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Electrochemical and electrocatalytic properties of hybrid films composed of conducting polymer and metal hexacyanoferrate

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Abstract

Hybrid organic/inorganic modified electrode, composed of poly 2-(4-aminophenyl)-6-methylbenzothiazole (PABT) matrix and Prussian blue (PB) like nickel hexacyanoferrate redox centers (PABT/NiHcF), showed reversible electrochemical behavior in aqueous electrolytes. Platinum disk (Pt) was used as a conductive substrate onto which the composite film was electrodeposited by potential cycling. Electrochemical behavior of the modified electrode was well characterized using cyclic voltammetry (CV). The voltammetric characteristics of the composite modified electrodes were also investigated in presence of different alkali metal cations (Li^+, Na^+, K^+ ,Ce^+ 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. Bilayer composite electrodes exhibit higher ionic conductivity, higher stability in comparison with pure inorganic (MeHcF) films. The inner electro active polymer chains in the film cause enhancement in the electric conductivity of the composite electrodes. The modified electrode presented a good electrocatalytic activity towards the oxidation of methanol (MeOH), and oxalic acid $(COOH)_2$.

Keywords: Modified electrodes, Electropolymerization, Nckel (π) hexacyanoferrate, Electro catalytic oxidation, Electrochemical stability, Composite electrode.

1. INTRODUCTION

Modification of electrode surfaces with electro active materials is an important and interesting area of research in electrochemistry for more than two decades. Various organic and inorganic modifiers have been immobilized on electrode surfaces to prepare chemically modified electrodes.[1–5] Among the inorganic materials, transition metal hexacyanoferrates (MeHcF) have been studied extensively because of their outstanding properties. These compounds show reversible insertion electrochemistry,[6,7] electrochromism,[8,9] the capability to be used in rechargeable batteries[10,11] and possess electrocatalytic activities.[12,13] Hybrid materials were obtained as a two layer composition with an organic polymer sub-film and inorganic MeHcF cover. Opposite geometry is also proposed in some cases.[14-18] Despite a sequence in the film preparation, an electrochemical way can be used for synthesis of both polymer and MeHcF., chemical way is also applied.[16,19,20] The electrochemical deposition process that leads to the formation of the hybrid modified electrode on the Pt electrode surface needs to be carefully controlled. The fabrication of a chemically modified film electrode is easily controlled by using consecutive cyclic voltammetry (CV) a synthetic procedure, in which an increase in the peak current of the film forms an appropriate redox couple for the modified film.[20] In our previous study, ABT was polymerized in non aqueous medium and give an electro active film, also the ABT can copolymerized with different concentration of aniline and give stable copolymers films with reasonable redox response.[21,22] Here we try to improve the PABT modified electrode, by formation a composite modified electrode the inner organic polymer film PABT and outer layer composed of inorganic NiHcF cover.[23-27] This layer can be formed as the equation (1).

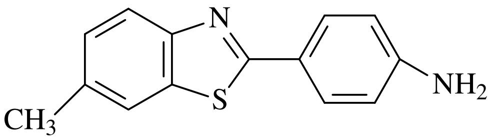
$$\begin{tikzcd}
{[\,Fe\,(CN)_6]^{-4} + Ni^{+2} + 2\,K^{+1}} \arrow[r, shift left] & {K_2\,Ni^{+2}\,[Fe(CN)_6]} \arrow[l, shift left, "\text{Chemical reaction}"] \arrow[d, shift right, "+e^-"'] \\
 & {K\,Ni^{+2}\,[Fe^{+3}(CN)_6] + K^+ + e^-} \arrow[u, shift right, "-e^-"']
\end{tikzcd} \quad \text{........ (1)}$$

Electrochemical reaction

This paper reports the successful preparation hybrid modified electrode on Pt electrode surface (Pt/PABT/NiHcF) by repetitive CV scans, to improve the electrochemical behavior of the prepared modified electrode. The influence of several parameters e.g.electrolyte composition, scan rate and potential limits as well as their behavior in various alkali metal electrolyte. The electrocatalytic oxidation properties of some organic compounds e.g. MeOH and $(COOH)_2$ will be examined.

