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Original Scientific Article

Composite Films of Metal Hexacyanoferrate and Poly(1,8-diaminonaphthaline) Derivatives: Electrosynthesis and Properties

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Abstract. The details of a potentiodynamic preparation method for a composite nickel(II) and copper(II) hexacyanoferrate (MeHcF) and poly[8-(3-acetylimino-6-methyl-2,4-dioxopyran)-1-aminonaphthaline] (PAMDAN) on a platinum electrode, (Pt|PAMDAN|MeHcF) are reported. The cyclic voltamograms recorded the direct deposition and growth of inner layer (PAMDAN) and the outer layer (MeHcF) from their solutions. The two composite electrodes show an improvement in the redox response. The voltammetric characteristics of the composite modified electrodes were also investigated in presence of different alkali metal cations (Li^+, Na^+, K^+ and NH_4^+). The heterogeneous electron transfer processes involving the composite and their stability were examined by subjecting the system to the long term cyclic voltammetric potential cycling in 0.2 M NaCl electrolyte also after exposing the modified electrode to air for about 48 h then cycled in 0.2 M NaCl solution. Bilayer composite electrodes exhibit higher ionic conductivity, higher stability in comparison with pure inorganic (MeHcF) films. The inner electroactive polymer chains in the film cause enhancement in the electric conductivity of the composite electrodes.

Keywords: composite electrode, cyclic voltammetry, electropolymerization, electrodeposition, hybrid films, modified electrode, prussian blue analogues

INTRODUCTION

In recent years hybrid materials constructed of transition metals hexacyanoferrates (MeHcF), prussian blue analogus (PB) and electroactive polymers have attracted attention of researchers working in different scientific areas. Hybrid systems consisting of conducting polymer and metal hexacyanoferrates are fabricated as films on a neutral electrode surface and are supposed to be uniform in the sub-micro scale. Such systems can't be achieved by separate layer by layer deposition.[1–3] The examples of hybrid organic-inorganic films are known,[4–10] and their practical advantages have been already appreciated. A composite material consisting of MeHcF impregnated in conducting polymer has been shown to have excellent properties. A system consisting of MeHcF and conductivity polymer is capable of mediating electrooxidation and electroreduction of several redox material.[6,11,12] An important feature of the composite organic-inorganic system is that the polymer matrix is electronically and ionically well conducting in potential range where the MeHcF redox species are electroactive. Consequently, propagation of charge to the MeHcF centers incorporated in the polymeric matrix is expected to be fast and the stability increase.[13–15] Ferromagnetic properties of hybrid systems were found to be advantageous in comparison with simple inorganic chemicals.[16,17] Inorganic-organic nanocomposite electrodes were tested for energy storage and conversion applications, especially in super capacitors,[18] solar cells,[19] electrochromic devices[20] and as a redox mediator for a glucose biosensor.[21,22]

Solid MeHcF are known to have lower diffusion constant in comparison with polymeric systems. Parameters characteristics for diffusion are drastically changed for a hybrid organic-inorganic material. Electroactive polymer chains in the film cause considerable enhancement in the electric conductivity of the material in comparison with pure inorganic net work. In our previous work we prepared PAMDAN in aqueous and non aqueous media.[23–25] In this work we focus our attention towards the electrochemical preparation of hybrid poly(MeHcF) (nickel, copper) and PAMDAN putting into consideration investigate their electrical properties by cyclic voltammetry.

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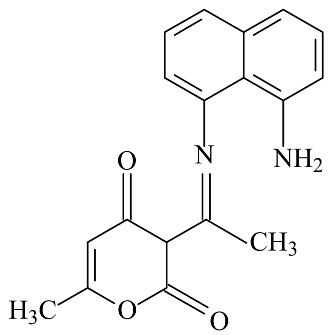

Figure 1. 8-(3-acetylimino-6-methyl-2,4-dioxopyran)-1-aminonaphthaline (AMDAN Schiff-base).

