

ELECTRODEPOSITION, CHARACTERIZATION AND APPLICATION OF Pt/P3MT/CoHCF MODIFIED ELECTRODE

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Using repetitive cyclic voltammetry a bilayer electrode Pt/P3MT/CoHCF has been prepared. Firstly, a poly(3-methylthiophene) film was electrodeposited on a bare Pt disk electrode to obtain a Pt/P3MT electrode; secondly, a Co(II) hexacyanoferrate film was electrodeposited on Pt/P3MT electrode film. The CME, Pt/P3MT/CoHCF, was then studied in different electrolyte solutions (NaCl 1 M, KCl 1 M, PBS pH=7 (0.2 M-0.2 M) and TBAPF₆ 0.1 M). Then the bilayer electrode was used for ascorbic acid DPV-oxidation and DPV-determination. In comparison with bare Pt electrode ($E_p=0.250$ V), Pt/P3MT ($E_p=0.080$ V) and Pt/CoHCF ($E_p=0.210-0.180$ V), the peak potential for the ascorbic acid DPV-oxidation is in the range $E_p=0.165-0.150$ V, decreasing with increasing ascorbic acid concentration. Between DPV-peak current and ascorbic acid concentration there is a linear dependence.

INTRODUCTION

In recent years, some interest has been directed to the investigations of bilayer electrodes (electrode substrate/film 1/film 2), both of the films being organic conductive films or inorganic conductive films or even organic and inorganic conductive films in an order or another.

In a bilayer electrode there are two different modalities of passing the charge from the electrodic substrate to solution and vice-versa: charge transfer steps take place at three interfaces (electrode substrate/film 1, film 1/film 2 and, of course, film 2/electrolyte solution the last two being regarded as electrodic interfaces endowed with charge transfer reactions) and, also, charge transport steps which are in fact “self exchange redox chemical reactions” ($O + R \rightleftharpoons R + O$) and diffusional steps of the counterions through the film accompanying the electrodic reactions in order to maintain the macroscopic electroneutrality of the film. It is very important that negligible barriers exist at each of the two electrodic interfaces: electrodic substrate/film 1 and film 1/film 2 in order to allow unhindered charge

transfer reactions. So the work function of the Pt and the highest occupied molecular orbital (HOMO) for film 1 must be almost at the same level. The same condition has to be fulfilled at the interface film 1/film 2 for the HOMO of film 1 and HOMO of film 2 to have unrestricted charge transfer reaction.

Among these organic conducting polymers, thiophene derivatives could be used.^{1,2} The P3MT coating of the electrode³⁻⁸ is relatively easy to be obtained, 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 case 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 neurotransmitters⁹⁻¹¹ or to eliminate the fouling of

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the electrode surface¹ or for its electronic properties¹² or for determining aminoacids.^{13,14} 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 (the polymer being positively charged) and their electrochemical reduction leads, for instance in the polythiophenes case, to "n-doped" state or even undoped state. In both "doped" states, the conducting polymer is very conductive.¹⁵ It is also possible to control the thickness of the polymer films as a function of the overall charge passed through the working electrode.

Among these inorganic conducting films the most investigated are the polynuclear transition metal-hexacyanoferrates, also known as Prussian Blue analogous.¹⁶⁻²⁰ The main fields of interest refer to their preparation and characterization and also to their electrochemical properties: good conduction (including electron and ions transfer),²¹⁻²³ electroanalysis and electrocatalysis.²⁴⁻³²

Polynuclear transition metal hexacyanoferrates can be obtained as inorganic conducting thin films deposited on a bare electrode surface by using different electrochemical techniques such as cyclic voltammetry, chronopotentiometry and so on. The inorganic conducting coating is obtained by electrodeposition of some electroactive species, which can coexist in aqueous solution in the presence of several cations that do not take part directly to their own electrode reactions but play an important role in the mechanism of electrodeposition and of operating of the resulting modified electrode during the electrochemical investigations.

