



ELECTROSYNTHESIS AND CHARACTERISATION OF A COBALT HEXACYANOFERRATE–POLY(3-METHYL- THIOPHENE) MODIFIED PLATINUM ELECTRODE USING CYCLIC VOLTAMMETRY

Ileana Sandu, Ioana Vlaicu, Alina Cristian and C. Mihailciuc *

abstract: The scope of the present paper is to prepare and to study a bilayer chemically modified electrode (BCME) synthesized by successive electrodeposition of an inorganic (inner) layer of cobalt hexacyanoferrate (CoHCF) and of an organic (outer) layer of poly(3-methylthiophene) (P3MT) on a platinum electrode surface and to investigate the electrochemical behaviour of this BCME in various transfer electrolyte solutions. Both the preparation and the characterization of the BCME were studied using cyclic voltammetry (CV) technique. The role of the doping/undoping cation used in the electrolyte solution is emphasised.

received: October 25, 2008

accepted: November 10, 2008

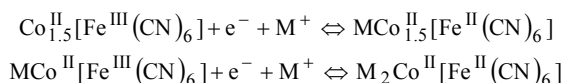
Introduction

In 1977, Heeger and MacDiarmid discovered that doping the polyacetylene with Lewis acids or bases endowed the polymer with metallic properties, including an increase of its electronic conductivity of 10 orders of magnitude [1]. Since then, many applications of conducting polymers, a very interesting class of electrode materials, have been investigated. Hence, conducting polymers are discussed as active battery electrodes, electronic and electrochromic displays, anti-corrosives, biological and chemical sensors or electrocatalysts, hole transport layers in organic light emitting diodes [2].

A multilayer electrode is a metallic electrode on which are deposited alternatively numerous layers, each layer being chemically different from its adjoining layers. The layer order drastically influences the electrochemical response of the system [3]. In the present work we study the phenomena occurring at a BCME from the angle of CV. Initially, the deposition of a CoHCF film on a platinum electrode surface was performed. The phenomenological aspects of this process consist, firstly, in the redox reaction that occurs at the electrode surface: $[\text{Fe}(\text{CN})_6]^{3-} + e^- \rightleftharpoons [\text{Fe}(\text{CN})_6]^{4-}$. Secondly, the formed complex containing

* University of Bucharest, Faculty of Chemistry, Department of Physical Chemistry,
4-12 Regina Elisabeta Blvd., District no. 3, 030018, Bucharest, Romania
corresponding author e-mail: cmpaul@gw-chimie.math.unibuc.ro

Fe^{II} (the reduced species), Co^{II} and M^+ ions (in different ratios) rapidly precipitate on the electrode surface forming the inorganic coating, the electroactive layer being cycled between its oxidized and reduced states. The following redox reactions involve M^+ as a doping ion (existing in the indifferent electrolyte) in order to maintain the electroneutrality of the layer [4]:



The structural properties of the film determine its electrochemical behaviour. As shown, it has the aptitude to store alkali-metal cation and to allow the charge transfer between the electrode surface and the solution [5].

A theoretical characterisation of the P3MT growth proposes a mechanism by analogy to the coupling reactions of aromatic compounds [6]. The first electrochemical step consists in the oxidation of the 3MT monomer to a radical cation at the electrode surface. Since the electron transfer reaction is faster than the diffusion of the monomer from the solution, a high concentration of radicals is maintained near the electrode surface. The second step involves the coupling of two radicals (that occurs in a very thin reaction layer) to produce a dihydro dimer dication which leads to a dimer after loss of two protons and rearomatization. Finally, the dimer, which is more easily oxidized than the monomer, occurs in its radical form and undergoes a further coupling with a monomeric radical. Electropolymerization proceeds then through successive electrochemical and chemical steps according to a general $\text{E}(\text{CE})_n$ scheme, until the oligomers become insoluble in the electrolytic medium (acetonitrile) and precipitates onto the surface of the first deposited inorganic layer.

The charging processes of the polymer can be associated with a ion doping because the process of oxidation or of reduction of the non-conducting state of these polymers generates mobile electronic charge carriers in the material. Charge neutrality has to be maintained by the appropriate exchange of an ionic charge with the electrolytic solution and this requires that a conducting polymer film of high charge/discharge activity should have good electronic and ionic conductivities [7].

In the present work we make a comparison between the electrochemical behaviour of the inorganic conducting film which acts either as outer (being in fact the single deposited film on the metallic conductive substrate) film in the Pt/CoHCF electrode case or as inner film in the Pt/CoHCF/P3MT electrode case. The outer organic film in the case of the bilayer shows conductive properties allowing the inner film to exhibit its own electrochemistry.

