

ELECTROCHEMICAL BEHAVIOR OF GC, Pt AND Au ELECTRODES MODIFIED WITH THIN FILM OF COBALT HEXACYANOFERRATE

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Abstract

A thin film of cobalt hexacyanoferrate (CoHCF), an analogue of mixed-valence Prussian blue, was deposited electrochemically on the glassy carbon, platinum and gold electrode surfaces in 0.5M KCl solution. The electrochemical behavior of these modified electrodes show three couples of redox peaks by CV in a supporting electrolyte solution of 0.5M NaCl, whereas for Au modified electrode only one couple of redox peaks is observed because of self-oxidation of gold substrate at more positive potentials. The effect of various factors such as cations and anions of supporting electrolyte, solution pH, scan rate and the limit of sweeping potential on the CV response of modified electrodes was also studied. It was shown that the electrodeposited CoHCF film is stable for several days, whether stored at open circuit in a 0.5M KCl or NaCl supporting electrolyte or in air.

Introduction

In recent years, there has been a growing interest in chemically modified electrodes and their potential use in electrochromic sensors, energy conversion and electrocatalysis [1-3]. Among the various compounds used as electrode surface modifiers, the hexacyanoferrates of transition metals have attracted much attention [4-21]. This may be due mainly to the good mechanical and electrical properties of these compounds. Some of the hexacyanoferrates such as Prussian blue (PB) [22-24] and cobalt hexacyanoferrate (CoHCF) [16] show two sets of redox couples, i.e. $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ and M_{ox}/M_r , during the variation of electrode potential. Such a characteristic favours the use of electrodes modified with these compounds as electron transfer mediators in the preparation of CMEs.

The first attempt in this domain was made by Neff and coworkers [22] in the preparation of iron(III)

hexacyanoferrate (Prussian blue) coated electrodes. Thereafter, electrodes modified by various hexacyanoferrates have been prepared by others [4, 9, 12, 16, 25-28]. Among these, the preparation of wax impregnated graphite electrodes, (WIGE), modified by a thin film of CoHCF has been reported by J. Joseph *et al.* [16]. Later, Z. Gao *et al.* reported the electrochemical and spectroscopic characteristics of CoHCF modified electrode prepared by derivatization of cobalt film deposited on a glassy carbon matrix in hexacyanoferrate solution [29]. However, the preparation of CoHCF on the surface of other electrodes such as GC, Pt and Au from an aqueous solution containing Co(II) and hexacyanoferrate has not previously been described. In the present study, a thin film of CoHCF was deposited electrochemically on the GC, Pt and Au electrodes and the properties of the said electrodes were studied in some detail.

Experimental Section

The electrodeposition cell was a conventional three-electrode system. The working electrodes were a platinum, gold or a glassy carbon disc (5 mm, 3 mm and 3 mm

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1 diameter respectively and from Beckman USA or Metrohm Switzerland). Each of the working electrodes was cleaned by polishing with 0.5 μm alumina and washed thoroughly with sulfuric acid, acetone and water successively before electrodeposition of CoHCF film. Reference and auxiliary electrodes were a KCl saturated calomel electrode (SCE) and platinum wire respectively.

Electrochemical measurements were performed with a potentiostat E626 (from Metrohm), used as potentiostat, connected to a function generator (VA Scanner E612 from Metrohm) and a Hewlett-Packard 7303A X-Y Recorder. The CoHCF thin film modified electrodes were prepared in an aqueous solution of 0.5M KCl containing 1 mM CoCl_2 and 0.5 mM $\text{K}_3\text{Fe}(\text{CN})_6$. The film deposition was implemented by cycling the potential between 0 and 1000 mV at 100 mVs^{-1} for the GC and Pt electrodes and between 0 and 800 mV at 100 mVs^{-1} for the Au electrode. By recording the voltammogram, evidence of film formation was observed on the first cycle and the growth of the film with time was apparent. The electrodes, after the deposition of a certain amount of CoHCF, were rinsed with water and immersed in an aqueous solution of 0.5 M NaCl for further examination.

Experiments were conducted at a temperature of $5(\pm 1)^\circ\text{C}$. All chemicals were of analytical grade, and solutions were prepared with bidistilled water.

Results and Discussion

Modification Process

Figure 1 shows the cyclic voltammograms obtained during the growth of CoHCF film on glassy carbon electrode from solution containing the components CoCl_2 , $\text{K}_3\text{Fe}(\text{CN})_6$ and KCl (see Experimental). Initially, two sets of redox peaks are observed, but as the film grows, the second anodic peak merges into the first one and appears as a shoulder of it. Moreover, by increasing the cycles of potential, the rate of film formation at electrode surface decreases gradually, probably because of the formation of sparingly soluble CoHCF in solution and a decrease in the concentration of film constituents. Such a situation is observed by a slackened growth in the height of the peaks as the number of the potential cycles reach about 15. Thus the film deposition on the surface of electrodes becomes practically negligible when the potential cycling exceeds this limit.