2. EXPERIMENTAL

The structure of ABT shown in Fig. 1, acetonitrile (CH_3CN), lithium perchlorate ($LiClO_4$), hydrochloric acid (HCl), nitric acid (HNO_3), sulfuric acid (H_2SO_4), nickel chloride ($NiCl_2$), potassium ferrocyanide [$K_3Fe(CN)_6$], potassium chloride (KCl), lithium chloride (LiCl), sodium chloride (NaCl), cesium chloride (CsCl), ammonium chloride (NH_4Cl), oxalic acid $(COOH)_2$ and methanol (MeOH) were analytical grade chemicals (Aldrich) and used without further purification. Aqueous solution was prepared from bidistilled water. Electrochemical measurements were carried out using the EG&G PAR computer measuring system (model 250) and X-Y Hewlett-Packarad recorder model 7440. A three electrode electrocatalytic cell (bioanalytical system, model C-1A) with a platinum disc electrode (Pt) 3.0 mm diameter was used as working electrode, a platinum sheet (area 2 cm^2) as a counter electrode and (Ag/AgCl) reference electrode. All experiments were done at room temperature. The structure of (ABT) is shown in Fig. 1.



2-(4-Amino phenyl)-6-methyl-benzotghiazole

Figure 1. The structure of monomer

3.RESULTS AND DISCUSSION

3.1. Electrochemical synthesis of Pt/PABT/NiHcF composite electrodes.

The working Pt electrode was polished on polishing cloth prior to use, the inner polymer film PABT was deposited onto the Pt electrode by using cyclic voltammetric technique in CH_3CN containing 0.1 M $LiClO_4$ and 10^{-3} M ABT monomer. The electrode potential was swept continuously at a scan rate 0.05 V/s for 20 scans in potential range between - 0.2 and 0.8 V vs. Ag/AgCl. The monomer electrooxidized irreversibly in one anodic peak at 660 mV (From the first potential scan).

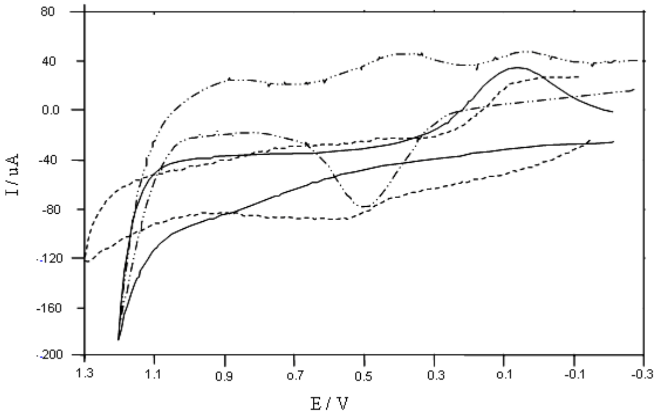


Figure 2. Cyclic voltammograms of .-.-.-.) Pt/PABT/NiHcF composite electrode in 0.2 M HCl. _____) The Pt/PABT, this layer formed from nonaqueous solution containing 10^{-3} M ABT and 0.1 M $LiClO_4$ in CH_3CN, using potential range – 0.2 to 0.8 V vs. Ag/AgCl for 20 scans at scan rate = 0.05 V/s, ------) the Pt/NiHcF, this layer formed from 0.4 M KCl, 0.4 M HCl, 0.05 M $K_3[Fe(CN)_6]$ and 10_{-3} M $NiCl_2$, using potential range - 0.3 to 1 V vs. Ag/AgCl for 30 scans at scan rate = 0.05 V/s.

On subsequent scans the anodic peak shifted to less positive potential with decreasing magnitude of the peak currents due to the consumption of monomer in the vicinity of the electrode. After the film formation, the electrode was rinsed thoroughly before being transferred to a solution of 0.2 M HCl. The redox response of the polymer was shown in Fig. 2 The electro deposition of outer coating layer NiHcF was achieved by applying CV in aqueous solution containing 0.4 M KCl , 0.4 M HCl, 0.05 M $K_3[Fe(CN)_6]$ and 10^{-3} M $NiCl_2$. Typically 30 full potential scans, starting from - 0.3 V and ending at 1 V, were applied at a scan rate of 0.05 V/s NiHcF layer electrooxidized irreversibly in one cathodic peak at 5.5 V .