Experimental Part

Instrumentation

Electrochemical experiments were carried out using the potentiostat-galvanostat system AutoLab PGStat 12, controlled by General Purpose Electrochemical System (GPES) electrochemical interface for Windows (version 4.9.007). Three electrodes in one-compartment cell (10 ml) were used in all experiments. Platinum disc electrode served as a

working substrate electrode. All potentials were measured and given referred to SCE electrode used as reference electrode. The counter electrode was a glassy carbon electrode. All measurements were performed under ambient conditions and no action was taken to remove oxygen.

Reagents and preparation of the BCME

All chemicals were reagent grade and used without further purification; the aqueous solutions have been prepared using distilled water. Before modification, the platinum substrate was polished with alumina slurry on a polishing pad, washed with distilled water and sonicated for a few minutes in doubly distilled water. The electrodeposition of CoHCF was carried out in a fresh aqueous solution containing 1 mM $\text{CoCl}_2 \cdot 6 \text{H}_2\text{O}$ (Sigma-Aldrich), 0.5 mM $\text{K}_3[\text{Fe}(\text{CN})_6]$ (Fluka) and 0.5 M KCl (Riedel-de Haën) as supporting electrolyte. The second layer was prepared by electrochemical polymerisation using an acetonitrile (Fisher Chemicals) solution containing 50 mM 3MT (Fluka) and 0.1 M Bu_4NPF_6 (Aldrich) as supporting electrolyte. The voltammetric parameters of the preparation are presented in the legend of Fig. 1.

Results and Discussion

The deposition processes involve adsorption, nucleation and growth steps [8]. The cyclic voltammogram illustrating the preparation of CoHCF film onto the platinum electrode surface by potential sweeping is presented in Fig. 1 (A). One may state that CoHCF film grows during repetitive scans. Hence, the increase in current with each cycle is a direct measure of the increase in thickness of the redox active film. The increasing height for both cathodic and anodic peaks indicates that the CoHCF film is obtained under the activated electroactive form. The shape of the successive voltammograms indicates that during the deposition of the CoHCF film, two reduction and one single oxidation processes take place.

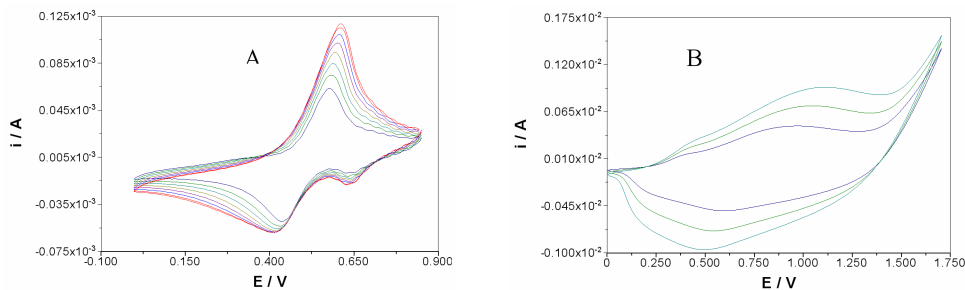


Fig. 1 Successive cyclic voltammograms for (A) the preparation of Pt/CoHCF chemically modified electrode (cycles 10-20-30-40-50-60-70-75, potential range 0.85 to 0.0 V vs. SCE, scan rate 100 mV/s) and for (B) the electropolymerization of P3MT (cycles 2-6-10, potential range 0.0 to 1.7 V vs. SCE, scan rate 50 mV/s).

The two cathodic peaks correspond at the two reduction processes mentioned above, illustrating the existence of the two stable forms, which are electroactive at different potentials (the peak situated at a lower value of the potential correspond at the $\text{KCo}_{1.5}^{\text{II}}[\text{Fe}^{\text{II}}(\text{CN})_6]$ forming).