Voltammograms obtained during the modification of Pt and Au surfaces with CoHCF are quite comparable with those of the GC electrode and all of these are in good agreement with the case reported for WIGE [16].

Electrochemical Behavior of CoHCF Modified Electrodes

Figure 2 shows the cyclic voltammograms obtained for

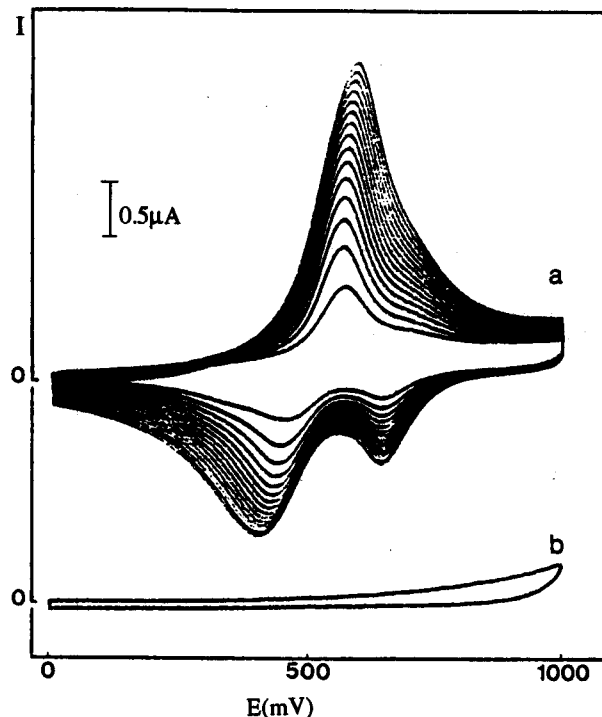


Figure 1. Cyclic voltammograms obtained a) during the electrodeposition of CoHCF on a GC disk electrode from a solution of CoCl_2 (1mM), $\text{K}_3\text{Fe}(\text{CN})_6$ (0.5mM) and KCl (0.5M), b) for bare electrode. Scan rate: 100 mVs^{-1}

GC modified electrodes prepared under identical conditions, except for the number of potential scans during modification process. These voltammograms were recorded by dipping the modified electrodes in 0.5M NaCl solution as electrolyte. As can be seen (Fig. 2a-2d), increasing the number of potential scans during the modification process, which can lead to an increase in CoHCF deposited on the electrode surface, has a profound effect on the CV characteristics of the modified surfaces. Comparison of the CV behavior of these electrodes reveals the features given below:

At least three main surface redox peaks can be designated with $E_m = [(E_a + E_c)/2]$ values of 0.290, 0.345 and 0.820 V/SCE (except for Fig. 2d). By increasing the number of potential scans, the first redox peak (a_1c_1) disappears at the expense of a considerable growth of the second redox peak (a_2c_2). However, such a situation is accompanied by the appearance of some shoulders on either side of the second redox wave. Unlike the case of the first redox process, the anodic and cathodic peak potentials for two other redox peaks shift positively and peak to peak separation also increases with increasing the film thickness. Thus it can be concluded that the potential shifts for anodic peaks are somewhat more pronounced than for cathodic peaks.

