating that a film was formed on the electrode surface, that it is obtained in an electroactive form, and that its thickness grows gradually. Fig. 1 shows the scans with number 1, 10, 20, 24 and 25 obtained by scanning the electrode potential. The shape of the voltammograms is in line with previous reported results [14] suggesting that the more negative anodic wave is determined by the oxidation of the dimer and oligomers formed by successive electrode steps and chemical steps starting from the initial monomer. The monomer can be oxidised less easily than the dimer and oligomers so that their waves appear at less positive potentials and, in addition, the waves overlap being very close one to another. The monomer is oxidised, by an electrochemical step, much faster, to its radical cation at the electrodic interface and, due to the fact that the radical cation of the monomer does not diffuse faster than it is generated, a coupling of two such radical cations occurs (in a very narrow reaction layer) and a dihydrodimer cation is formed by a chemical step. This dihydrodimer produces a dimer by losing two protons, again by a chemical step.

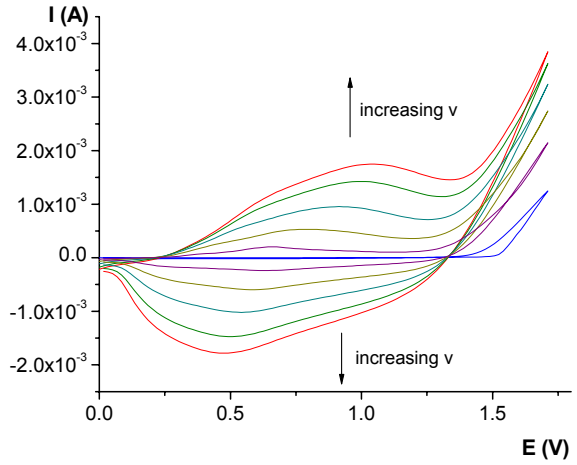

Fig. 1 – The scans with number 1, 4, 7, 10, 13 and 15 during the electropolymerization of P3MT film from a solution containing 0.05 M 3MT and 0.1 M $TBAPF_6$ in acetonitrile, on Pt working electrode at 50 mV/s between 0.0 V and 1.7 V.

Electropolymerization proceeds through successive electrochemical and chemical steps [15,16] according to a general $E(CE)_n$ scheme. Due to the fact that, after a certain size, the oligomers become insoluble in the organic solvent they precipitate onto the electrode surface. Once the oxidation of the monomer starts the entire electropolymerization occurs and the electrode Pt/P3MT is prepared with the organic film in its electroactive state. In the oxidized state, being positively charged, the polymer is doped with PF_6^- counteranion.

The electrode Pt/P3MT obtained in this way was studied in the electrolyte solution (0.1 M $TBAPF_6$ in CH_3CN) at different scan rates the shape of the cyclic voltammograms being the same as those already reported.[14] The cyclic voltammograms present an anodic wave and a cathodic wave which shift anodically, respectively cathodically, with increasing scan rate. The redox behaviour is determined by the participation of the film to electrodic processes: in its oxidized form being p-doped and playing its electrocatalytic role and in the reduced form being undoped. During the oxidation the counteranion penetrates inside the film to assure the electroneutrality condition and during the reduction the counteranion is expelled out from the film.

The electrocatalytic activity of the Pt/P3MT modified electrode (versus that of Pt electrode) was tested towards oxidation of ascorbic acid at different concentrations of the electroactive species on one hand and of epinephrine at a single concentration on the other hand by using CV technique. The CV oxidation of ascorbic acid at Pt/P3MT is illustrated in Fig. 2(A) and at Pt electrode in Fig. 2(B), both of them in 0.5 M sulphuric acid. As can be seen the Pt/P3MT plays the expected role of an electrocatalyst, the anodic peak due to the oxidation of ascorbic acid being both anticipated in position on potential axis and increased in intensity in comparison to the anodic peak obtained on Pt bare electrode. The same behaviour, especially as concern the height of the anodic peak current, was observed for both electrodes towards the oxidation of epinephrine (Fig. 3).

