



ELECTROCHEMICAL PREPARATION AND CHARACTERIZATION OF POLY (3-METHYLTHIOPHENE)-COBALT HEXACYANOFERRATE-MODIFIED PLATINUM ELECTRODE USING CYCLIC VOLTAMMETRY

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abstract: Using consecutive cyclic voltammetry (CV), cobalt (II) hexacyanoferrate (CoHCF) and cobalt (II) hexacyanoferrate/poly (3-methyl thiophene) (CoHCF/P3MT) films have been prepared in fresh solutions formed between CoCl_2 1mM, $\text{K}_3[\text{Fe}(\text{CN})_6]$ 0.5 mM and KCl 0.5 M for the Pt/CoHCF electrode and DMSO as a solvent, TBAPF₆ 0.1M and 3MT 50mM for the Pt/P3MT/CoHCF electrode. Then, using different cyclic voltammetry techniques, chemically modified electrodes, Pt/CoHCF and Pt/P3MT/CoHCF, were used to study their response in a phosphate buffer system of 7.2 pH and in ascorbic acid of various concentrations.

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Introduction

Electrodes containing modified chemical films are used in different fields of chemistry and material science [1,2], in the application areas of electroanalysis and electrocatalysis [3,4], in studies on interfacial charges and electron transfer [5,6], and in research on surface chemical composition. Conducting polymeric films are also used as chemical sensors. The electrochemical deposition process that leads to the formation of the metal hexacyanoferrate on the electrode surface needs to be carefully controlled. Fabrication of a chemically-modified electrode is easily controlled by consecutive cyclic voltammetry as a synthesis process in which an increase in the peak current of the film forms an appropriate redox couple for the modified film. These systems have the general formula $\text{M}^I_{\text{A}}[\text{M}^{\text{II}}(\text{CN})_6]_{\text{B}}$ and possess properties resembling those of redox organic polymers [7], zeolitic and intercalation materials [8]. Above all, chemically modified electrode Fe (II) hexacyanoferrate (FeHCF) received the greatest attention, for preparing chemically modified electrodes, which are Prussian Blue analogues, due to the large purpose of electrochemical studies, and their further application. A few electrodes showed good results as Prussian Blue did. From the

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large area of MeHCF, CoHCF is exceptional, as it has similar reversible redox centre with those of Prussian Blue. Two types of film were found regarding CoHCF. One type has a redox couple, while the other presents two redox couples. Voltammetric researches and studies using an EQCM (electrochemical quartz crystal microbalance) indicated that CoHCF has a rigid, cubic, zeolitic structure formed from three orthogonal chains Fe-CN-Co, and both Fe and Co are octahedral coordinated of six carbon atoms, and six nitrogen atoms. Chemical lattice of Co (II), in CoHCF structure, especially Co-N bond, depends upon the nature and the area of the alkaline metallic counter cation included in CoHCF structure. The thick inorganic film, which was electrochemically synthesized on a platinum electrode, using potentiostatic conditions, -0.4 V, in aqueous solution, behaves as it contains molecular magnets. Regarding the structure of bilayer film electrodes, a metal hexacyanoferrate of stoichiometric formula $A_xM_y[Fe(CN)_6]qH_2O$ (where M is a metal, A represents a counter cation, and x, y, q are stoichiometric coefficients) forms an almost cubic three-dimensional framework of repeating -NC-Fe-CN-M-NC units, in which the cyan moiety with its carbon atom coordinating to an iron ion and the nitrogen atom to an M ion forms the edge of the cube. Iron and M ions alternate at the lattice sites, while the counter cation and the water molecules are situated at the interstices in the cavity or the ionic channel of the cube.

The purpose of this paper is to emphasize the conducting properties of the P3MT (inner) organic layer in the Pt/P3MT/CoHCF chemically modified electrode, being involved in electron transfer reactions between CoHCF (outer) inorganic layer and platinum electrode substrate and to compare its electrochemistry with that of the P3MT (simultaneously outer and single) organic layer in the Pt/P3MT chemically modified electrode.