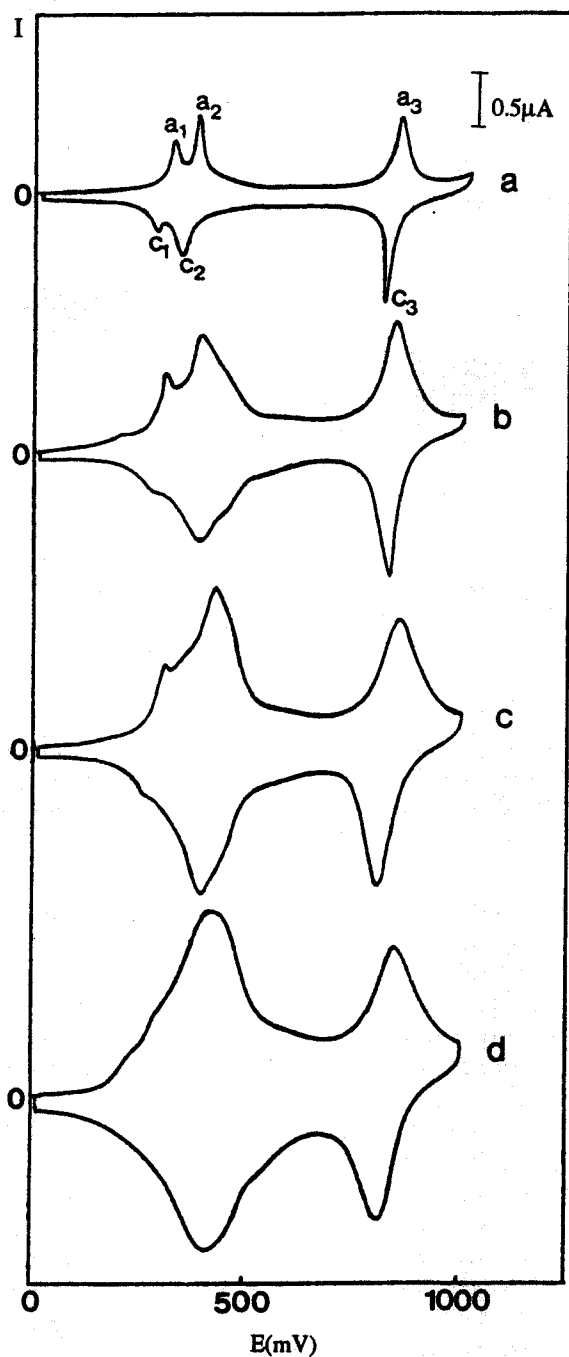


Figure 2. Cyclic voltammograms of GC-CoHCF modified electrodes prepared with: a)1; b)5; c)10 and d)15 cycles of potential. Supporting electrolyte: NaCl 0.5M. Scan rate: 20 mVs⁻¹.

The half width of the voltammograms begins to increase with increasing the film thickness, yielding lower values for the low coverage and higher values for the high coverage of electrodes. Similar behavior is obtained for Pt-CoHCF modified electrode with respect to the number of

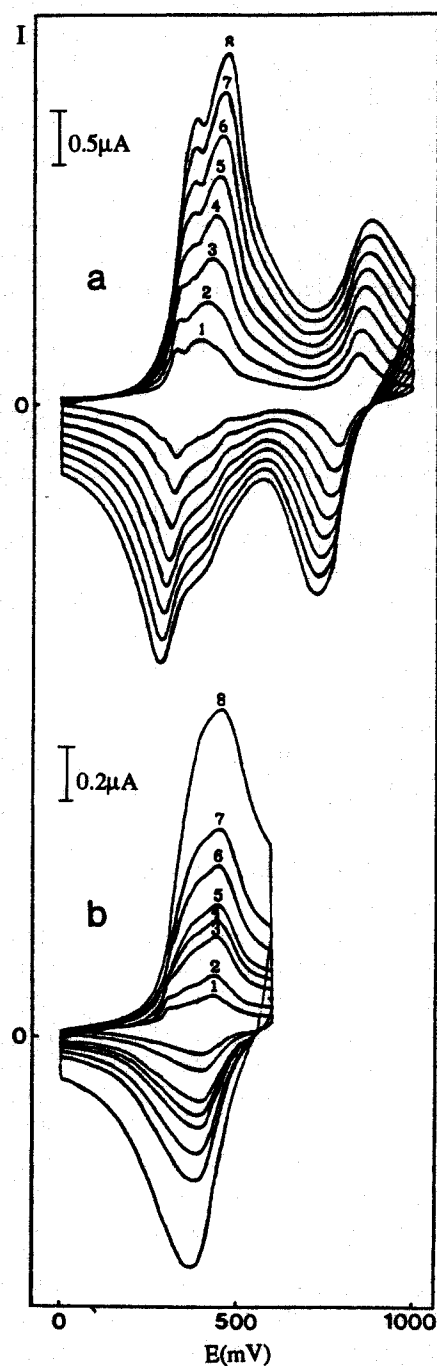


Figure 3. Cyclic voltammograms of CoHCF modified electrodes prepared with 15 cycles of potential in various sweeping rates: a)Pt-CoCHF, 1) 10; 2)20; 3)30; 4)40; 5)50; 6)60; 7)70 and 8)80 mVs⁻¹. b)Au-CoHCF, 1)10; 2)20; 3)40; 4)60; 5)80; 6)100; 7)200 and 8) 400 mVs⁻¹. Supporting electrolyte: NaCl 0.5M.

redox peaks and their evolution in connection with the thickness of the deposited film. However, in the case of Au electrode, because of a limited potential range, only the a₁c₁ and a₂c₂ redox peaks are observed (Fig. 3).