The redox response of pt/NiHcF, Pt/PABT, and Pt/PABT/NiHcF composite electrodes were recorded in 0.2 M HCl and the results are illustrated in Fig. 2 which shows that Pt/PABT give cathodic peak at ~ 0.09 V, the Pt/NiHcF give redox polymer at 0.09 V for cathodic peak and its anodic response at 0.55 V. The Pt/PABT/NiHcF give a redox response the anodic peak appear at 0.4 V and cathodic peak at 0.5 V. This indicates that Pt/PABT/NiHcF electrode was improving the electrochemical response compared to Pt/PABT modified electrode and to Pt/NiHcF. The composite electrode film showed a modification in current peak height which reflects 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 (PABT) to attract the negatively charged cyanometallate polynuclear inorganic species (MeHcF). This was illustrate the higher ionic conductivity, higher stability of the composite electrodes compared to the single one as previously reported.[28,29,30]

3.2. Electrochemistry of the Pt /PABT/NiHcF composite modified electrode

In order to analyze the effect of the presence of a layer on the other one, the electrochemical behavior of Pt/PABT/NiHcF electrode has been studied in aqueous solution. Fig. 2 shows the CVs response of the bilayer modified electrode in 0.2 M HCl. The voltammogram illustrates that, the appear of a pair of redox couple (oxidation peak at 0.5 V and the corresponding cathodic peak at 0.4 V. These redox couple correspond to $Fe^{+3}[(CN)_6]^{-3}/Fe^{+2}[(CN)_6]^{-4}$ system.[31,32] Comparison with the response of Pt/PABT in a similar solution is possible by looking at Fig. 2 The obtained results show that NiHcF layer greatly improves the electrochemical properties of the Pt/PABT electrode and the hybrid (Pt/PABT/NiHcF) modified electrode exhibits faster electron transfer rate. In order to study the nature of electrode process occurring at the electrode surface, CVs were recorded for the modified electrode at various scan rates (0.005 to 0.3 V/s). The results obtained are shown in Fig. 3. It is observed that as the scan rate increases the peak current as well as peak-to-peak separation increases (at scan rate 0.005 V/s oxidation peak at 0.45 V and reduction peak at 0.4V, at scan rate 0.3 V/s oxidation peak at 0.65 V and reduction peak at0.45 V). The peak-to-peak separation varies from 0.1 to 0.25 V on varying the scan rate from 0.005 to 0.3 V/s. For ideal behavior of the modified electrode, the peak-to-peak separation should be zero. The higher peak separation and larger peak width are normally observed with all modified electrodes are attributed to the non ideal behavior of the electrode. The peaks are not perfectly symmetrical about the E value, probably resulting from the difference in the background currents plus some kinetic limitations in the redox reaction. Further, the peaks are quite broad and it is not clear to what extent the brooding is due to the repulsive interactions between the electro active sites and/or the electrochemical non equivalence of the sites.[33,34]

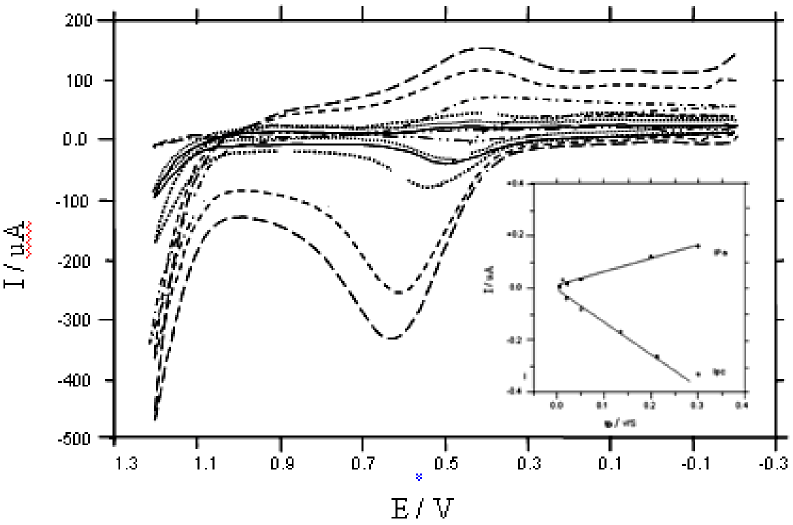


Figure 3. Cyclic voltammograms of Pt/PABT/NiHcF composite electrode in 0.2 M HCl at various scan rates, –··–··–) 0.005 V/s, ··········) 0.01 V/s, _____) 0.02 V/s, ···· ····) 0.05 V/s, , ------) 0.2 V/s and —— ——) 0.4 V/s. Inset shows the dependence of the anodic peak current (Ipa) and cathodic peak current (Ipc) on the scan rate of Pt/PABT/NiHcF composite electrode. The composite film formed as in Fig. 2.