On the other side, Fig. 1 (B) shows the successive cyclic voltammograms of the growth of P3MT film onto the first deposited inorganic layer of CoHCF. With increasing the film thickness, the film morphology changes from a dense structure to a porous one, property that makes the film surface sensible to conditioning electrolyte concentration [9]. The shape of the voltammogram is similar to that obtained at the preparation of Pt/P3MT electrode, which leads to the conclusion that the inner film allows the charge transfer (due to its conductive properties), mediating the electrochemical communication between metallic substrate and electrolytic solution. The cathodic wave of the CV shows a single peak assigned to be the undoping process. The anodic branch of the voltammogram, which corresponds to the doping process, exhibits two peaks: a broad oxidation peak and an anodic shoulder. The large peak (at a higher potential value) corresponds to the oxidation process of the monomer. The other peak is correlated to the oxidation of the dimer and of the other formed oligomers, because the conjugated systems such as polymers (as a result of the interactions between charged oligomeric segments, the reactivity of the polymeric chain depends on its charge) are much easier oxidized or reduced than their monomeric precursors and their oxidation waves generate a large area. Therefore, the correspondent peak is situated at lower values of the anodic potential. The peak potentials are displaced one from each other, due to a slow solvent/electrolyte exchange, and the current keeps high well after the redox peak, which is attributed to a capacitive behaviour of the conducting material. Moreover, the materials prepared in the presence of different supporting electrolytes have different redox properties, and simultaneously, the nature of the doping anion strongly affects the morphology and the electrodeposition of P3MT layer [10].

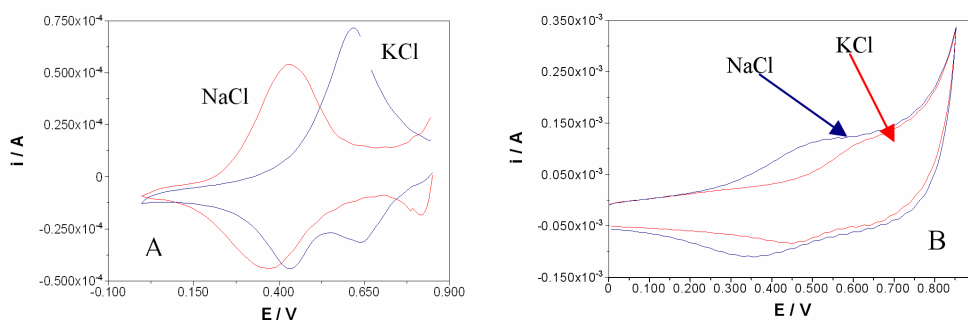


Fig. 2 Comparison between two cyclic voltammograms illustrating the characterisation in KCl (1 M) and in NaCl (1 M) solutions of the Pt/CoHCF (potential range 0.85 to 0.0 V vs. SCE, scan rate 100 mV/s) - (A) and comparison between two cyclic voltammograms illustrating the characterisation in KCl (1 M) and in NaCl (1 M) solutions of the Pt/CoHCF/P3MT (potential range 0.0 to 0.85 V vs. SCE, scan rate 100 mV/s) - (B).

The cyclic voltammogram presents an accentuated hysteresis due to a distribution of redox states (as their energies increase) or to a capacitive charging current. Also, the hysteresis depends upon the concentration and also upon the nature of the indifferent electrolyte. This aspect explains the important capacity of conductive polymers to store ionic charge, used in various applications (e.g. redox capacitors because the kinetics of the doping/undoping processes is generally fast, with the charge being stored throughout the bulk volume of the material) [11].

After the electrosynthesis of the CoHCF film, the electrode was dipped successively in two transfer electrolyte solutions (KCl 1M and NaCl 1M) and characterised by CV. For the sake of comparison, the voltammograms illustrating the behaviour of the Pt/CoHCF modified electrode in each electrolyte are plotted in Fig. 2.A. It is obvious that the formal potentials of the systems and the shapes of cyclic voltammograms depend on the nature of the chosen electrolyte cation.

The electrode reaction occurs much more easily in NaCl electrolyte than in KCl electrolyte. This can be observed comparing the half-wave potential for K^+ ($E_{1/2,K^+} = E_{K^+}^0 = 0.525\text{ V}$) and for Na^+ ($E_{1/2,Na^+} = E_{Na^+}^0 = 0.407\text{ V}$) respectively, ions that are present in the two solutions. The difference between the peak potentials is smaller for NaCl electrolyte ($\Delta E_p = 0.08\text{ V}$) than for KCl ($\Delta E_p = 0.185\text{ V}$) electrolyte and $\Delta E^0 = E_{K^+}^0 - E_{Na^+}^0 = 0.1185\text{ V}$.

One observes, on the one hand, that the voltammetric response in NaCl electrolyte shows a set of peaks at potentials of about 0.4 V; a lower amount of K^+ ions is present in the layer structure, this cation being replaced with Na^+ (which has a smaller radius). This experimental reality is in concordance with the fact that the electron transfer is accompanied by the simultaneous displacement of a counter-cation. On the other hand, the cyclic voltammogram acquired in KCl exhibits a couple of cathodic peaks and a single anodic peak.

