

ELECTRODEPOSITION, CHARACTERIZATION AND APPLICATION OF Pt/P3MT MODIFIED ELECTRODE

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Poly(3-methylthiophene) film has been prepared on Pt disk electrode in acetonitrile and its electrochemical behaviour in the electrolyte solution, containing only the supporting electrolyte, was studied. The Pt/P3MT modified electrode was used for ascorbic acid DPV-determination in 0.5 M phosphate buffer solution of pH 7.0. The peak potential (around 0.08 V) is anticipated in comparison with Pt bare electrode case (around 0.22 V). Two intervals of concentrations with a linear dependence between differential pulse voltammetric anodic current peak and ascorbic acid concentration could be found with correlation coefficients of 0.997 and 0.998, respectively. A detection limit (S/N=3) value of 25 μ M has been obtained.

INTRODUCTION

Ascorbic acid (AA) is an important biologically active compound in body fluids and the understanding of its electrochemistry is very important 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 dopamine which displays reversible behaviour) 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.¹ 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.² The P3MT coating of the electrode³⁻⁷ 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 surface¹ or for its electronic properties¹⁰ 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 polythiophenes case, to “n-doped” state or undoped state. In both states, the

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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), TBAPF₆ (Merck), ascorbic acid (Merck), as well as the components (Carlo Erba) of the phosphate buffer system 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 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 (25 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 TBAPF₆ 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 phosphate buffer system of pH 7.0 by using differential pulse voltammetry (DPV) 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 (25 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 TBAPF₆ in acetonitrile. As one can see in Fig. 1A, 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. 1A shows the scans with number 1, 10, 20, 24 and 25 obtained by scanning the electrode potential. There are two anodic waves (a large peak relatively well defined and an anodic shoulder ill-defined, respectively a large cathodic peak and a shoulder ill-defined). 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. Electropolymerization proceeds through successive electrochemical and chemical steps^{14,15} 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 PF₆⁻ counteranion.

The electrode Pt/P3MT obtained in this way was studied in the electrolyte solution (0.1 M TBAPF₆ in CH₃CN) at different scan rates (20, 30, 40, 50, 60, 70, 80, 90 and 100 mV/s) in the range from 0.0 V to 1.7 V. The cyclic voltammograms in Fig. 1B 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.

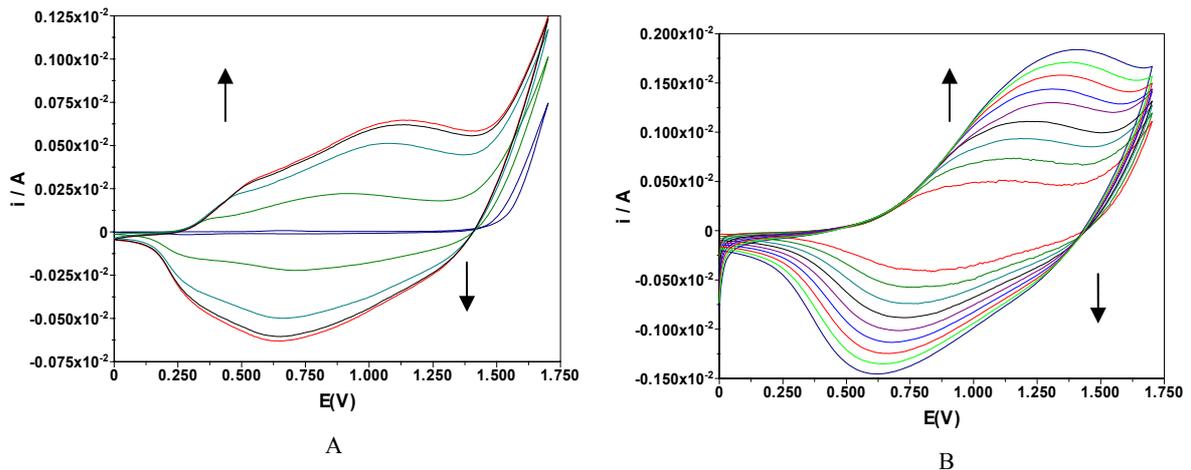


Fig. 1 – The scans with number 1, 10, 20, 24 and 25 during the electropolymerization of P3MT film from a solution containing 0.05 M 3MT and 0.1 M TBAPF₆ in acetonitrile, on Pt working electrode at 50 mV/s between 0.0 V and 1.7 V (A) and the cyclic voltammograms of Pt/P3MT modified electrode in the electrolyte solution (0.1 M TBAPF₆ in CH₃CN) at different scan rates (20, 30, 40, 50, 60, 70, 80, 90 and 100 mV/s) in the range from 0,0 V to 1,7 V (B).