By comparing the redox behavior of Pt-PB [30] and TG-CoHCF [16] modified electrodes in aqueous 0.5M Cl and NaCl solutions respectively with that of GC, Pt and Au electrodes modified by CoHCF in 0.5M NaCl (see above), we assigned the peak a_2c_2 at 0.345 V/SCE to the $Co^{2+} \rightarrow Co^{3+}$ transition and the redox peak a_3c_3 occurring at 0.820 V/SCE to the $Fe(CN)_6^{4-} \rightarrow Fe(CN)_6^{3-}$ transition in CoHCF. The additional redox couple of a_1c_1 , whose peak heights are relatively smaller, can be assigned to the presence of a different form of CoHCF, arising in the course of electrodeposition. The variation of peak height dependence on potential scan rate and peak separation between anodic and cathodic peaks at low scan rate (see below) are the criteria that conform to the expected surface

processes.

The Effect of Scan Rate

Figure 4 shows the cyclic voltammograms of CoHCF film modified electrodes (prepared with 1 and 10 cycles of potential) at different scan rates. The peak currents of all redox processes observed in 0.5M NaCl solution exhibit a linear relationship with the sweep rate up to 100 mVs⁻¹ as expected for a surface bound species behavior [31]. This also indicates that the heterogeneous electron transfer at the interface between GC substrate and CoHCF film, and the counterions exchange process between CoHCF film and NaCl solution are sufficiently fast, hence the whole redox process proceeds swiftly at this range of potential sweep.