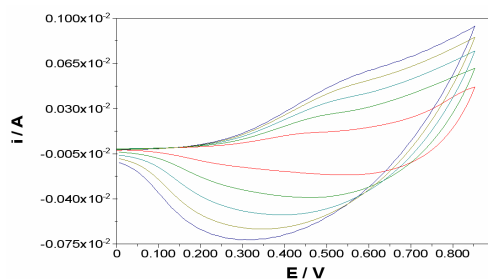


Fig. 3 Cyclic voltammograms illustrating the characterisation of Pt/CoHCF/P3MT in $Bu_4NH_4PF_6$ (0.1 M) solution acquired at different scan rates (20, 40, 60, 80, 100 mV/s). Potential range: 0.0 to 0.85 V.

The same treatment was applied to the Pt/CoHCF/P3MT, in order to compare the electrochemical behaviour of the monolayer and of the bilayer modified electrode in each transfer electrolyte solution (Fig. 2.B). As mentioned, Na^+ and K^+ are ions with an important role in doping/undoping processes. The electrode reaction occurs easier for Na^+ than for K^+ . That is why the voltammogram for NaCl has the cathodic peak corresponding at the forming of $NaCo_{1.5}^{II}[Fe^{II}(CN)_6]$ at a lower peak potential (0.33 V) than for KCl voltammetric response (0.473 V).

The redox behaviour of the BCME is determined also by the organic (outer) film deposition in electrodic process. In its oxidized state this is p-doped. Referring to the inorganic (inner) layer in Pt/CoHCF/P3MT, while oxidation reaction occurs, the counter-cation (Na^+ or K^+) is rejected out the layer lattice for providing the electroneutrality state. During the reverse reaction (reduction), the counter-cation penetrates into the film. In KCl electrolyte one may

observe one anodic peak and two cathodic peaks, but these are much indistinct than for the Pt/CoHCF modified electrode, characterised in the same solution. The explanation is that P3MT film being interposed between inorganic film and electrolytic solution, the CoHCF film becomes more inaccessible to K^+ ions, able to participate at the doping/undoping phenomena. However, the outer film allows the chemical communication between inner film and solution, because the shape of the voltammograms is alike. A similar interpretation could be given for the electrochemical behaviour of the BCME in NaCl solution.

The Pt/CoHCF/P3MT was also studied in the conditioning solution, containing 0.1 M Bu_4NPF_6 in acetonitrile (but without 3MT monomers) in order to enhance the voltammetric response of the BCME in an electrolyte transfer solution containing PF_6^- (a small ion derived from a strong acid). Analysing Fig. 3 one observes that the shapes of the successive cyclic voltammograms show a large hysteresis, experimental fact explained by the property of conducting polymers to store ionic charge. This hysteresis depends upon the nature and upon the concentration of the indifferent electrolyte. The nature of the anion affects also the electrodeposition (while the nature of the cation influences the doping/undoping processes).

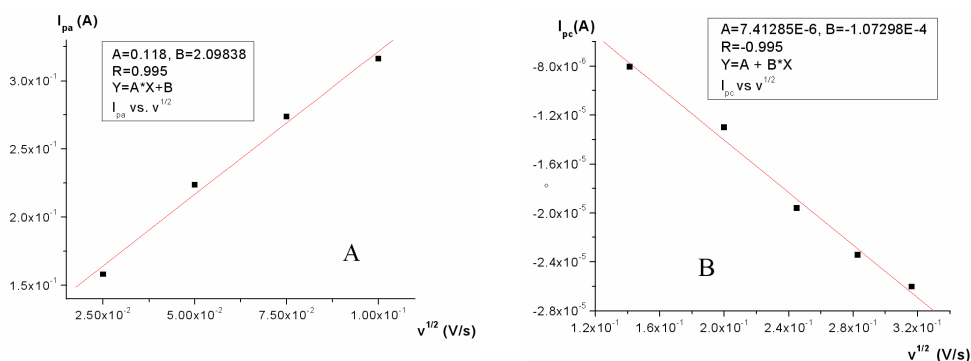


Fig. 4 Linear dependences representing: I_{pa} vs. $v^{1/2}$ for the Pt/CoHCF modified electrode, at different scan rates: 25, 50, 75, 100 mV/s (A), and for I_{pc} vs. $v^{1/2}$ for the Pt/CoHCF/P3MT modified electrode at several different scan rates: 20, 40, 60, 80 and 100 mV/s (B) both for characterisation in KCl solution (1 M).

We propose for exemplification two linear dependences versus the square root of the scan rate for the cathodic and anodic peak currents, respectively (Fig. 4). These representations enhance the role of the doping/undoping diffusing ion (K^+) at the working electrode from the electrolytic solution, despite the fact that in doping process the used solution is very concentrated (1 M).