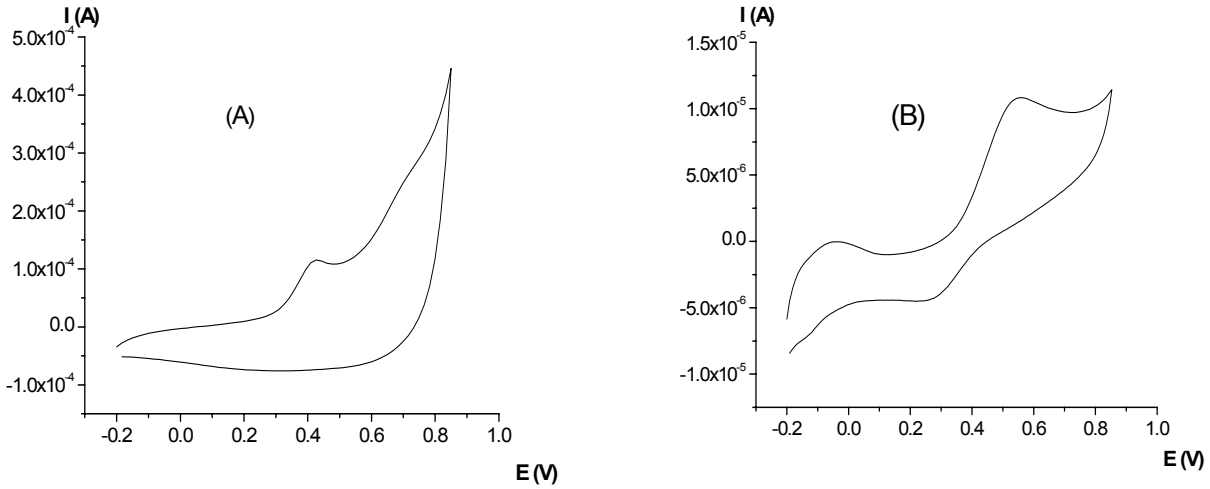

Fig. 2 – CV behaviour of 1.66 mM ascorbic acid in 0.5 M sulphuric acid at Pt/P3MT electrode (A) and at Pt electrode (B) (potential range -0.20 V - +0.85 V, scan rate 25 mV/s).

As can be seen from Fig. 2(A), an anodic peak appears at ca. 0.44 V --- 0.41 V which has an intensity from $2.5 \cdot 10^{-5}$ A (for 0.44 mM ascorbic acid) to $10.7 \cdot 10^{-5}$ A (for 1.66 mM ascorbic acid) on Pt/P3MT electrode in comparison to Pt electrode case (peak potentials from 0.44 V for 0.45 mM ascorbic acid to 0.41 V for 1.66 mM ascorbic acid and peak currents from $5 \cdot 10^{-6}$ A for 0.45 mM ascorbic acid to $10.8 \cdot 10^{-6}$ A for 1.66 mM ascorbic acid). On the reverse scan, in Fig. 2(B), a cathodic peak appears at potential peak close to 0.25 V, probably due to reduction of the product of ascorbic acid oxidation. The small value of the peak current is probably due to some deactivation of the active sites of the film which can be in some extent blocked by the adsorption of some anodic reaction product.

Fig. 4 shows the cyclic voltammograms obtained by studying the behaviour of Pt/P3MT modified electrode towards a solution containing 1.66 mM ascorbic acid and 0.5 mM epinephrine in 0.5 M sulphuric acid in comparison to both a solution containing only 1.66 mM ascorbic acid in 0.5 M sulphuric acid and a solution containing only 0.5 mM epinephrine in 0.5 M sulphuric acid.

Same kinds of CV experiments were performed at four other different ascorbic acid concentrations: 0.44 mM, 0.83 mM, 1.15 mM, 1.42 mM. All cyclic voltammetric responses show the appearance of the

anodic peak due to ascorbic acid oxidation and the anodic peak with a shoulder look due to the epinephrine oxidation. The disappearance of the latter peak is due to the increase of the capacitive charging current [17] contribution which is very specific to the organic films cyclic voltammograms, the anodic peak being followed by a large residual current plateau.