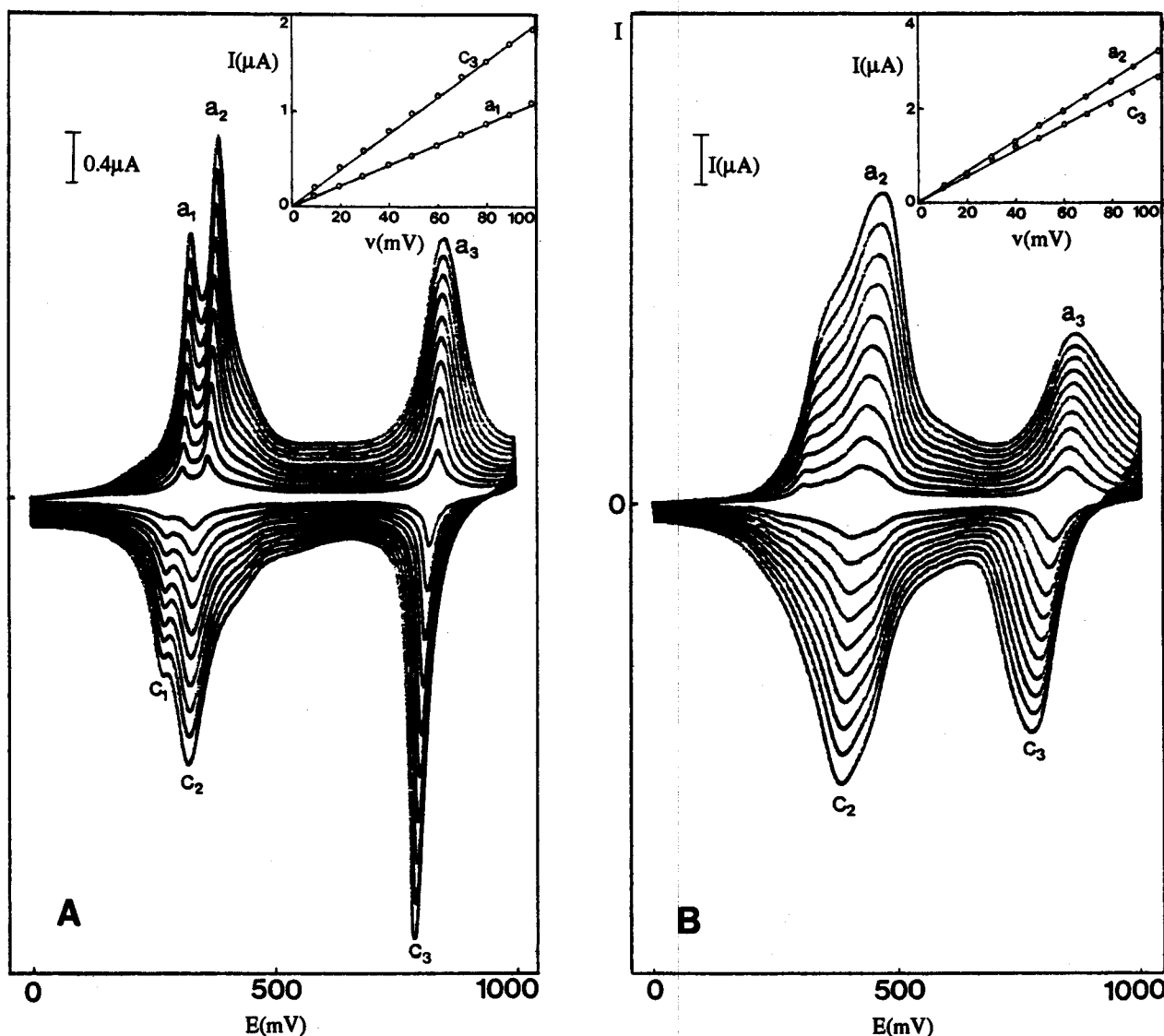


Figure 4. Cyclic voltammograms of GC-CoHCF modified electrode prepared with: a) 1 cycle of potential, b) 10 cycles of potential, in scan rates between 10-100 mVs⁻¹. Supporting electrolyte: NaCl 0.5M. Linear graphs show the variation of peak currents vs. scan rates.

At relatively higher scan rates, the peak currents depend on the square root of scan rates. This means that at higher scan rates, the peak current is controlled by a diffusional process which is the diffusion of counterions in the modifying layer. It is interesting to note that with increasing the film thickness, the i_p vs. $v^{1/2}$ proportionality appears at lower sweep rates. For example, for electrodes prepared with 1, 5 and 15 cycles of potentials this proportionality is observed at above 400, 300 and 200 mVs^{-1} respectively. At scan rates between 10-100 mVs^{-1} , the peak potentials and peak separations ($E_{p,a} - E_{p,c}$) for all redox waves are small, but increase with increasing sweep rates. The peak separation also increases with increasing film thickness, however this value for electrodes possessing low coverage is smaller than that for high coverage electrodes. These phenomena can be related to the effect of ohmic drop inside the CoHCF film, which increases with increasing the film thickness [1, 32, 33].

Ion Effect on the Electrochemical Behavior of CoHCF Film Modified Electrode

The nature of ions has a considerable effect on the electrochemical behavior of modified electrodes. Indeed, the penetration of ions into or out of the immobilized layer is necessary for electroneutrality of the modified film during the electrochemical process.

The electrochemical behavior of CoHCF film modified electrode was examined in 0.5M solutions of HCl, LiCl, KCl, NaCl, NH_4Cl and 0.25M solutions of MgCl_2 , CaCl_2 and BaCl_2 as supporting electrolytes for elucidating the effect of various cations. Figure 5 shows the cyclic voltammograms obtained from these solutions. From this figure, it follows that:

i) The peak potentials and the shape of the voltammograms are strongly affected by the nature of the cations of the supporting electrolytes. This indicates that CoHCF such as PB has a zeolitic nature [23].

ii) All cations, except for NH_4^+ , can penetrate into or out of CoHCF film during the variation of electrode potential.

iii) In KCl, LiCl, MgCl_2 , CaCl_2 and BaCl_2 solutions, the shape of the voltammograms is similar. However, if the height of the anodic peak is considered as a measure of the ion permeability in the film, the order of cation incorporation into CoHCF film would be different from each other.

iv) It can be seen qualitatively from Figure 4 that CV curves of CoHCF film modified electrodes in NaCl solution are very different from those in other solutions. In 0.5M NaCl solution, the CV curves are well defined and the electrochemical reactions of the modified electrode are reversible; whereas in 0.5M solutions of other cations the CV curves are poor and the electrode reactions are somewhat irreversible. This can arise from a relatively difficult penetration of these ions into the film.