EXPERIMENTAL

The chemicals, 1,8-diaminonaphthaline, dehydroacetic acid, acetonitrile, lithium perchlorate, copper nitrate, nickel nitrate, nitric acid, perchloric acid, sodium chloride, lithium chloride, potassium chloride, ammonium chloride, calcium chloride, sodium bromide, sodium sulfate, sodium nitrate, sodium acetate and potassium hexacyanoferrate were analytical grade chemicals (Aldrich) and used without further purification. Aqueous solutions were prepared from bidistilled water.

Electrochemistry was performed using the EG&G PAR computer measuring system model 250 and a Hewlett-Packard X-Y recorder model 7440. Cyclic voltammetry was conducted using a three-electrode electrolytic cell (Bioanalytical system, model C-1A) in which a platinum disc electrode (Pt) (3.0 mm diam.), was used as working electrode, a platinum sheet (area 2 cm^2) as counter electrode and Ag|AgCl as reference electrode. All experiments were done at room temperature. AMDAN Schiff base was previously prepared and characterized[23,24] and the structure is shown in Figure 1.

RESULTS AND DISCUSSION

Electrochemical Preparation of Films

Composite films were synthesized electrochemically on a platinum disc electrode. Synthesis of material proceeded in two steps. The first step was electropolymerization of AMDAN by using sweeping cyclic voltammetry technique (CV). The polymerization solution was 1×10^{-3} M AMDAN in 0.1 M $LiClO_4$ in acetonitrile. Repetitive cyclic voltamograms for the anodic polymerization of AMDAN in potential range between −0.3 and 0.8 V (E), at scan rate 0.05 V s^{-1} (v) and for 20 scans (Figure 2a) was carried out. The first cycle in Figure 2a shows a broad peak at 0.6 V which was attributed to the oxidation of the amino group.[24] On repeating the potential scan, a pair of symmetrical peaks at 50 mV starts to appear and grow, this is due to the formation of polymer film. In the second step, the electrochemical deposition of MeHcF films was performed by continuous cycling of the potential of the working electrode (Pt|PAMDAN) in a defined potential range in a suitable aqueous