Moreover, the inset of Fig. 3 illustrates that the anodic peak current and cathodic peak current (Ip_a, Ip_c) have a linear relation with scan rate, also with square root of scan rate (not shown) which corresponding to a diffusion controlled quasi reversible reaction and indicating that the electrode reactions of the film are phenomenological equivalent to those of surface attached redox species.

3.3. NiHcF film deposition in different univalent metal chloride solution.

The electrochemical deposition of second layer (NiHcF) films were prepared using consecutive CVs in different 0.2 M univalent metal solution e.g. Li^+, K^+, Na^+, Cs^+ and NH_4^+ aqueous chloride solutions. It was found that the electrochemical response of the composite modified electrode depended on the monovalent cation in the electrolyte used in the synthesis conditions. Fig. 4 shows the redox response of the prepared films in 0.2 M HCl. The results show that the redox response of films were cation dependent. So the profile of redox response of the monocations different from each other depending on the ionic radii of $Li^+ < K^+ < Na^+ < NH_4^+ < Cs^+$. The redox response of the film in case of small radii Li^+, Na^+ and K^+ were electroactive (as shown in Fig. 4). While in case of large ionic radii e.g. Cs^+ film is inactive.[31,35]

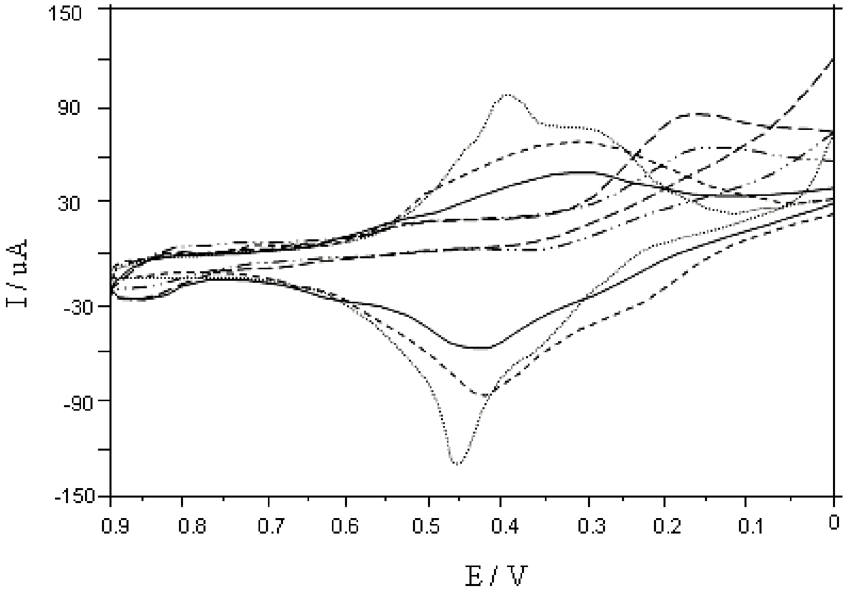


Figure 4. Cyclic voltammograms of Pt/PABT/NiHcF composite electrode in 0.2 M HCl of different cations of chloride solution, ––––) 0.4 M CsCl, –··–··) 0.4 M NH_4Cl ------) 0.4 M KCl, ·········) 0.4 M LiCl and ———) 0.4 M NaCl at scan rate = 0.1 V/s. The composite film as in Fig. 2.

3.4. *Effect of nature of supporting electrolyte.*

It is well known that the electrochemical behavior of hybrid modified electrodes is affected also by the type of the cations in the supporting electrolytes.