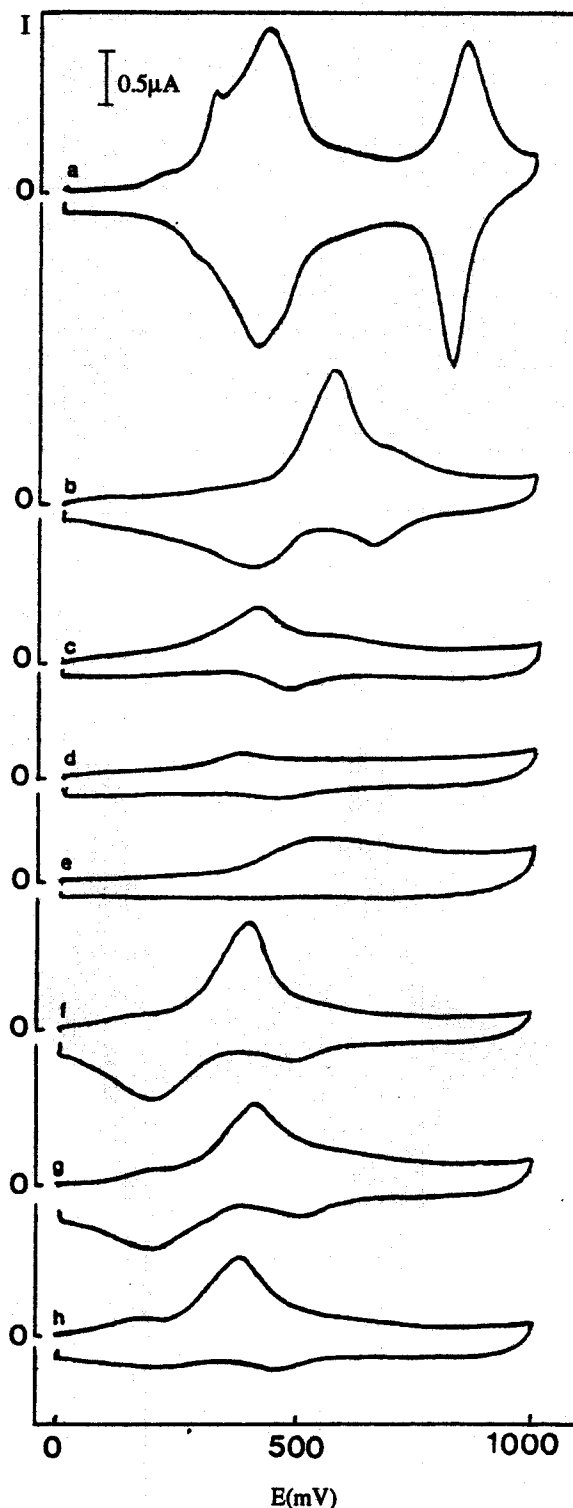


Figure 5. Cyclic voltammograms of GC-CoHCF modified electrode prepared with 10 cycles of potential, in various supporting electrolytes: a) NaCl 0.5M; b) KCl 0.5M; c) LiCl 0.5M; d) HCl 0.5M; e) NH_4Cl 0.5M; f) CaCl_2 0.25M; g) MgCl_2 0.25M; h) BaCl_2 0.25M. Scan rate: 20 mVs^{-1}

v) In contrast to the PB film, which shows highest ionic permeability for NH_4^+ [30, 34], the Na^+ was found to penetrate the CoHCF film more readily than the other cations (as can be seen from the height of the anodic peaks in the presence of different cations).

vi) The permeability of CoHCF film with respect to H^+ and Ba^{++} ions is less than that using other cations.

vii) During the repeated cycling of potential, the redox processes are not blocked in the presence of the fairly large hydrated ions, Li^+ , Ca^{++} and Ba^{++} ions; this is in contrast with the behavior of PB film [34].

viii) In the case of NH_4^+ ion, the redox process is stopped immediately after one scan of potential from 0.0V to 1.0V and no reoxidation wave was observed. But its electrochemical behavior was regained after its transportation into the 0.5 M NaCl solution.

ix) The voltammograms are stable after the initial scan, except for those in HCl and BaCl_2 solutions, which slowly decay upon repeated scanning.

x) Independent of the oxidation involved, the process is completely reversible in that, changing the supporting electrolyte cation from Na^+ to others and then back to the first, reproduces the original cyclic voltammogram. This can be attributed to the reversible penetration of Na^+ ions to CoHCF film and can be regarded as a sign of the high affinity of the surface layer towards Na^+ ions.

xi) Finally, unlike the PB film which shows ion permeability in the following sequence [9, 35]:

$\text{NH}_4^+ > \text{K}^+ > \text{Cs}^+ > \text{Na}^+ > \text{Li}^+ > \text{Ba}^{++} > \text{Ca}^{++} > \text{H}^+$
The order of ion permeability in the CoHCF film is as follows:

$\text{Na}^+ > \text{K}^+ > \text{Ca}^{++} > \text{Mg}^{++} > \text{Li}^+ > \text{Ba}^{++} > \text{H}^+ > \text{NH}_4^+$

In conclusion, as is the case with other metal hexacyanoferrate modified electrodes, the ion transportation in the CoHCF modified surfaces is very sophisticated and cannot be explained simply in terms of hydrated ionic radius and the system's channel size, as was done for the PB modified electrode [4].

The electrochemical behavior of CoHCF film modified GC electrode was also examined in 0.5M solution of HCl , NaClO_4 , NaNO_3 , and 0.25M solution of Na_2SO_4 (Fig.