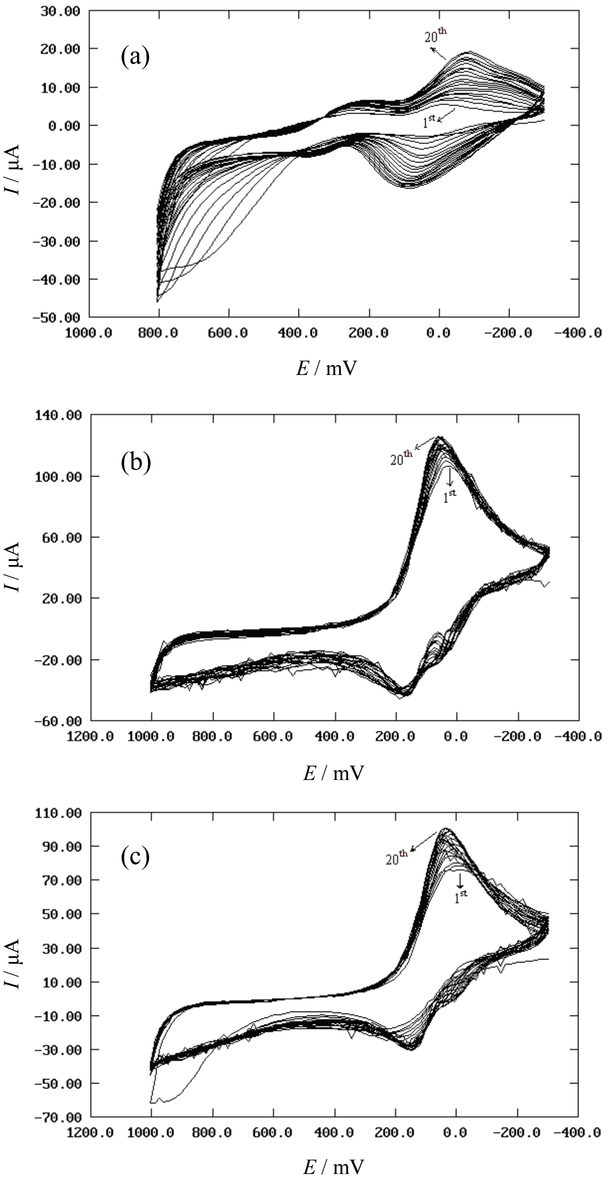

Figure 2. (a) Cyclic voltamograms of electrodeposition of PAMDAN films (inner layer) on Pt electrode from acetonitrile containing 1×10^{-3} M AMDAN and 0.1 M $LiClO_4$ at scan rate 0.05 V s^{-1} in potential range between −0.3 and 0.8 V. (b) Repeated cyclic voltamograms of electrodeposition of CuHcF on Pt|PAMDAN from aqueous solution containing 1×10^{-3} M $Cu(NO_3)_2$, 0.1 M HNO_3 and 1×10^{-3} M $K_3[Fe(CN)_6]$ at scan rate 0.05 V s^{-1} in potential range between −0.3 and 1 V. (c) Repeated cyclic voltamograms of electrodeposition of NiHcF on Pt|PAMDAN from aqueous solution containing 1×10^{-3} M $Ni(NO_3)_2$, 0.1 M HNO_3 and 10^{-3} M $K_3[Fe(CN)_6]$ at scan rate 0.05 V s^{-1} in potential range between −0.3 and 1 V.

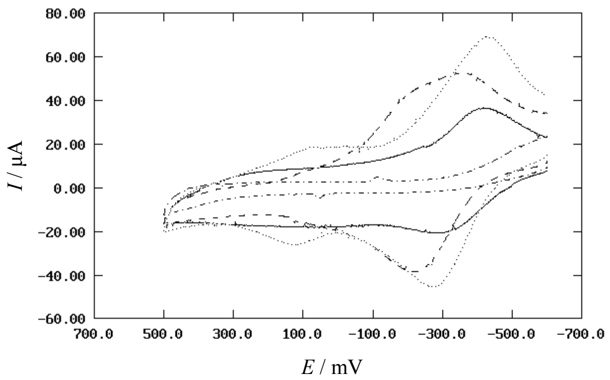

Figure 3. The cyclic voltamograms of Pt (··–··–··), Pt|PAMDAN (———), Pt|PAMDAN|CuHcF (··········) andPt|PAMDAN|NiHcF (- - - -) electrodes in 0.2 M NaCl at scan rate 0.1 V s^{-1} in potential range between −0.6 and 0.5 V. The electrodes were prepared as described in Figure 2.

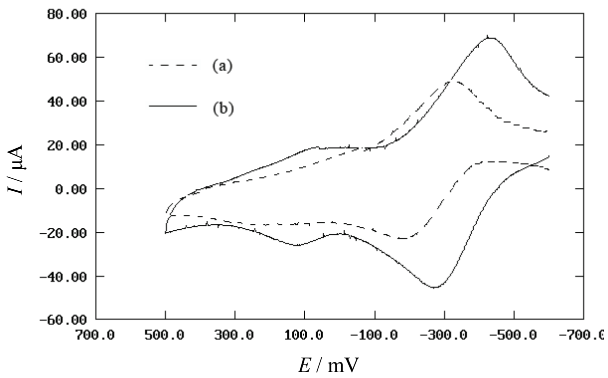

Figure 4. (a) Cyclic voltamograms of Pt|PAMDAN|CuHcF modified electrode in 0.2 M NaCl in which the inner layer (PAMDAN) prepared in 0.2 M $HClO_4$ (aqueous solution). (b) The same as in (a) except the inner layer (PAMDAN) is prepared in 0.1 M $LiClO_4$ in CH_3CN (non-aqueous solution).

solution. Typical electrochemical formation of CuHcF and NiHcF films was performed by repetitive cyclic voltammetry of the working electrode (Pt|PAMDAN) in a potential range between −0.3 and 1.0 V in a supporting electrolyte aqueous solution containing HNO_3, $K_3[Fe(CN)_6]$ and Cu^{2+} or Ni^{2+} nitrate ions respectively. By this method, composite electrodes Pt|PAMDAN|CuHcF and Pt|PAMDAN|NiHcF were prepared (Figures 2b and 2c). Single broad redox couple where obtained in two cases with a difference in peak position so for CuHcF the redox peak appear at 0.17 V and 0.08 V and at 0.15 V and 0.05 V for the redox peak in case of NiHcF. These single redox could be attributed to the M(II)-CN-Fe(III)/M(II)-CN-Fe(II) reaction.[26–28]