Experimental Part

Apparatus

The electrochemical measurements were performed using a PGSTAT 12 potentiostat/galvanostat, a system controlled by General Purpose Electrochemical System interface, designed for Windows 4.9.007 version. A three-electrode single-compartment electrochemical cell was used. The working electrode was a platinum disc of 2 mm diameter, the reference electrode was a saturated calomel electrode (all electrode potentials quoted in this paper refer to this reference electrode) and the counter electrode was a glassy carbon electrode. All measurements were carried out at room temperature.

Reagents

The water was double distilled. All other reagents: $K_3[Fe(CN)_6]$ (Fluka), $CoCl_2$ (Sigma-Aldrich), NaCl (Riedel-de Haën), KCl (Riedel-de Haën), a buffer phosphate solution of certain pH, acetonitrile solvent (Aldrich), 3-methylthiophene and tetrabutylammonium hexafluorophosphate (TBAPF₆, Fluka) were used without further purification and were analytical reagent grade.

Deposition of the inorganic and organic/inorganic films

The platinum bare 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. The Pt/CoHCF modified electrode was prepared by potentiodynamic procedure using the multi-cycling of the electrode potential (75 and 100 scans) by cyclic voltammetry (CV) technique, at a scan rate of 100 mV/s, in a potential range from +0.85 V to 0.00 V, in a freshly aqueous solution containing 1 mM CoCl_2 , 0.5 mM $\text{K}_3[\text{Fe}(\text{CN})_6]$ and 0.5 M KCl. After the deposition of CoHCF film, the modified electrode was rinsed with double distilled water and dried in air. Then, the obtained Pt/CoHCF modified electrode was studied in three different solutions containing KCl or NaCl at 1 M concentration and respectively PBS at pH 7 (0.2 M-0.2 M). The Pt/P3MT/CoHCF modified electrode was prepared, firstly depositing the organic film and then the inorganic film. The organic film was deposited from a solution containing ACN, 0.1 M TBAPF₆ and 50 mM 3MT, sweeping the potential from 0.0-1.6 V using a scan rate of 25 and 50 mV/s (7 scans) and after was deposited the inorganic film from a solution containing 1 mM CoCl_2 , 0.5 mM $\text{K}_3[\text{Fe}(\text{CN})_6]$ and 0.5 M KCl, using the same technique as for the monolayer electrode. Then, the obtained Pt/P3MT/CoHCF modified electrode was studied in three different solutions containing KCl or NaCl at 1 M concentration and respectively PBS at pH 7 (0.2 M-0.2 M). 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 discussions

The Pt/CoHCF electrode was obtained by multi-cycling (100 scans) the electrode potential between +0.85 V and 0.00 V at a scan rate of 100 mV/s. As one can see in Fig.1(A) 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, that it is obtained in an electroactive form, and that its thickness grows gradually. Fig. 1(A) shows the scans with number 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100. Fig. 1(B) shows the preparation of bilayer electrode, for the scans with the number 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100. The Pt/P3MT/CoHCF bilayer electrode was obtained, firstly, by electrodeposition of the organic film at a scan rate of 25 mV/s, cycling the potential between 0.0-1.6 V (7 scans) and, secondly, by electrodeposition of the inorganic film. As one can see, the inner organic film, did not modify the voltammogram allure for the deposition of the outer inorganic film, as it resembles with the single layer electrode. It can be observed just a little decrease of the anodic peak, also the second cathodic peak, the one from negative values of the potential is also not so good deposited.

After the two films were deposited on the electrode surface, they were characterized in solutions that contained different counteranions, in order to study their responses. In Figs. 2, 3 and 4 is given a comparison between the cyclic voltammograms for the two electrodes in solutions that contain 1M NaCl, 1M KCl and 0.2-0.2 M PBS. All characterizations were carried out at different scan rates 10, 20, 30, 40, 50, 60, 70, 80, 90, 100 mV/s), sweeping the potential between 0.0-0.85 V. In the following, the cyclic voltammograms obtained at

100 mV/s are used for comparison. In Fig.2, on the Pt/CoHCF in NaCl conditioning solution can be seen that in the direct sweeping of the potential there are two anodic peaks, very close one to another, while on the Pt/P3MT/CoHCF there is only one peak.