Plotting the peak current against the square root of the sweep rate (Fig. 2), straight lines for both anodic and cathodic current peaks are obtained. This behaviour is consistent with a diffusion limiting process and probably can be explained by considering that the nature itself of the counteranion, which moves inside the electrolyte solution in a solvated state, could be forced to lose, at least partially, solvent molecules from the solvation shell cell to be able, having appropriate size, to enter to the film lattice.

The electrocatalytic activity of the Pt/P3MT modified electrode was tested towards oxidation of ascorbic acid by DPV technique at different concentrations of the electroactive species (from 2 μ M to 488 μ M) in phosphate buffer solution

(pH 7.0). The DPV trace voltammograms are presented in Fig. 3. As can be seen in Fig. 3, the anodic peak potentials describing the ascorbic acid oxidation shifts negatively with increasing ascorbic acid concentration, from 0.080 V to 0.075 V.

Plotting the anodic peak current against the ascorbic acid concentration one gets the linear dependences from Fig. 4 showing the existence of two different regions of linearity. For low ascorbic acid concentrations (2 μ M to 93 μ M) there is a linear dependence only for the last four values, with a correlation coefficient of 0.997. For higher ascorbic acid concentrations (from 116 μ M to 488 μ M) the linear dependence has a correlation coefficient of 0.9989. A detection limit of 25 μ M has been obtained.

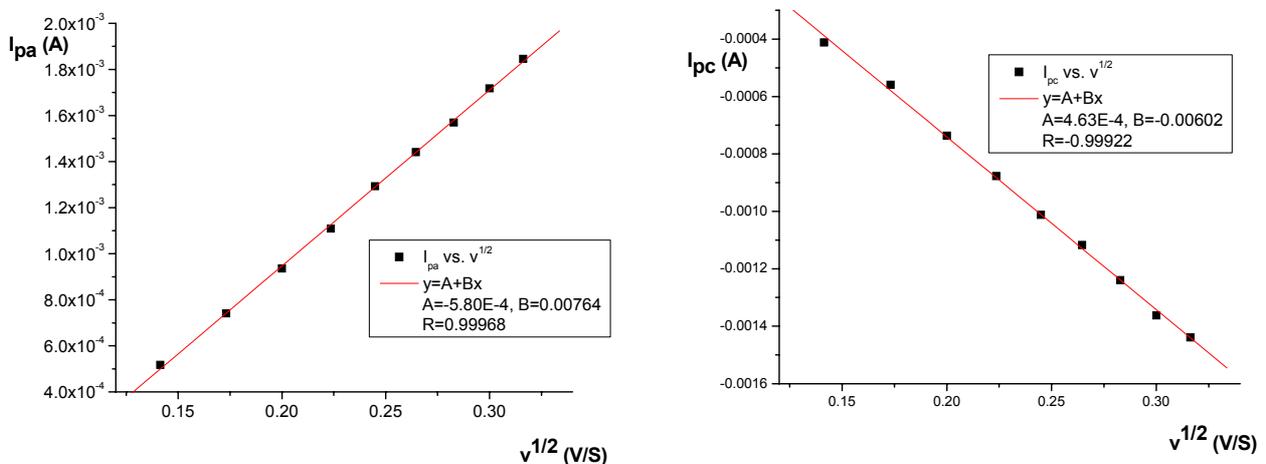


Fig. 2 – The linear dependences of anodic and cathodic peak currents upon the square root of the scan rate for the cyclic voltammograms of Pt/P3MT modified electrode in the electrolyte solution (0.1 M TBAPF₆ in CH₃CN) from Fig. 1.