The redox response of bare Pt, Pt|PAMDAN, and Pt|PAMDAN|CuHcF composite electrodes were recorded in 0.2 M NaCl and the results are illustrated in Figure 3. This indicates that Pt|PAMDAN|CuHcF electrode was improve the electrochemical response compared to Pt|PAMDANmodified electrode. The composite electrode film showed a modification in current peak height which reflect the fast ionic transfer due to the presence of inner conducting polymer layer. We explore here the concept of electrostatic stabilization originating from the ability of the positively charged conducting polymer backbone (PAMDAN) to attract the negatively charged cyanometallate polynuclear inorganic species (MHcF). This was illustrate the higher ionic conductivity, higher stability of the composite electrodes compared to the single one as previously reported.[16,17]

The effect of the film thickness (no. of cycles) on the composition and electrochemical characteristics of the resulting films was investigated. The peak current of the redox peaks was taken as an index following the thickness increase of the polymer film with the number of cycles used in the polymer formation. It was found that for first layer (PAMDAN), the higher no. of cycles scans decrease the response of the composite film. This observation is in agreement with our previous results[23] that thicker films of poly(AMDAN) are more insulating than thinner ones. The optimal film thickness for first layer was found to be 20 scans. The optimal condition of the second layer thickness was also investigated and it was found to be 20 cycles for both CuHcF and NiHcF.

The influence of potential range for first and second layers was studied. It was found that the higher redox currents were obtained when polymerization potential range for the first layer was between −0.3 and 0.8 V at scan rate 0.05 V s^{-1} while for the second layer the potential range was between −0.3 and +1 V, also at scan rate 0.05 V s^{-1}.

The electrodeposition of the second layer was carried out from an aqueous solution containing 10^{-3}M $Cu(NO_3)_2$, 0.1 M HNO_3 and 10^{-3}M $K_3[Fe(CN)_6]$. In case of NiHcF layer $Cu(NO_3)_2$ was replaced by $Ni(NO_3)_2$. The mechanism of the formation of the second layer was proposed by several authors.[3,12] First, the reduction of hexacyanoferrate (III) proceeds during negative potential scan at potential below 0.3 V.

$$\mathrm{Fe^{III}(CN)_6^{3-} + e^- \rightleftarrows Fe^{II}(CN)_6^{4-}}$$

Hexacyanoferrate (II) ions which are generated in the vicinity of the electrode surface react with metal ion (Me^{II}) and the following reaction can be proposed.[27–33]

$$\mathrm{Fe^{II}(CN)_6^{4-} + Me^{2+} + 2\,K^+ \rightleftarrows K_2\left[Me^{II}\left[Fe^{II}(CN)_6\right]\right]}$$

The polymerization medium of the inner layer plays an important role in the electroactivity of the composite films. Therefore, the inner layer (PAMDAN) was prepared in acidic aqueous solution (0.2 M $HClO_4$) and non aqueous medium (CH_3CN) while the other parameters