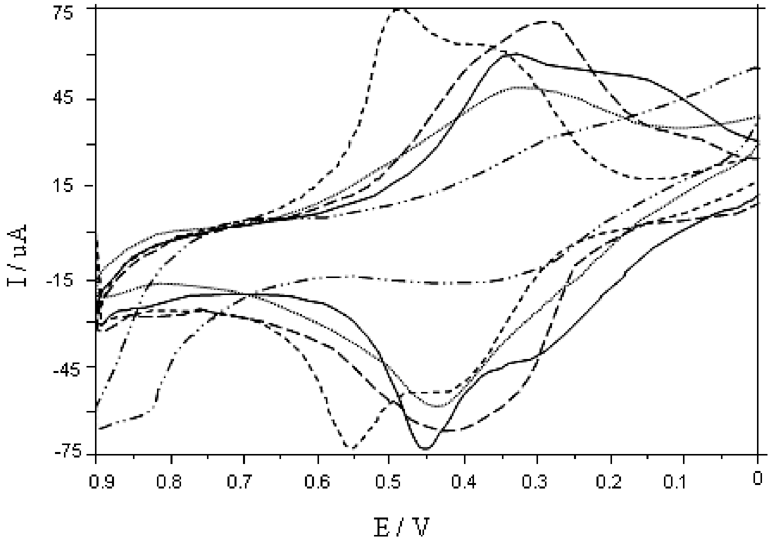


Figure 5. Cyclic voltammograms of Pt/PABT/NiHcF composite electrode in 0.2 M of different cations of chloride solution at scan rate = 0.1 V/s, ·········) HCl, ———) LiCl, ------) NaCl, –––––) KCl and –··–··–) CsCl. The film formed as in Fig. 2.

Fig. 5, presents comparative cyclic voltammograms for the modified electrode in six kinds of solutions with different supporting electrolytes. It is well known that NiHcF film is permeable membrane for cations such as H^+, Li^+, K^+, Na^+, Cs^+ and NH_4^+. These cations can react with inorganic film by incorporation into their net structures, to maintain charge balance, The redox process observed is accompanied by the incorporation of cations from the electrolyte solution. During the PABT/NiHcF oxidation/reduction process the cations in corporation is a complicated problem, so several reports indicate that the permeability of HcF depends on hydrated ionic radii of cations.[36-42] However other reports indicate that the permeability not in according with the order of hydrated ionic radii.[42-45] Thus the hydrated ionic radius of the insertion ion is not exclusively the determining factor. The permeability of MeHcF towards counter-cations is such 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 HcF. The interactions between the cation and the NiHcF, including electrostatic interactions the ionic polarities, and the dehydration ability of the cation before entering the channel of HcF, etc.[46,47] It seems that Na^+ ion matches the ion channel of NiHcF most closely and NiHcF possesses the best selectivity for Na^+ ion as a counter ion of the above monocations. This property of the hybrid NiHcF may be used for cation recognition.[45] The effect of anions of the electrolyte on the electrochemical behavior of the Pt/PABT/NiHcF modified electrode was also studied in solution of different anions, viz. Cl^-, NO_3^-, SO_4^{2-}, ClO_4^- and CH_3COO^- ions and the results are shown in Fig. 6.

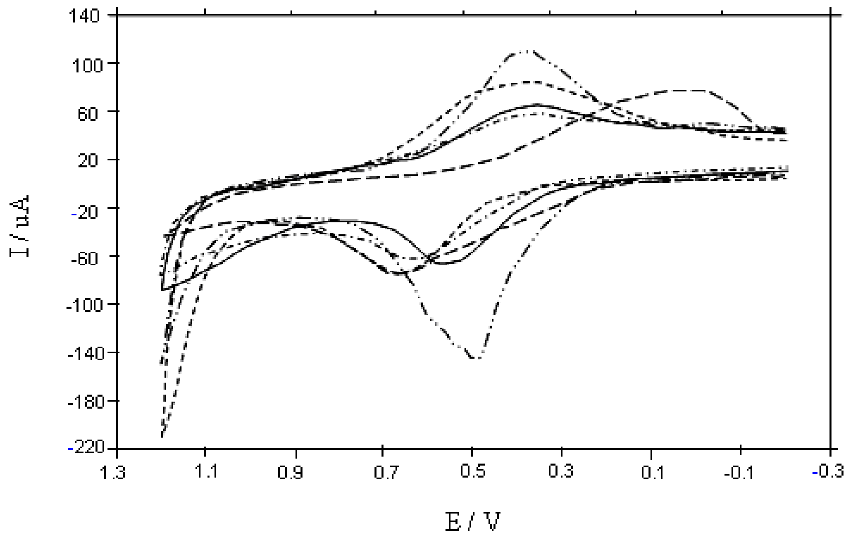


Figure 6. Cyclic voltammograms of Pt/PABT/NiHcF composite electrode in 0.2 M of different anions at scan rate = 0.1 V/s, –··–··–) HCl, ----) $HClO_4$, ——) HNO_3, ··–·–·) H_2SO_4 and - – –) CH_3COOH. The composite electrode prepared as in Fig. 2.