In particular, the metal hexacyanoferrates films obtained on the very common electrode surface, even if they are not enough stable for different applications,³³⁻³⁵ are easily prepared by consecutive CV and the increase in the peak currents at each repetitive scan is a valuable indication of their electrodeposition.

In electroanalysis, a challenging goal is to determine the level of ascorbic acid (AA) into a sample because its electrochemistry on usual electrodes is rather difficult to accomplish due to some drawbacks such as: the electrode reaction is irreversible, the electrode surface does not resist to fouling by the electrode reaction products, the

ascorbic acid can interfere in electrochemical detection of different other biochemical electroactive species of interest.

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 attain this purpose a deliberate modification of the electrode surface with an organic or inorganic or both organic and inorganic conducting polymer could be chosen.

EXPERIMENTAL

Apparatus: Electrodeposition of P3MT and CoHCF films was performed by using a potentiostat/galvanostat Autolab 12 (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.

Chemicals: All electrolyte solutions for P3MT film electrodeposition were prepared in acetonitrile (Carlo Erba) (LC degree) used without further purification and all aqueous electrolyte solutions were prepared in doubly distilled water. All other reagents: 3-methylthiophene (Merck), TBAPF₆ (Merck), ascorbic acid (Merck), CoCl₂·6H₂O (Carlo Erba), K₃[Fe(CN)₆] (Carlo Erba), KCl (Carlo Erba), NaCl (Carlo Erba), 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/CoHCF

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 for 5 min and finally dried in air.

Firstly, the Pt/P3MT modified electrode was prepared by potentiodynamic procedure using multi-cycling of the electrode potential (25 scans) by CV 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 50 mM 3MT and 0.1 M TBAPF₆ in acetonitrile as indifferent electrolyte. Then the Pt/P3MT was rinsed with acetonitrile and then dried in air.

The Pt/P3MT/CoHCF modified electrode was prepared by potentiodynamic procedure using the multi-cycling of the electrode potential (75 scans), at a scan rate of 100 mV/s, in the potential range from +0.85 V to 0.00 V, in a freshly aqueous solution containing 1 mM CoCl₂, 0.5 mM K₃[Fe(CN)₆] and 0.5 M KCl. After the deposition of CoHCF film, the modified electrode was rinsed with doubly distilled water and dried in air. Then, the obtained Pt/P3MT/CoHCF modified electrode was used to study its response in two different solutions containing 1 M potassium ion and 1 M sodium ion. On another hand the obtained Pt/P3MT/CoHCF modified electrode was used to study its response in different concentrations of ascorbic acid in phosphate buffer system of pH 7 by using differential pulse voltammetry (DPV).

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 the experiment.

RESULTS AND DISCUSSION

The Pt/P3MT electrode was obtained as one can see in Fig. 1A, upon sequential cycles, there was a gradual increase in the current intensity (either cathodic or anodic), indicating that a film was formed on the electrode surface, which 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. As concerns the shape, the cyclic voltammograms show no important difference from those already reported.³⁶ As it was discussed, electropolymerization proceeds through successive electrochemical and chemical steps^{34,35} according to a general $E(CE)_n$ scheme. 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 inorganic conducting film was grown, as one can see in Fig. 1B, upon sequential cycles; there was a gradual increase in the current intensity (either cathodic or anodic), indicating that a film was formed on the electrode surface, it is obtained

in an electroactive form, and that its thickness grows gradually. Fig. 1B shows the scans with number 5, 15, 25, 35, 45, 55, 65 and 75 obtained by scanning the electrode potential.

The presence of the inner film (P3MT) influences the shape of the cyclic voltammograms, because the charge transfer/transport through the organic conductive film and the charge transfer at the two electroodic interfaces (Pt/P3MT and P3MT/CoHCF) occur at the level of not very high conductive film (in comparison with Pt substrate). Especially, the anodic peak becomes larger and it is shifted to more positive potentials in comparison with Pt/CoHCF case. Also, the redox hysteresis is much larger for Pt/P3MT/CoHCF than in the Pt/CoHCF case illustrating a greater ability of storing charges as capacitors.