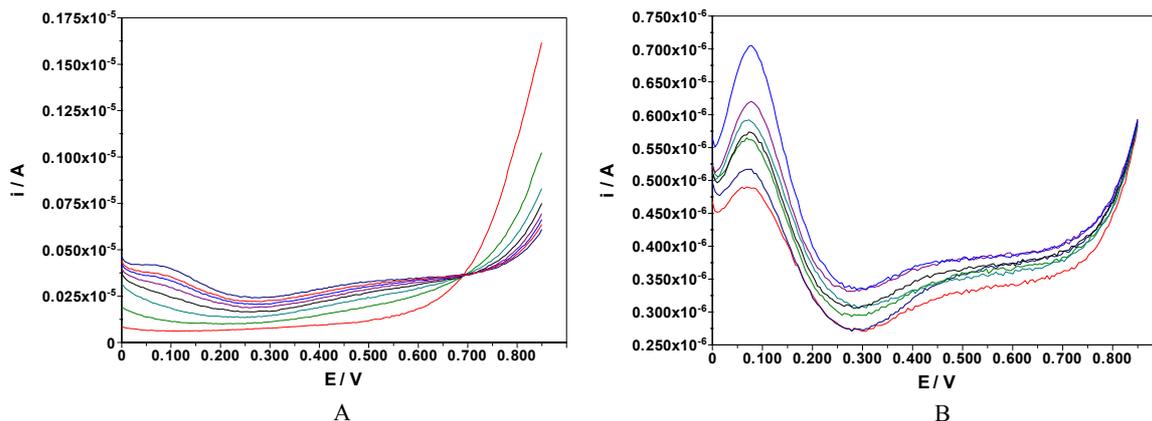


Fig. 3 – DPV trace voltammograms of ascorbic acid in 0.5 M PBS, pH= 7 at different concentrations of ascorbic acid (A): 0, 2; 7; 15; 25; 38; 54; 71 and 93 μM ; (B) 116; 182; 226; 276; 334; 429 and 488 μM .

The precision of peak current determinations was situated within the interval 2.40% (for 25 μM ascorbic acid) and 2.04% (for 93 μM ascorbic

acid) and 1.23% (for 116 μM ascorbic acid) and 1.12% (for 488 μM ascorbic acid) expressed as the relative standard deviation.

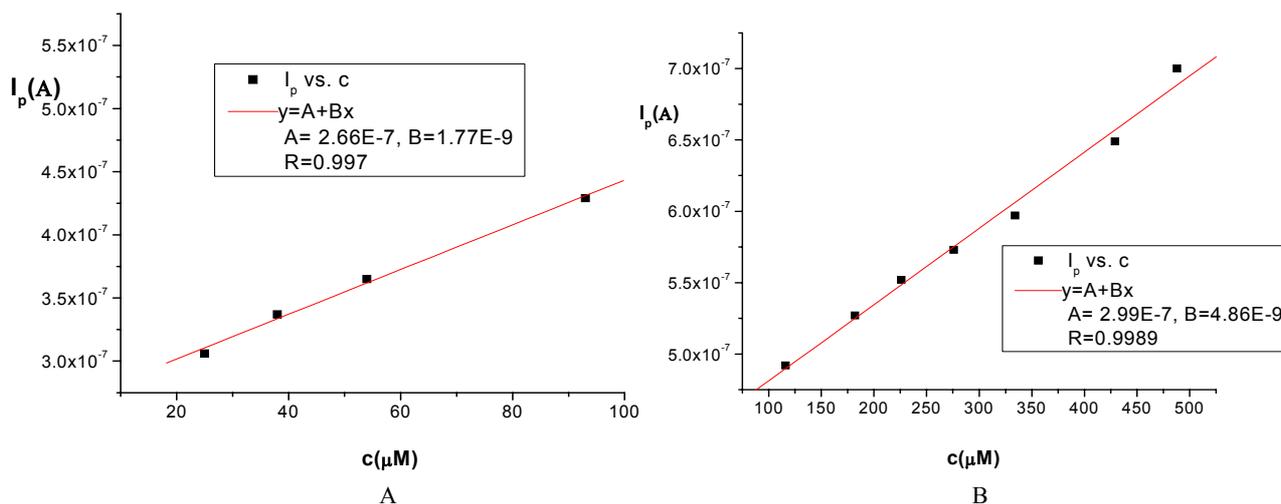


Fig. 4 – The linear dependences of the anodic peak current upon the ascorbic acid concentration (A): from 25 μM to 93 μM ; (B): from 116 μM to 488 μM .

CONCLUSION

By using consecutive cyclic voltammetry technique, P3MT film was electrosynthesized from a solution containing 0.05 M 3MT and 0.1 M TBAPF₆ in acetonitrile and also characterized in a solution containing 0.1 M TBAPF₆ in acetonitrile, both in deaerated solution under ambient conditions. The P3MT film exhibits electrocatalytic activity towards ascorbic acid oxidation, the anodic peak being anticipated in comparison with the case of Pt bare electrode. The anodic peak current depends linearly upon the concentration of ascorbic acid for two different concentration ranges.

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