As can be seen, the heights of the anodic and cathodic peaks in the presence of SO_4^{2-} , NO_3^- and ClO_4^- anions are greatly increased in comparison with NaCl electrolyte. The E_p values are affected only slightly by the nature of the ions. Unlike the PB electrode, repeated cycles in the presence of these ions (about 10 cycles) do not result in the degradation of thin film. This behavior is in contrast with that of the PB film in the presence of these anions [35]. A change from Cl^- to SO_4^{2-} , NO_3^- and ClO_4^- and vice versa is reversible. In addition to the main redox peaks, one should appear on the positive side of the cathodic peak of a_2c_2

redox wave, the height of which is higher in NaCl solution than in other electrolytes. Consequently, it can be concluded that unlike the reports on the behavior of many other hexacyanoferrate modified electrodes, the anions of supporting electrolyte can also diffuse into or out of the CoHCF film during the redox reactions.

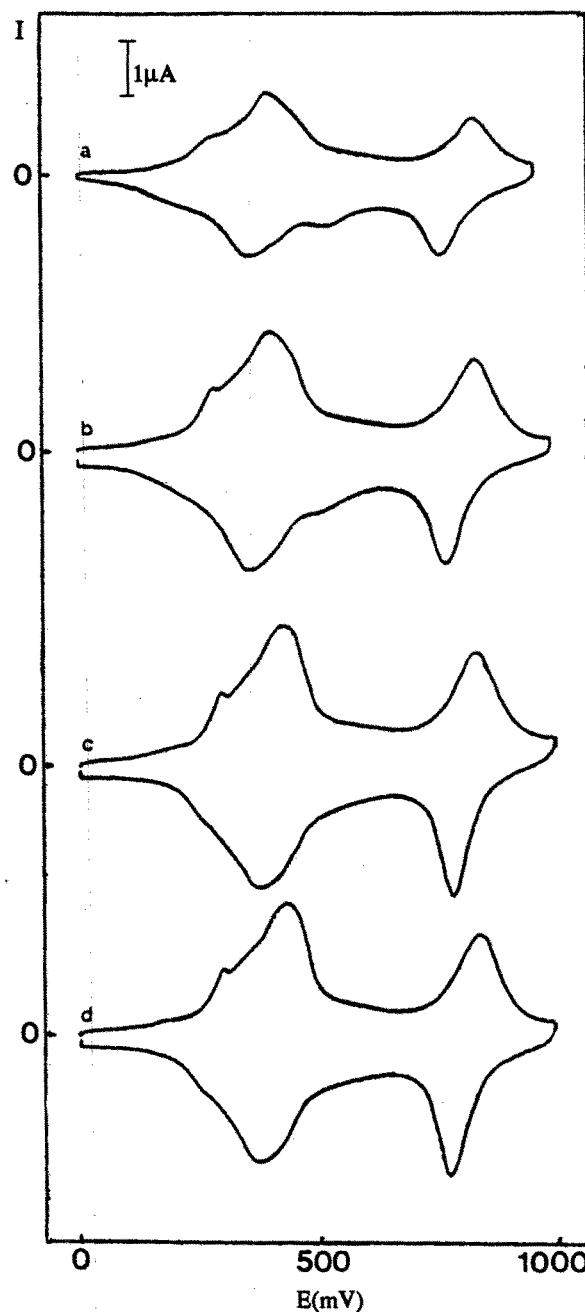


Figure 6. Cyclic voltammograms of GC-CoHCF modified electrode prepared with 15 cycles of potential in supporting electrolytes with different anions: a) NaCl 0.5M; b) Na_2SO_4 0.25M; c) NaClO_4 0.5M; d) NaNO_3 0.5M. Scan rate: 20 mVs^{-1}

Effect of Supporting Electrolyte Concentration

The redox potentials of the CoHCF film modified electrode are dependent on the concentration of sodium ions in background electrolyte, which shifts in a Nernstian manner with the Na^+ concentration. Such a behavior is also reported for PB [4, 23] and ruthenium purple [34] modified electrodes towards K^+ and NH_4^+ and K^+ ions respectively. It is found that the redox peak potentials decrease by ca. 60 mV per decade of decreasing Na^+ ion concentration, whereas the peak current stays almost constant. If the Na^+ ion concentration in the solution is reduced below 0.1M, the shapes of the curves for high coverage electrodes begin to alter and the half widths for the anodic and cathodic peaks increase, whereas the behavior of electrodes prepared at low coverage is unchanged. This suggests that as much as the film thickness is increased, the electrolyte concentration must also be increased.