Obviously, the shape of the cyclic voltammograms obtained at the electrodeposition of the P3MT film is the same well-known³⁶ but the shape of the cyclic voltammograms obtained at the electrodeposition of the CoHCF film is more or less the same as for the obtaining of Pt/CoHCF electrode.³⁷ The cathodic peak separation is the same $\Delta E_p = E_{pc,2} - E_{pc,1} = 0.240V$, but each cathodic peak is shifted in the cathodic direction with almost 20 mV, in comparison to Pt/CoHCF case. The anodic peak is larger and shifted with almost 50 mV in the anodic direction. The redox hysteresis is more accentuated for Pt/P3MT/CoHCF case in comparison with Pt/CoHCF case due to the existence of the inner organic film.

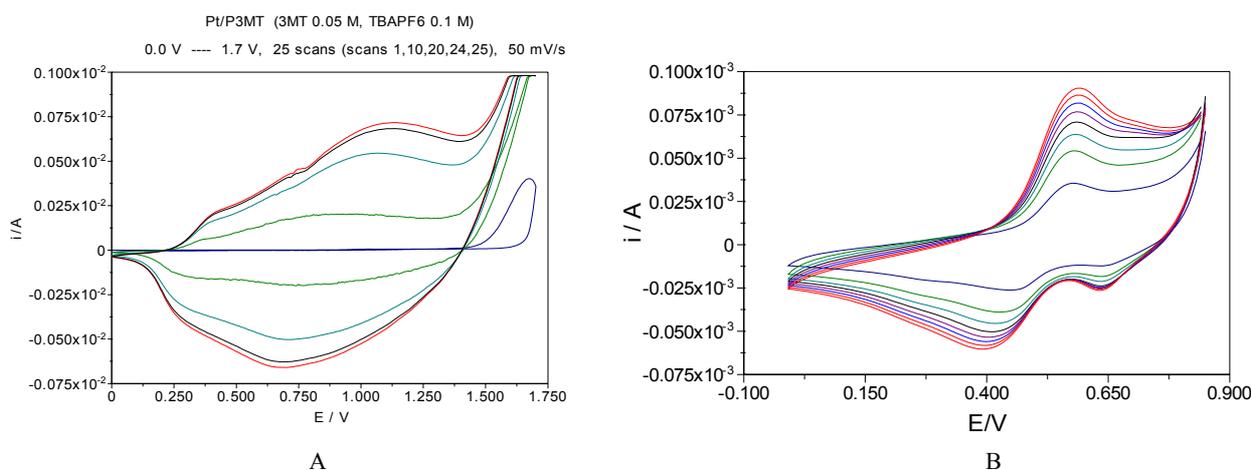


Fig. 1 – A. The scans with number 1, 10, 20, 24 and 25 during the electrodeposition of P3MT film on Pt working electrode at 50 mV/s scan rate, between +0.0 V and 1.7 V. Electrolyte solution: 0.05M 3MT, 0.1M TBAPF₆ in acetonitrile. B. The scans with number 5, 15, 25, 35, 45, 55, 65 and 75 during the electrodeposition of CoHCF film on P3MT film electrodeposited on Pt/P3MT working electrode at 100 mV/s scan rate between +0.85 V and 0.00 V. Electrolyte solution 1 mM CoCl₂, 0.5 mM K₃[Fe(CN)₆], 0.5 M KCl in water.