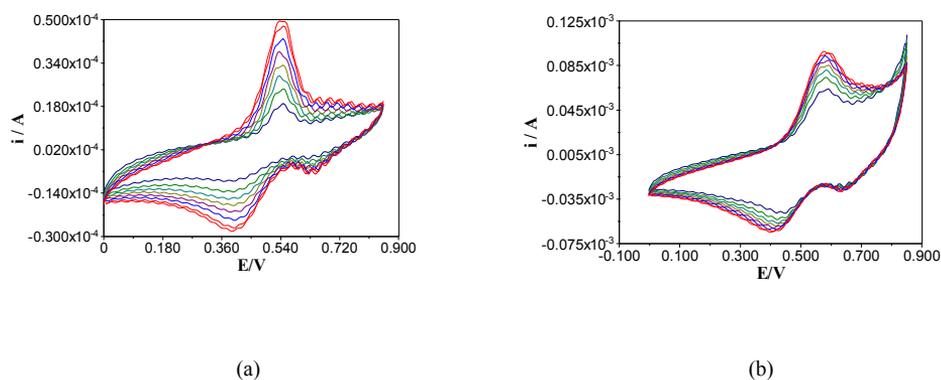


Fig. 1 Preparation of Pt/CoHCF (a) and Pt/P3MT/CoHCF (b).

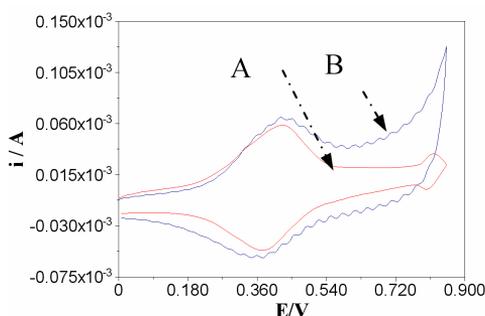


Fig. 2 Comparison between Pt/CoHCF (A) and Pt/P3MT/CoHCF (B) in NaCl solution.

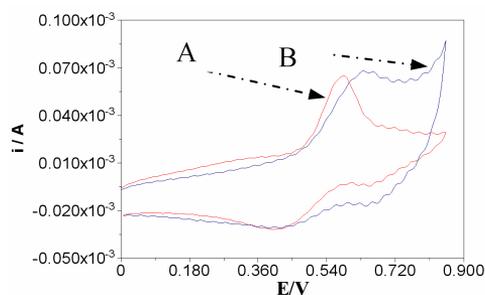


Fig. 3 Comparison between Pt/CoHCF (A) and Pt/P3MT/CoHCF (B) in KCl solution.

Fig. 3 presents the voltammogram characterizing the two electrodes in KCl solution. It can be seen that the anodic peak of the bilayer electrode is a little bit shifted to a more positive potential, also the cathodic peak is not so well evidenced, compared with the one of the single layer electrode, where there are two peaks, well separated. This can be attributed to the existence of the organic film of the bilayer electrode.

Fig. 4 releases the voltammetric response of the two electrodes in PBS of pH 7 (phosphate buffer solution, 0.2 M-0.2 M).

Here the resembling of the two is almost the same, with a little exception on the anodic and cathodic peaks of the Pt/P3MT/CoHCF, which are little higher than the one on the Pt/CoHCF electrode. The voltammograms allure is almost the same, which means that there is an electrochemical communication between the two organic and inorganic films. Fig. 5 presents an overlapping of the scans for the characterization of the two electrodes in the all three solutions. The difference is visible, between the two electrodes, and also for the same

electrode, which indicates that the doping/undoping ion is very important. As one can observe, there is a similarity between the characterization of the both electrodes in NaCl and PBS solution due to the existence of the same doping ion, that is Na^+ .

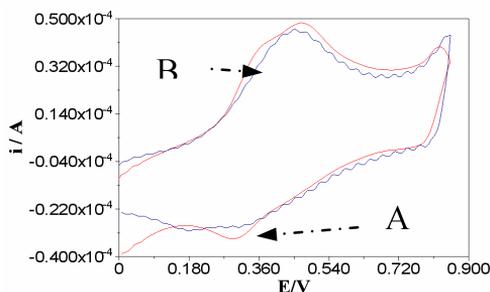


Fig. 4 Comparison between Pt/CoHCF (A) and Pt/P3MT/CoHCF (B) in PBS solution.