The anion mobility within the hybrid film would be limited by the cavity size and would then determine the electrochemical activity on the redox process of the hybrid film. Fig. 6 shows that the electro activity of the hybrid film is clearly influenced by the nature of anion in electrolyte solution and the activity decrease in order $Cl^- > ClO_4^- > NO_3^- > SO_4^{2-} > CH_3COO^-$. The explanation of such behaviour is that when the anion size increased the mass transport and the mobility of anion within the hybrid film tends to diminish and consequently the redox current decreases.[48-51]

3.5. Effect of supporting electrolyte concentration

The effect of electrolyte concentration on the redox response of the composite electrode was investigated.[52,53] For this reason the redox response of the composite electrode was measured at different concentration of NaCl in the range between 0.1 to 1 M. These results show the participation and involvement of electrolyte ions in the redox process.

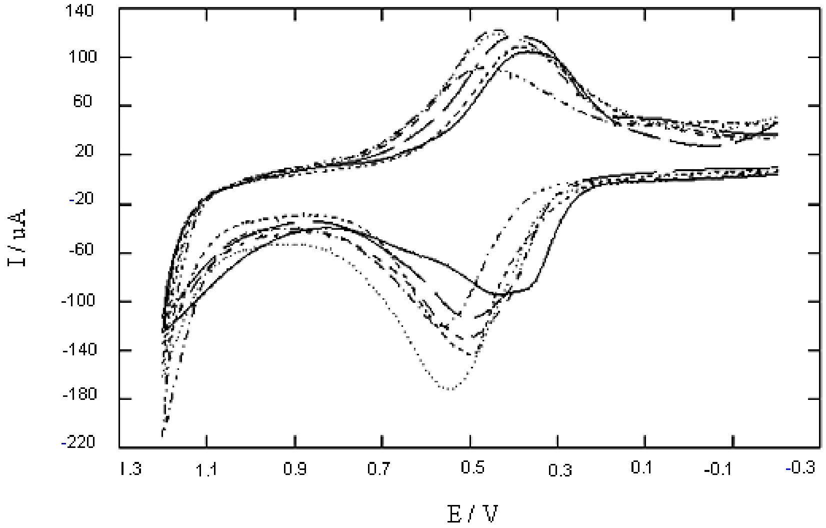


Figure 7. Cyclic voltammograms of Pt/PABT/NiHcF composite electrode in different concentrations of NaCl electrolyte solution at san rate = 0.1 V/s ,——) 0.1 M, - - - -) 0.2 M, — —) 0.4 M, - – -) 0.6 M, ······) 0.8 M and - · – · –)1 M. The composite electrode prepared as in Fig. 2.

Fig. 7 shows the cyclic voltammmgrams of the hybrid (Pt/PABT/NiHcF) modified electrode in NaCl solutions of different concentration (0.1 to 1 M) at scan rate of 0.1 V/s in potential range -0.2 V to 0.1 V. The figure illustrates that each redox cyclic voltammograme give single redox response with anodic peak and cathodic peak. It can be observed that both anodic and cathodic peak currents increase with increasing in the concentration of NaCl in range (0.1 to 0.8 M), after that the peak current decrease with increase in concentration, This may be due to the interaction in the electrolyte solution between positive and negative ions.

3.6. Stability of the hybrid modified electrode

The stability of the Pt/PABT/NiHcF modified electrode was studied during potential cycling and long-term usage. The effect of potential cycling on the hybrid modified electrode was carried out for this purpose. The repetitive cyclic voltammograms were recorded as the potential was scanned between 0 and 0.9 V (vs. Ag/AgCl) with scan rate of 0.1 V/s. It is noticeable that the deposited film is stable for more potential cycles. The peak current of the hybrid film was considered as a factor indicating the stability of the modified electrode. The anodic peak potential at 0.55 V unchanged but the anodic peak current changed some what the modified electrode in 0.1 M NaCl repeated for 200 cycles. The modified electrode showed good stability in acidic solution was shown in the Fig. 8. The above results indicate that the hybrid modified electrode is fairly stable; this confirmed the formation of hybrid film increase and improve the stability of the modified electrode.