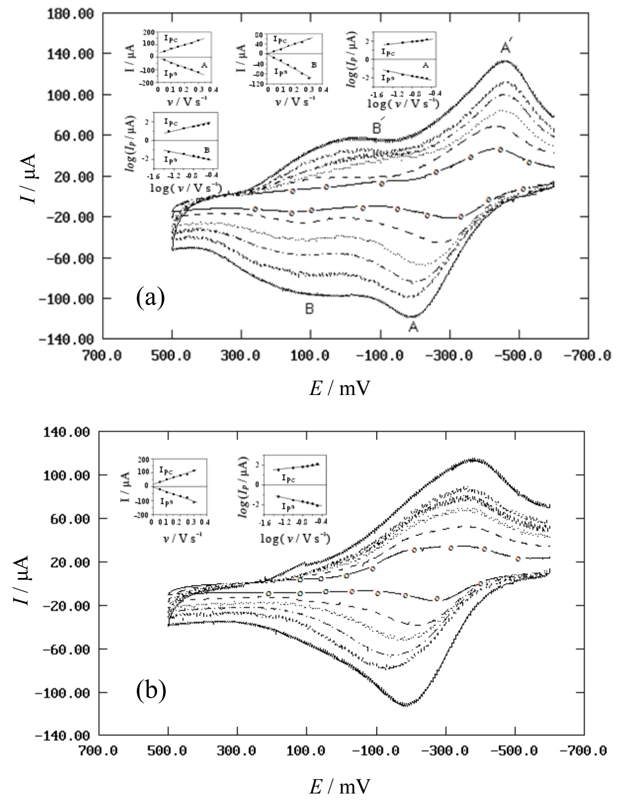

Figure 5. (a) Cyclic voltamograms of Pt|PAMDAN|CuHcF composite modified electrode at different scan rates in 0.2 M NaCl: 0.05 V s^{-1} (-o—o-),0.1 V s^{-1} (- - - -), 0.15 V s^{-1} (············), 0.2 V s^{-1}(-·-·-·-), 0.25 V s^{-1} (- - - - - -) and 0.3 V s^{-1} (———) The insets show the dependence of the anodic peak current I_{pa} and the cathodic peak current I_{pc} of Pt|PAMDAN|CuHcF on the scan rate and the plots of log I_p *vs.* log *v*. (b) Cyclic voltamograms of Pt|PAMDAN|NiHcF composite modified electrode in 0.2 M NaCl. The scan rates are the same as in (a). The insets show the dependence of the anodic peak current I_{pa} and the cathodic peak current I_{pc} of Pt|PAMDAN|NiHcF on the scan rate and the plot of log I_p *vs.* log *v*.

of preparation were kept constant. The resulting composite electrode was tested in 0.2 M NaCl as shown in Figure 4. It was clear that the composite electrode with inner layer prepared in non aqueous medium has higher response, so two redox peak appear with high peak current, compared to the composite electrode with inner layer prepared in aqueous medium which give one broad (or two overlapping redox) peak. This was attributed to the partial oxidative degradation of the inner deposited film in aqueous medium.[25,34–37] Moreover, the inner deposited film prepared in aqueous medium can hold water via hydrogen bonds in its structure, this water could provide a reservoir for the degradation side reaction, which cause low redox response.[38]

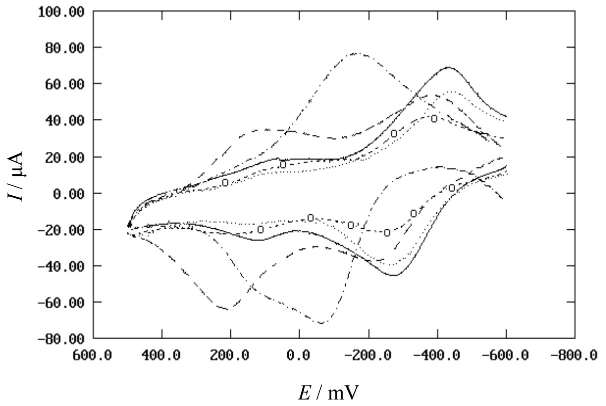

Figure 6. Cyclic voltamograms of Pt|PAMDAN|CuHcF composite modified electrode in 0.2 M of different cation electrolyte at scan rate 0.1 V s^{-1}: LiCl (············), NaCl (———), KCl (- - - -), NH_4Cl (-·-·-·-) and $CaCl_2$ (-o-o-o-). The composite electrode is prepared as shown in Figure 2b.

Electrochemistry of Pt|PAMDAN|MeHcF Composite Modified Electrodes

The electrochemical properties of the composite modified electrodes were studied in pure NaCl aqueous solution by cyclic voltammetry. Figure 3 shows the redox response of Pt, Pt|PAMDAN, Pt|PAMDAN|CuHcF and Pt|PAMDAN|NiHcF electrodes in 0.2 M NaCl. The CV of Pt|PAMDAN|CuHcF exhibits two sets of redox peaks, one at −0.3 V and the other around 0.1 V. The first peak could be attributed to the oxidation of polymer film, The second peak is due to Fe(III)|Cu(II)-CN-Fe(II) oxidation/reduction reaction.[28] In the case of Pt|PAMDAN|NiHcF electrode, single broad peak appear and there is a decreased in current height, the broadness of the cathodic peak appear clearly.