Effect of Acidity of Supporting Electrolyte

The voltammetric behavior of the CoHCF film modified electrode in pure electrolyte solution is not affected significantly by variation of pH (from ~0.2 to ~5) as long as the solution contains an excess of Na^+ as supporting electrolyte, and the peak potentials are almost the same. In more acidic solutions, however, the height of the peaks decrease and the half-width of them increase, and finally the redox reactions are slowly blocked. It seems that in solutions with a $C_{\text{H}^+}/C_{\text{Na}^+}$ ratio greater than 1.2, the affinity of CoHCF film for H^+ ions is greater than for Na^+ ions. At higher pH values (pH 5), a_1, c_1 peaks disappear and the peak potentials of a_2, c_2 and a_3, c_3 peaks move at about 20-30 mV towards less positive values, whereas ΔE_p values increase with increasing pH. Although at pH >5 the height of the peaks decreases considerably, by transferring the electrode to 0.5M NaCl solution it finds again its initial behavior. Therefore, it can be concluded that the decrease in electrochemical reactivity of CoHCF film in elevated pHs arises from a provisional and reversible blocking of electrode process in the presence of OH^- ions or the anions of used buffer without any deteriorating effect on the modifying layer. It must be noted that the pH at which the blocking effect appears depends on the thickness of the polymeric film and it is manifested at higher pHs for thicker layers.

Stability Test

The stability of CoHCF deposited on Au, Pt and GC electrodes was examined against various parameters. The stability of these electrodes, irrespective of their storage in air or supporting electrolyte, is good (Fig. 7), but their stability in KCl solution under repeated scanning is better than in NaCl solution, which arises from its higher affinity for K^+ ion. For GC matrix, the variation of electrode

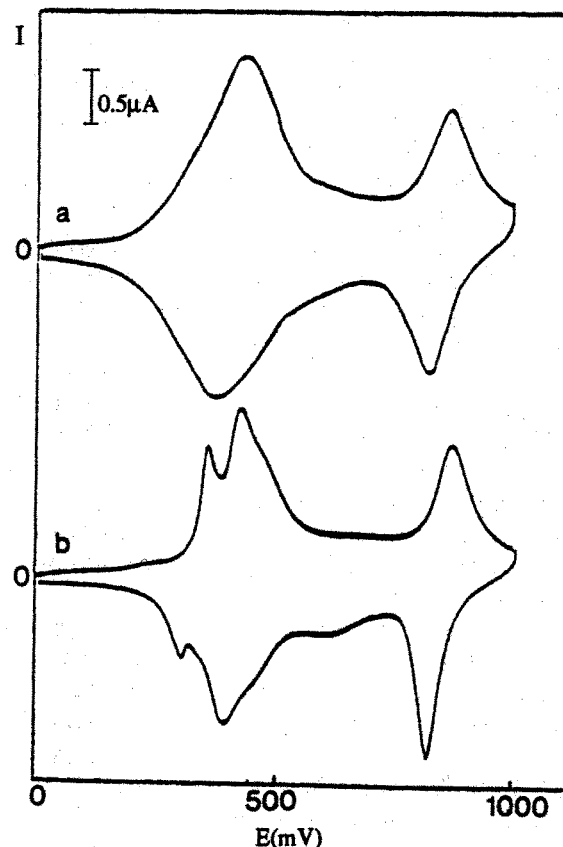


Figure 7. Cyclic voltammograms of GC-CoHCF modified electrode prepared with 15 cycles of potential, in 0.5M NaCl: a) after 48h storage in air, b) after 14h storage in 0.5M NaCl. Scan rate: 20 mVs^{-1}

potential range up to 1.1 V and down to -1.3 V does not result in degradation of the film. In the case of Pt and Au matrix, CoHCF film remains intact if the electrode potential varies only inside the electroactivity range of bare electrodes.

Conclusion

Cobalt hexacyanoferrate modified electrodes can be prepared by cyclic voltammetry using various matrices such as GC, Pt and Au. The electrodeposited layers show in general two redox sites due to the transformations $\text{Co}^{2+} \rightarrow \text{Co}^{3+}$ and $\text{Fe}(\text{CN})_6^{3-} \rightarrow \text{Fe}(\text{CN})_6^{4-}$. These transformations are accompanied by cation transfer between electrode surface layer and adjacent electrolyte. Therefore, the electroactivity of deposited film depends strongly on the nature of transferring cation. The highest electroactivity is observed with 0.5M NaCl solution, whereas the greatest affinity is obtained for K^+ ions. It has been shown that the electrochemical behavior of such electrodes is affected to a certain extent by the nature of the anion present in the electrolyte. These modified electrodes also show a satis-

factory degree of stability and thus can be used as a reaction bed in the investigation of electrocatalysis.

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