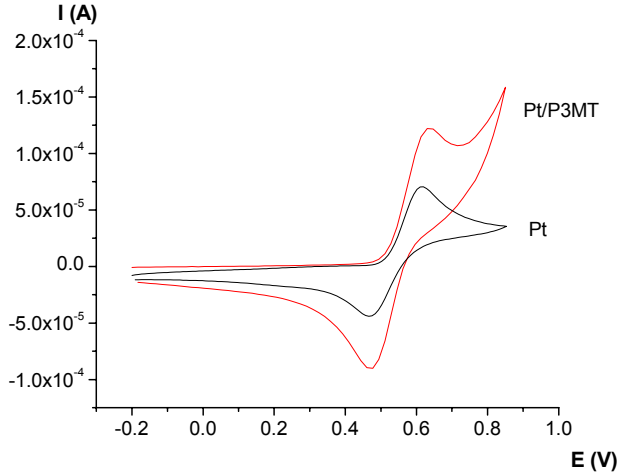

Fig. 3 – CV behaviour of 1.66 mM ascorbic acid in 0.5 M sulphuric acid at Pt/P3MT electrode and at Pt electrode. (potential range -0.20 V - +0.85 V, scan rate 25 mV/s).

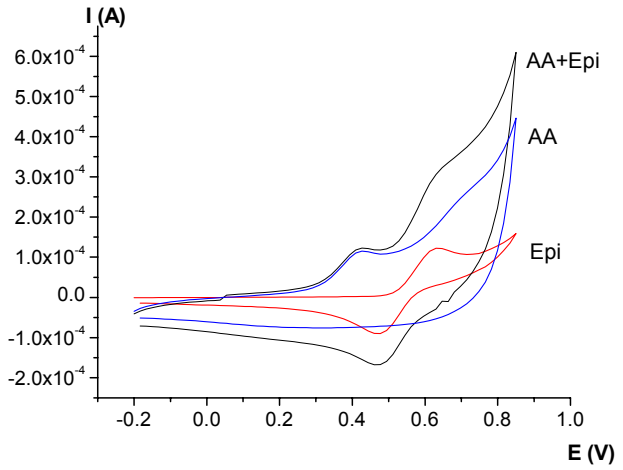

Fig. 4 – CV behaviour of 0.5 mM epinephrine in 0.5 M sulphuric acid, of 1.66 mM ascorbic acid in 0.5 M sulphuric acid and of 1.66 mM ascorbic acid and 0.5 M epinephrine in 0.5 M sulphuric acid at Pt/P3MT electrode (potential range 0.20 V - +0.85 V, scan rate 25 mV/s).

Alternatively, this large shape of the cyclic voltammogram was interpreted by a distribution of redox states with increasingly higher energies.[18] This very large charging current appears both in the cyclic voltammograms of the solution containing 1.66 mM ascorbic acid in 0.5 M sulphuric acid and in the cyclic voltammograms of the solution containing 1.66 mM ascorbic acid and 0.5 mM epinephrine in 0.5 M sulphuric acid.

Plotting the peak current against the ascorbic acid concentration a straight line was obtained with a correlation coefficient of 0.997, the equation of the line being $I_{pa} = -4.52 \cdot 10^{-6} + 6.56 \cdot 10^{-2} c$. The peak potential was in the range 0.44 V for 0.45 mM ascorbic acid and 0.41 V for 1.66 mM ascorbic acid, a negative shift with increasing concentration being noticed.

CONCLUSION

By using consecutive cyclic voltammetry technique, P3MT film was electrosynthesized from a solution containing 0.05 M 3MT and 0.1 M $TBAPF_6$ in acetonitrile and also characterized in a solution containing 0.1 M $TBAPF_6$ in acetonitrile, both in deaerated solution under ambient conditions. The P3MT film exhibits electrocatalytic activity towards ascorbic acid oxidation in the presence of epinephrine, the anodic peak of ascorbic acid oxidation being both anticipated and enhanced in comparison with the case of Pt bare electrode. The anodic peak current depends linearly upon the concentration of ascorbic acid in the studied concentration range.

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