The improvement of the redox response in case of composite film could be due to the propagation of charge to the MeHcF centers incorporated in the polymeric matrix is expected to be fast and the stability increase.[2,13–15] In addition, the effect of scan rate potential on the electrochemical properties of Pt|PAMDAN|CuHcF and Pt|PAMDAN|NiHcF were studied in 0.2 M NaCl aqueous solution by cyclic voltammetry (Figures 5a and 5b) and the insets show that the plot of the anodic (I_{pa}) and cathodic (I_{pc}) peak current against the scan rate (*v*), as can be seen I_p varies linearly with the scan rate. This is typical behavior of a strongly attached, electrochemically active site and was intensively reported for thin films of conducting and redox polymers. A plot of log I_p *vs.* log *v* is indicated in the inset of Figure 5a. It can be observed that, the slopes approach unity, as predicted for an adsorbed species of film electrodes with thin film electrodes with thin-layer behavior.[24,25,26]

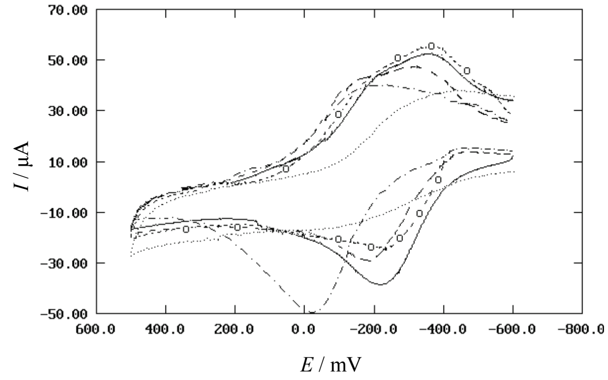

Figure 7. Cyclic voltamograms of Pt|PAMDAN|NiHcF composite modified electrode in 0.2 M of different cation electrolyte at scan rate 0.1 V s^{-1}: LiCl (············), NaCl (———), KCl (- - - -), NH_4Cl (-·-·-·-) and $CaCl_2$ (-o-o-o-). The composite electrode is prepared as shown in Figure 2c.

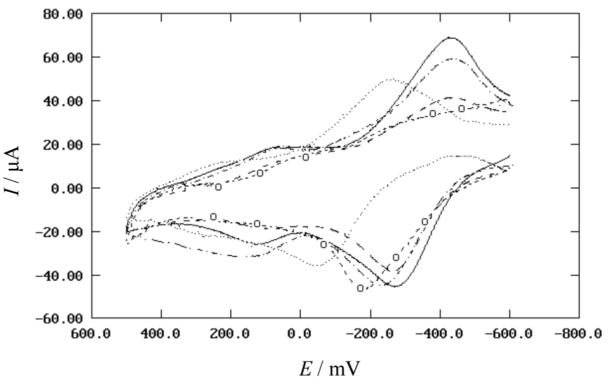

Figure 8. Cyclic voltamograms of Pt|PAMDAN|CuHcF composite electrode in 0.2 M of different anion electrolyte at scan rate 0.1 V s^{-1}: NaCl (———), NaBr (············), $NaNO_3$ (- - - -), Na_2SO_4 (-·-·-·-) and CH_3COONa (-o-o-o-). The composite electrode is prepared as in Figure 2b.

Permeability of Composite Modified Electrode Towards Counter Ion

It has been established that metal hexacyanoferrates show selective permeability towards the cations in the supporting electrolyte, such as alkali metal ions and other monovalent and divalent cations.