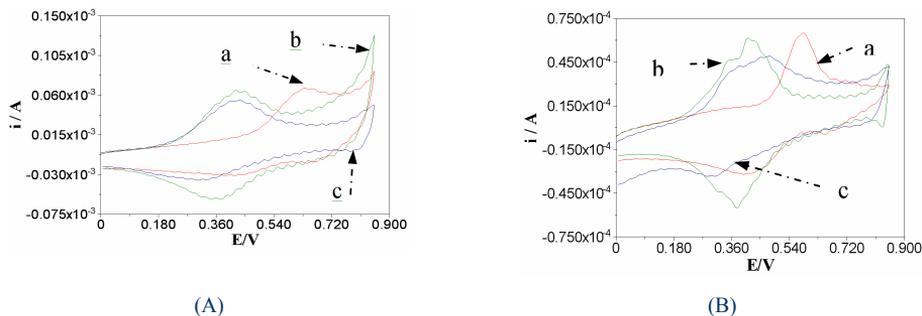


Fig. 5 Overlap of the scans for the characterization of the Pt/P3MT/CoHCF, fig. 5 A, and Pt/CoHCF fig. 5 B in NaCl (a), KCl (b) and PBS (c), for a scan rate of 100 mV/s in a range potential between 0.0-0.85 V.

It is also obvious, for both electrodes, that the electrode reactions take place more easily on the Pt/P3MT/CoHCF/NaCl electrode than on the Pt/P3MT/CoHCF/KCl or on Pt/CoHCF/NaCl than on Pt/CoHCF/KCl, because the electrochemical mobility of the Na^+ ion is higher than the one of the K^+ ion, and because the migration of the ions in/from the film to/from the electrode surface depends on this mobility. As we can see, because the anodic potential goes in the anodic ways for both electrodes, get us to the conclusion that the undoping process, which comes during oxidation, is diffusionaly controlled. The electrode reaction takes place at a potential which is higher for the characterizations of the two electrodes in KCl, than in NaCl, which is in concordance with the electrochemical mobility of Na^+ ion which is higher than that of the K^+ ion.

The plot of the peak current vs. square root of the scan rate for the monolayer modified electrode (obtained after 100 cycles) in NaCl solution, shows linear dependence both for the cathodic and for anodic current. The behavior is in concordance with a diffusional controlled process, and it can be explained probably, by the fact that these doping counterions (in a state that depends upon their nature) have to penetrate the film in order to assure its electroneutrality. The counterions travel inside the electrolyte solution in a hydrated state, but they can be forced to loose, at least partially, the solvent's molecules

from the hydrated cover, so they can be able to penetrate inside the interstitials of the polymer.

These representations enhance the role of the doping/undoping diffusing ion (here Na^+) at the working electrode from the electrolytic solution, despite the fact that in doping process the used solution is very concentrated (1 M). Representation of the cathodic and anodic peak currents versus the square root of the scan rate, for Pt/CoHCF modified electrode in a NaCl solution (scan rate 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 mV/s) in a potential range between 0.00-0.85 V, leads to a linear dependence, with correlation coefficients 0.99 for I_{pc} vs. $v^{1/2}$, and respectively - 0.95 for I_{pa} vs. $v^{1/2}$.

Conclusions

A bilayer chemically modified electrode Pt/P3MT/CoHCF was prepared by cyclic voltammetry technique and then studied by cyclic voltammetry technique in different electrolyte solution containing doping as counterion either Na^+ or K^+ ions. The behaviour of the outer layer in the bilayer case was, more or less, the same with the behaviour of the monolayer for the Pt/CoHCF electrode. The inner layer in the case of the bilayer electrode allows the electrochemical communication between the platinum substrate and the outer inorganic conducting layer. The formal electrode potential and the cyclic voltammograms allure are doping cation dependent. Also the results indicate that the redox process was performed near the last/outer electrodic interface, which is another proof of the immobilization of the conducting CoHCF film and P3MT/CoHCF films on the bare electrode surface.

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