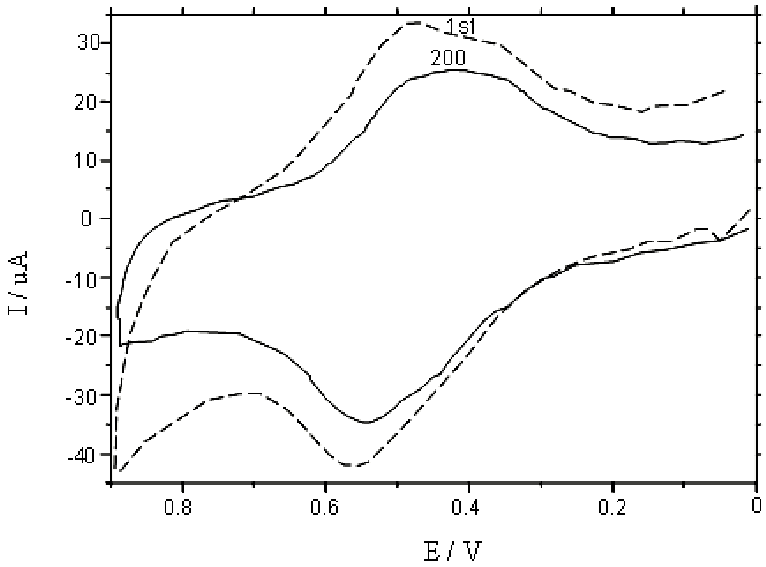


Figure 8. Cyclic voltammograms of Pt/PABT/NiHcF composite electrode in 0.1 M NaCl for 200 scans at scan rate = 0.1 V/s. The composite electrode prepared as in Fig. 2.

3.7. Electro catalytic behavior of Pt/PABT/NiHcF hybrid film

The electro catalytic behavior of Pt/PABT/NiHcF hybrid modified electrode towards the oxidation of MeOH and $(COOH)_2$ was examined.

3.7.1. Mediated oxidation of MeOH at hybrid modified electrode

The catalytic oxidation of MeOH at hybrid Pt/PABT/NiHcF modified electrode is demonstrated in Fig. 9. The oxidation of MeOH occurs at about 0.68 V and the reduction peak appear at 0.65 V at Pt/PABT/NiHcF hybrid modified electrode. The methanol not oxidized at bare Pt electrode as shown in Fig. 9. The cyclic voltammograms illustrate that the hybrid film able to catalyse the oxidation of MeOH .The modified electrode showed good stability for scan repetition (200 scans) in MeOH solution as shown in the Fig. 9.

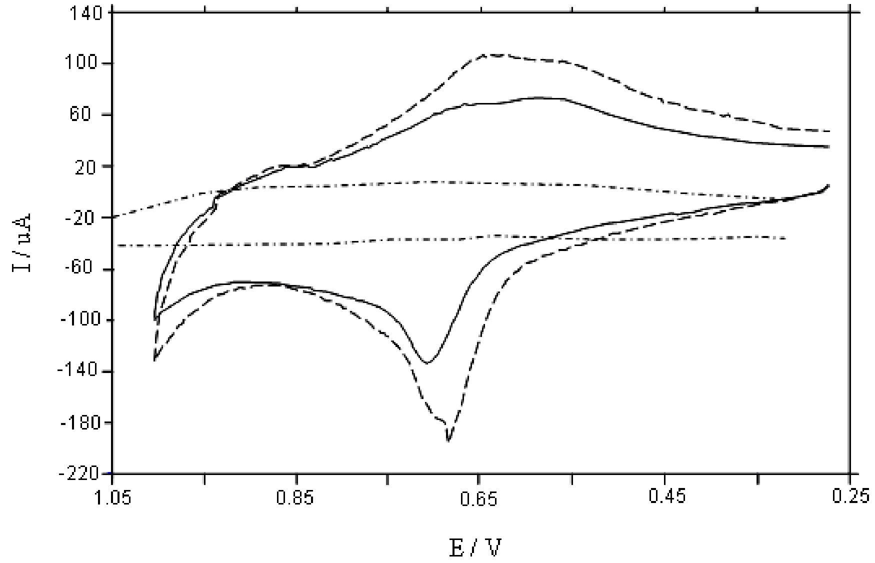


Figure 9. Cyclic voltammograms of ----) Pt/PABT/NiHcF in 0.1 M methanol soluble in 0.2 M NaCl after one cycle, ———) Pt/PABT/NiHcF in 0.1 M methanol soluble in 0.1 M NaCl after 200 cycles and -·-·-) bare electrode in the same solution. The composite electrode prepared as in Fig. 2.