The study of the Pt/P3MT/CoHCF in 1.0 M KCl and, respectively, in 1.0 M NaCl shows a similar behaviour of the bilayer electrode as for the study of the Pt/CoHCF electrode itself (Figs. 2A and 2B). The Pt/P3MT/CoHCF electrode was studied both in 1 M KCl (see Fig. 2A) and 1 M NaCl (see Fig. 2B) electrolyte solutions by cyclic voltammetry technique at different scan rates. In the case of Pt/P3MT/CoHCF/KCl (1 M) electrode, the doping/undoping ion is K^+ and the average peak electrode potentials are $E_p^a=617$ mV and $E_p^c=423$ and 695 mV, with a formal electrode potential $E^{o'}=E_{K^+}^{o'}=520$ mV and a peak

separation $\Delta E_p=520$ mV. In the case of Pt/P3MT/CoHCF/NaCl (1 M) electrode the doping/undoping ions are Na^+ and K^+ the former in the studying solution, the latter being already inside the film as a result of preparation from the solution of preparation containing K^+ and the average peak electrode potentials are $E_p^a=423$ mV and $E_p^c=334$ mV, with a formal electrode potential $E^{o'}=E_{Na^+}^{o'}=378$ mV and a peak separation $\Delta E_p=89$ mV.

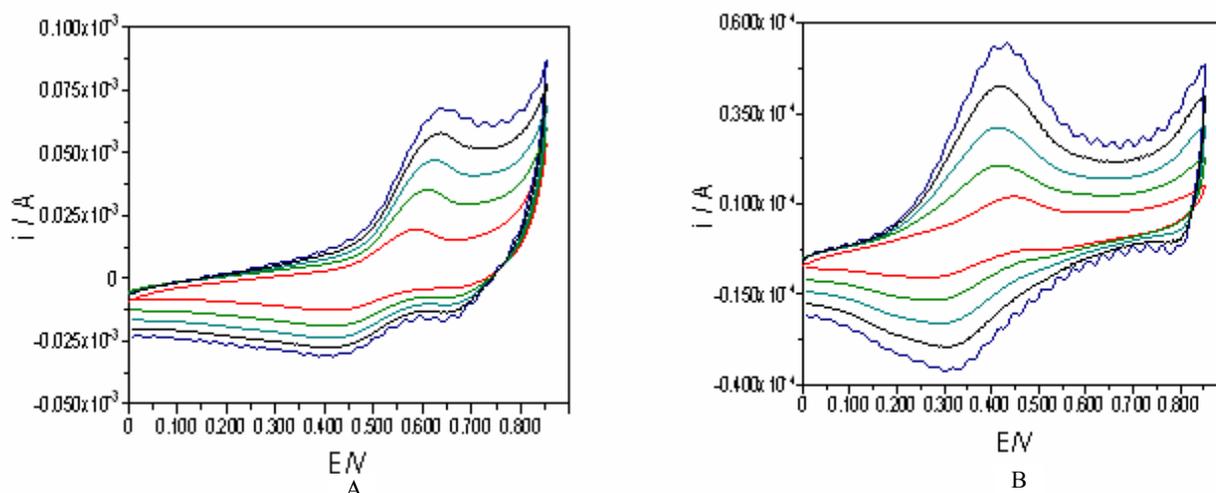


Fig. 2 – The behaviour of Pt/P3MT/CoHCF/KCl(1 M) (A) and Pt/P3MT/CoHCF/NaCl(1 M) (B) with the increasing sweep rate: 20, 40, 60, 80 and 100 mV/s in the range from 0.00 V to 0.85 V.

It is obvious that the electrode reactions occur easier ($\Delta E^o = E_{K^+}^{o'} - E_{Na^+}^{o'} = 150$ mV) at the Pt/P3MT/CoHCF/NaCl electrode than at Pt/P3MT/CoHCF/KCl electrode due to the fact that the electrochemical mobility of sodium ion is greater than that of potassium ion and the migration into and out of the film depends upon the electrochemical mobility. Of course, in the presence of the inner film the cyclic voltammograms of Pt/P3MT/CoHCF electrode in Na^+ -containing electrolyte solution, respectively in K^+ -containing electrolyte solution look almost similarly with those of Pt/CoHCF electrode due to the fact that the doping/undoping processes involve the same counteranions K^+ , respectively Na^+ (for both electrodes Pt/P3MT/CoHCF and Pt/CoHCF)

at a similar ending electrodic interface CoHCF/electrolyte solution.