Figures 6 and 7 show the cyclic voltamograms of Pt|PAMDAN|CuHcF and Pt|PAMDAN|NiHcF electrodes in 0.2 M aqueous LiCl, NaCl, KCl, NH_4Cl and $CaCl_2$ solutions. The results illustrate that, the shape of the voltamograms depends on the cation present and metal in hexacyanoferrate layer. Figure 6 shows that in case of NaCl and KCl give two defined redox centers are observed with Pt|PAMDAN|CuHcF electrode, and for LiCl and $CaCl_2$ the first peak appear while the second peak is decreased while NH_4Cl give one broad redox center and there is a shoulder beside the anodic peak. Figure 8 shows also the dependence of the shape of voltamograms on the cations and all of them give one redox center, while LiCl shows the poor response. From the above results we conclude that the permeability depends on the cation and the type of MeHcF, these confirmed with the results reported in the literature. For example PB shows permeability in the order of $K^+ > Na^+ > Li^+$, similarly to the order of the radii of hydrated ions of Li^+, Na^+, and K^+ whose values are 0.12, 0.18 and 0.235 nm respectively.[39] Gao *et al.*[40] reported a permeability order of $K^+ > Na^+ > Li^+$ for CoHcF.[41,42] These permeability orders are in accord with the order of the hydrated ionic radii. However, Wu *et al.*[44] reported that the permeability of MeHcF towards supporting cations is in the order of $K^+ > Li^+ > Na^+$ which is not in accord with the order of the hydrated ionic radii.[44,45] Thus, the hydrated ionic radius of the insertion ion is not exclusively the determining factor. The permeability of MeHcF towards counter cations is such a complicated problem that there is a great difference in the permeability of the hexacyanoferrates. Besides the radius of the cation, the major factors influencing the permeability of the cation also include the radius of the ion channel in hexacyanoferrates, the interactions between the cation and the hexacyanoferrate, including the electrostatic interactions and ionic polarities and the dehydration ability of the cation before entering the channel of the hexacyanoferrate.[46,47]

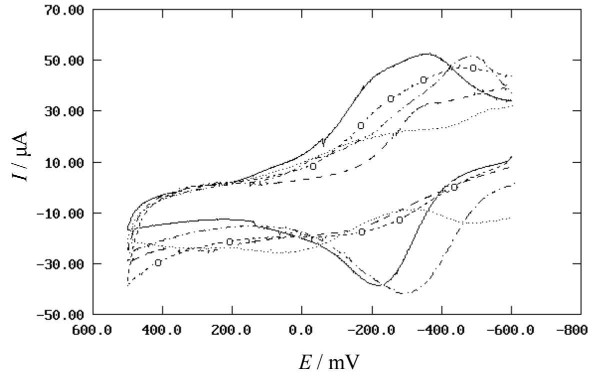

Figure 9. Cyclic voltamograms of Pt|PAMDAN|NiHcF composite electrode in 0.2 M of different anion electrolyte at scan rate 0.1 V s^{-1}: NaCl (———), NaBr (············), $NaNO_3$ (- - - -), Na_2SO_4 (-·-·-·-) and CH_3COONa (-o-o-o-). The composite electrode is prepared as in Figure 2c.

The redox response of the composite electrodes was found depends also on the nature of the anion of the supporting electrolyte, Figures 8 and 9 illustrate the influence of nature of anion on the redox response of the composite electrodes, the results show that the shape of the voltamograms depends on the anion used in the supporting electrolyte which reflect the role of the anion mobility within the composite electrode also the nature of metal in MeHcF layer affect on the change in radius of the ion channel in HcF.[11,28,48–50]

Effect of Electrolyte Concentration on the Redox Response of Composite Modified Electrodes

The electrolyte concentration was investigated to study its influence on the redox response of composite electrode. Therefore, NaCl solution was used in concentration range between 0.1 and 1 M. Figure 10 shows the cyclic voltamograms of the composite Pt|PAMDAN|CuHcF in different NaCl concentration. The results illustrate that the best response of the composite film was given with 0.2 M NaCl. It can be observed that both anodic and cathodic peak currents depend on the electrolyte concentration, which indicate that the electrochemical reaction of CuHcF is accompanied by the transfer of an electron and Na^+ ion (counter cation) to maintain charge balance during the electrochemical reaction process of CuHcF.[28,41,42,45] The same results obtained in case of Pt|PAMDAN|NiHcF composite electrode.