3.7.2. Mediated oxidation of $(COOH)_2$ *at hybrid modified electrode*

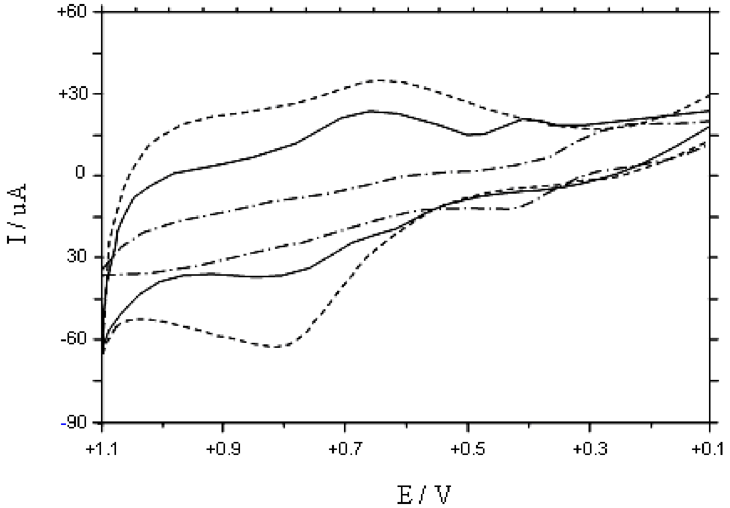


Figure 10. Cyclic voltammograms of ----) Pt/PABT/NiHcF in 0.1 M oxalic acid soluble in 0.2 M NaCL after one cycle, ———) Pt/PABT/NiHcF in 0.1 M in 0.1 M oxalic acid soluble in 0.8 M NaCL after 200 cycles and -·-·-) bare electrode in the same solution. The composite electrode prepared as in Fig. 2.

The electro catalytic activity of the hybrid Pt/PABT/NiHcF modified electrode was examined for the electrooxidation of $(COOH)_2$ at hybrid modified electrode is presented in Fig. 10 the film gives one anodic peak at 0.8 V and two cathodic peaks at 0.95 V and 0.6 V. As seen, the modified electrode catalyze the oxidation process compared to the bare Pt electrode ,also the film shows a stability towards scan repetition(200 scans)in the$(COOH)_2$ solution as showen in the Fig.. The above results illustrate that the electrocatalytic oxidation of MeOH and $(COOH)_2$ occurred at hybrid modified electrode. We can conclude that the hybrid modified electrode can catalyze the oxidation of MeOH and $(COOH)_2$.

4. CONCLUSION

Using consecutive CVs, Pt/PABT/NiHcF hybrid modified electrode was successfully synthesized directly by deposition of PABT and then NiHcF on the electrode surface. The NiHcF depends on the type of the monovalent cation of electrolyte during layer-deposition also the nature of electrolyte during the redox response. The nature of supporting electrolyte (cations and anions) in the redox response process has an important effect on the redox reaction and consequently on the current peak . Hybrid organic/inorganic material can be obtained by direct synthesis of inorganic redox networks on an organic polymer layer. One may conclude that formation of composite system between redox networks and organic polymer is a simple manner for producing stable material showing fast ion transport and increased chemical stability in comparison with single pure layer films, exhibit redox couple activity at a potential dependent on the kind of the inorganic part of the hybrid material. Hybrid material exhibits high stability and faster ionic transport in comparison with pure inorganic film and pure polymer layer film. Stability of the hybrid modified electrode can be studied by using repeating scan method, the composite films show good stability compared to the pure one. Electrodes modified with PABT/NiHcF have good electrocatalytic effect towards, oxalic acid and MeOH electro oxidation.

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