In Fig. 3 one can see the behaviour of Pt/P3MT/CoHCF electrode in a studying solution containing 0.1 M TBAPF₆ in acetonitrile. The cyclic voltammogram is very similar³⁶ to that obtained in the same electrolyte solution but for Pt/P3MT electrode. This behaviour is consistent with the fact that each film plays a conductive role facilitating the charge (electrochemical) communication from an interface to another. What is the mechanism of passing of doping/undoping counteranion PF₆⁻ through CoHCF film remains rather to be explained.

The two cyclic voltammograms for Pt/P3MT/CoHCF electrode in 1 M KCl and in 1 M NaCl are quite different and remember the shapes of the two cyclic voltammograms for Pt/CoHCF

electrode in the same studying solutions. In the case of Pt/P3MT/CoHCF/NaCl (1 M) the shape is more or less symmetrical around the $E^{0'}$ value. In addition, one can notice that the pair of peaks is broad. This observation regarding the behaviour of the Pt/P3MT/CoHCF modified electrode obtained in the presence of K^+ counterion in the studying solution containing Na^+ and K^+ counterions is similar with the results found for Pt/CoHCF itself.

Plotting the peak currents against the square root of the sweep rate one obtains straight lines for both anodic and cathodic peaks and for

Pt/P3MT/CoHCF modified electrode both in K^+ -containing and, respectively, Na^+ -containing supporting electrolyte (figures not shown here). This behaviour is consistent with a diffusion limiting process and probably can be explained by considering the nature itself of the counteraction, which moves inside the electrolyte solution in a hydrated state, but could be forced to lose, at least partially, solvent molecules from the hydration shell to be able, having appropriate size, entering the crystal lattice.³⁸

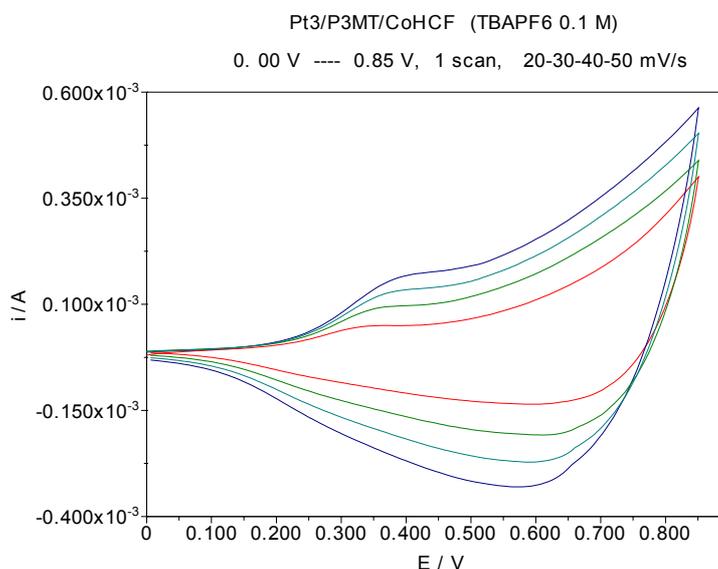


Fig. 3 – The behaviour of Pt/P3MT/CoHCF in 0.1M TBAPF₆ in acetonitrile with increasing sweep rate 20, 30, 40 and 50 mV/s in the potential range 0.0 V ---- +0.85 V.

The electrocatalytic activity of the modified Pt/P3MT/CoHCF electrode was tested towards oxidation of ascorbic acid by DPV technique at different concentrations of the electroactive species in phosphate buffer solution (pH 7). The DPV trace voltammograms are presented in Fig. 4. As can be seen from Fig. 4, the anodic peak potentials corresponding to the ascorbic acid oxidation shifts very slightly in the negative direction with increasing ascorbic acid concentration, and they can be localized in the range from 0.160 V to 0.165 V.