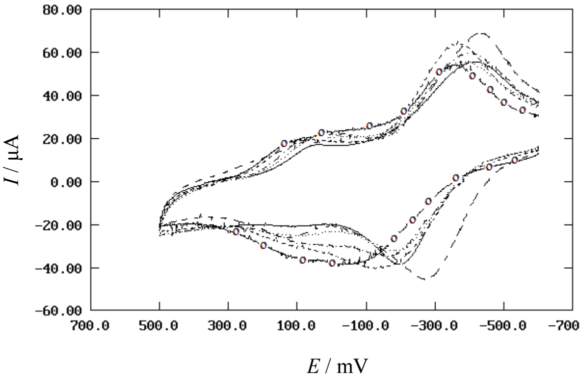

Figure 10. Cyclic voltamograms of Pt|PAMDAN|CuHcF composite electrode in different concentration of NaCl electrolyte solution: 0.1 (———), 0.2 (- - - -), 0.3 (··········), 0.4 (-·-·-·-) and 1 mol dm^{-3} (-o-o-o-). The composite electrode is prepared as in Figure 2b.

Stability of the Composite Modified Electrodes

For many applications, the stability of the modified electrode is of a great importance so the stability of the prepared electrodes was investigated by cyclic voltammetry. The peak current was considered as a factor indicating the stability of the modified electrodes at various conditions of operation. It was found that the modified electrodes when subjecting to the long term cyclic voltammetric potential cycling in 0.2 M NaCl aqueous solution, and to air for about 48 h after that tested in NaCl solution. In both cases the modified electrodes showed a constant response without much change in peak potential and peak current, which reflect the stability of the modified electrodes. This is especially useful for the electrocatalytic study and in energy storage application batteries.[12,18,19,51]

CONCLUSION

We demonstrate here the possibility of preparation of composite films containing MeHcF within PAMDAN matrix that are capable of fast delivery of charge to the metal hexacyanoferrate redox centers the attractiveness of the composite system concerns the fact that the formal potential of Mehcf redox process lies in the potential range where PAMDAN is conductive.

Hybrid organic-inorganic materials can be obtained by electrodeposition using potential cycling method. The electrochemical behavior of the composite modified electrodes were studied in electrolyte solution containing various cations *e.g.* Li^+, Na^+ ,K^+, NH_4^+ *etc.* Also the nature of anion in electrolyte was examined. One may conclude that formation of composite systems between redox networks and electroactive polymers is a simple manner for producing stable material showing fast ion transport and increased chemical stability in comparison with simple inorganic predisposed MeHcF films. Finally, the whole concept of fabrication of such hybrid films may lead to the development new materials for charge storage devices (capacitors), charge mediators (relays) and electrocatalysies systems. Further research is necessary along this line.

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SAŽETAK

Složeni tanki slojevi metalnog heksacijanoferata i derivata poli(1,8-diaminonaftalina): elektrosinteza i svojstva

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Opisane su pojedinosti potenciodinamičke metode pripreme tankih slojeva smjese heksacijanoferata nikla (II) i bakra (II) (MeHcF) i poli[8-(3-acetilimino-6-metil-2,4-dioksopiran)-1-aminonaftalina] (PAMDAN) na površini platinske elektrode (Pt|PAMDAN|MeHcF). Cikličkom voltametrijom praćen je rast unutrašnjeg (PAMDAN) i vanjskog sloja (MeHcF) taloženjem iz otopine. Modificirana elektroda ima poboljšane redoks odzive. Njene voltametrijske karakteristike istražene su u otopinama Li$^+$, Na$^+$, K$^+$ i NH$_4^+$ iona. Heterogeni prijenos elektrona i stabilnost modificirane elektrodne površine istraženi su višestrukom cikličkom voltametrijom u 0,2 M NaCl. Eksperiment je ponovljen nakon izlaganja elektrode zraku tokom 48 sati. Složeni tanki sloj ima višu ionsku vodljivost i veću stabilnost, nego čisti sloj MeHcF. Veću vodljivost uzrokuju molekule elektroaktivnog polimera u unutrašnjem dijelu tankog sloja.