This behaviour is according with a diffusion-controlled process and it may be explained considering the partial desolvation of the counteranion in order to be able to penetrate in the conducting film lattice. Figure 5 illustrates the comparison between two voltammetric responses (of Pt/CoHCF and of Pt/CoHCF/P3MT respectively) which correspond on the linear dependences above, for marking the different electrochemical behaviour of the two modified electrodes.

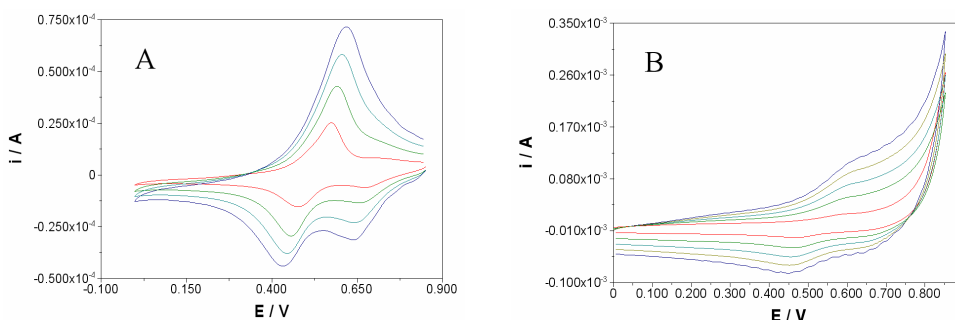


Fig. 5 Comparative voltammograms for (A) Pt/CoHCF (scan rates: 25, 50, 75, 100 mV/s, potential range 0.85 to 0.0 V) and for (B) Pt/CoHCF/P3MT (scan rates: 20, 40, 60, 80, 100 mV/s, potential range 0.0 to 0.85 V) illustrating the characterisation in KCl solution (1 M).

Conclusions

The conducting films have similar features as those of immobilised species exhibiting reversible electrochemical behaviour. Due to its conductivity peculiarities, a CoHCF film deposited onto a metallic surface allows the electronic transfer between a second conducting layer of P3MT and the substrate with metallic conduction, fact that results comparing the cyclic voltammograms acquired in different studying solutions. Concerning the nature of the doping ion, the transfer phenomena generate different voltammetric responses, depending mainly on the ion size, on its charge and electrochemical mobility.

The comparison between the electrochemical behaviour of the inorganic conducting film which acts either as outer (being in fact the single deposited film on the metallic conductive substrate) film in the Pt/CoHCF electrode case or as inner film in the Pt/CoHCF/P3MT electrode case shows, more or less, the same shape of the cyclic voltammograms in the studied electrolyte solutions depending mainly on the nature of the doping/undoping counteraction. The outer organic film in the case of the bilayer shows conductive properties allowing the inner film to exhibit almost its own electrochemistry.

REFERENCES

1. Shirakawa, H., Louis, E.J., MacDiarmid A.G., Chiang, C.K. and Heeger, A.J. (1977) *J. Chem. Soc. Chem. Commun.* **578**.
2. Tang, H., Zhou, Z., Zhong Y., Liao, H. and Zhu, L. (2006) *Thin Solid Films* **515**, 2447-51.
3. Diard, J.-P., Glandut, N., Montella, C., Sanchez, J.-Y. (2005) *Journal of Electroanalytical Chemistry* **578**, 247-57.
4. Chen, S.-M. (2002) *Journal of Electroanalytical chemistry* **521**, 29-52.
5. Kulesza, P.J., Malik, M.A., Zamponi, S., Berrettoni, M. and Marassi, R. (1995) *Journal of Electroanalytical Chemistry* **397**, 287-92.
6. Ambrose, J. F. and Nelson, R.F. (1968) *J. Electrochem. Soc.* **115**, 1161-82.
7. Schmitz, R.H.J. and Jüttner, K (1998) *Electrochimica Acta* **44**, 1627-43.

8. Benedetti, E. J., Canobre, S.C., Fonseca, C. P. and Neves, S. (2007) *Electrochimica Acta* **52**, 4734-41.
9. Tolstopyatova, E. G., Sazonova S.N., Malev, V.V. and Kondratiev, V.V. (2004) *Electrochimica Acta* **50**, 1565-71.
10. Roncali, J. (1992) *Chem. Rev.* **92**, 711-38.
11. Jüttner, K., Schmitz, R.H.J. and Hudson A. (1999) *Electrochimica Acta* **44**, 4177-87.