Plotting the DPV-anodic peak current against the ascorbic acid concentration one gets the linear dependences 5 showing the existence of two different regions of linearity. For low ascorbic acid concentrations but starting with 10 μ M, in the range from 10 μ M to 91 μ M (A) there is a linear

behaviour, with a correlation coefficient of 0.993, the equation of the line being $I_{pa} = 0.220 + 9.59 * 10^{-4} c$. For high ascorbic acid concentrations, in the range from 167 μ M to 445 μ M (B), the linear dependence has a correlation coefficient of 0.999, the equation of the line being $I_{pa} = 0.235 + 1.109 * 10^{-4} c$.

The anodic peak in DPV-voltammograms appears in the potential range 0.160-0.165 V, being anticipated in comparison with the ascorbic acid oxidation peak obtained on Pt bare electrode ($E_p=0.250$ V) and on Pt/CoHCF electrode ($E_p=0.210$ -0.165 V).

The latter response is probably due to the supplementary catalytic effect of the inner film P3MT. Obviously, the very large anodic peak appeared around 0.650V is probably due to the

electrode reactions involving the two stable forms of CoHCF ($\text{KCo}^{\text{II}}[\text{Fe}^{\text{II}}(\text{CN})_6]$ and $\text{K}_2\text{Co}^{\text{II}}[\text{Fe}^{\text{II}}(\text{CN})_6]$) which are electroactive at not too different electrode potentials; the two anodic peaks overlap.

In addition, in the PBS the concentration of the counteranion is less than in the electrolyte solution used for studying the chemically modified electrode and this depletion requires larger overvoltages to drive electrooxidation. As a

consequence, the peak potential is positively shifted. As it was mentioned³⁶ the protons seem to not be able to participate to doping/undoping process in order to maintain the electroneutrality of the film during electrode reactions.

The electrocatalytic effect of the Pt/P3MT/CoHCF electrode is due to the fact that the inorganic conductive film is obtained in an oxidate state (the last half-cycle begins at 0.00 V and ends at 0.85 V).

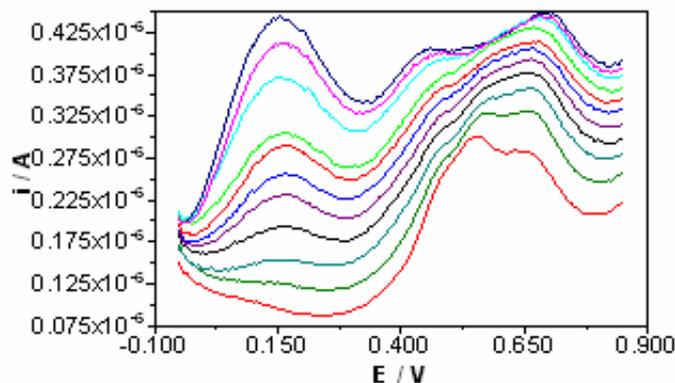


Fig. 4 – DPV voltammograms for ascorbic acid oxidation (in PBS of pH=7) at Pt/P3MT/CoHCF electrode with increasing concentration of ascorbic acid from 0 to 445 μM . DPV parameters are SP=5 mV, PA=10 mV, potential range is from 0.00 V to 0.85 V.

CONCLUSIONS

Using consecutive cyclic voltammetry technique, a bilayer electrode consisting of P3MT film (as inner film) and CoHCF film (as outer film) was electrodeposited onto Pt electrode surface in K^+ -containing solution and also characterized in K^+ -containing, Na^+ -containing solution and also PBS (Na^+ containing counteranion). The formal electrode potentials of the inorganic film were determined in both electrolyte solutions. The bilayer electrode exhibits electrocatalytic activity towards the oxidation of ascorbic acid, the anodic oxidation peak being anticipated in comparison with the bare Pt electrode and Pt/CoHCF electrode. The DPV-anodic peak current depends linearly upon the concentration of ascorbic acid.

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