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Preparation of a cobalt hexacyanoferrate film-modified aluminum electrode by chemical and electrochemical methods: enhanced stability of the electrode in the presence of phosphate and ruthenium(III)

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Abstract Modification of an aluminum electrode by means of a thin film of cobalt hexacyanoferrate (CoHCF) using electroless and electrochemical procedures is described. The modification conditions of the aluminum surface, including the electroless deposition of metallic cobalt on the electrode surface from $\text{CoCl}_2 + \text{NaF}$ solution and the chemical derivatization of the deposited cobalt to give a CoHCF film in 0.25 M KCl + 0.25 M $\text{K}_3[\text{Fe}(\text{CN})_6]$ solution, have been determined. The modified Al electrodes prepared under optimum conditions show one or two well-defined redox couples in phosphate buffer solutions of pH 7.2, depending on the preparation procedure, due to the $[\text{Co}^{\text{II}}\text{Fe}^{\text{III/II}}(\text{CN})_6]^{-2-}$ system. The effect of pH, alkali metal cations, and anions of the supporting electrolyte on the electrochemical characteristics of the modified electrode were studied. Diffusion coefficients of hydrated Na^+ in the film, the transfer coefficient, and the transfer rate constant for electrons were determined. The stability of the modified electrodes under various experimental conditions was studied and their high stability in the sodium phosphate buffer solutions was confirmed. Enhanced stability was observed when the modified electrode was scanned in fresh solutions of RuCl_3 between 0 and 1 V for at least 20 cycles, due to the formation of mixed hexacyanoferrates of cobalt and ruthenium.

Keywords Aluminum-modified electrode · Cobalt hexacyanoferrate film-modified electrode · Electroless modification · Ruthenium-cobalt hexacyanoferrate film

Introduction

One important group of inorganic compounds utilized for electrode modification is the transition metal hex-

acyanoferrates. The modification on the electrode surface with these compounds is possible in eight different ways [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14]. These ways may be divided into three main groups:

1. By immersing a conductive substrate surface in a solution containing cyanoferrates and transition metal ions, allowing formation of insoluble metal cyanoferrates by a simple chemical reaction [1] or electrochemical reaction, cycling the electrode over a range of potentials [2, 3, 4].
2. By immersing the transition metal electrode surface, or some plated conductive substrates with a transition metal, in a solution containing cyanoferrate ions and then derivatizing the electrode surface to obtain insoluble metal cyanoferrates by chemical [5, 6, 7] or electrochemical methods [8, 9, 10].
3. By immobilizing mechanically the metal hexacyanoferrates as microparticles on the surface of an appropriate electrode, e.g. a paraffin-impregnated graphite electrode (PIGE) [11, 12, 13], a carbon paste electrode (CPE), or a conductive polymer-coated electrode [14].

Electrodes modified with cobalt hexacyanoferrate (CoHCF) have been prepared where two different types of film were reported. One type has a redox couple [15] and the other has two redox couples [16], depending on the preparation procedure and nature of the substrate used.

CoHCF exhibits not only electrocatalytic or mediator activities via slow electrochemical reactions [17, 18, 19, 20], but also a specific ion exchange capability, and electrochromic [21] and thermochromic characteristics [22]. In most of these investigations, common substrates such as Pt, Au, GC, Ni or, recently, Al were used for the preparation of the modified electrodes.

The present study is a continuation of our program which has the general object of using aluminum as a substrate, since it is less expensive, more available, and particularly suitable for electroless preparation of some transition metal cyanoferrate film-modified electrodes [6, 7, 23, 24, 25]. In this paper, preparation of CoHCF/

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Al modified via the electroless and electrochemical methods and a comparative study of the electrochemical behavior of the electrodes are reported.

Experimental

Chemicals and instrumentation

An aluminum bar with a purity of $99.9 \pm 0.2\%$ was used as the substrate for the electrode matrix. CoCl_2 , NaF, $\text{K}_3[\text{Fe}(\text{CN})_6]$, HNO_3 , and NaOH were of analytical grade (Merck). The phosphate buffer solution was made up from NaH_2PO_4 and adjusted to pH 7.2 by NaOH. The electrochemical experiments were carried out using an EG&P $>1^\circ\text{C}$. A saturated calomel electrode (SCE), a platinum wire, and an aluminum disk modified electrode (CoHCF/Al; $A = 0.125 \text{ cm}^2$) were used as reference, auxiliary, and working electrodes, respectively.

Electrode preparation

The electrodes were modified via electroless and electrochemical methods. For this purpose the aluminum surface, fitted into a Teflon tube [7], is polished to a mirror finish, first by sandpaper (P320) and then by $0.05 \mu\text{m}$ alumina powder. The CoHCF film preparation was carried out in two different steps, including deposition of metallic cobalt on the aluminum substrate and then derivatization of the surface to give the CoHCF film. The electroless deposition of metallic cobalt was carried out by dipping the cleaned surface of the electrode in a solution containing 2 M CoCl_2 plus NaF (saturated) for 2–7 min, depending on the desired thickness. The aluminum electrode covered by metallic cobalt was derivatized to CoHCF film by immersing it in 0.25 M KCl plus 0.25 M $\text{K}_3[\text{Fe}(\text{CN})_6]$ for 2–30 min.

Modification of the electrodes by an electrochemical method was also achieved in two steps. First, the electrodeposition of metallic cobalt on the aluminum surface was performed in 0.1 M CoCl_2 by an amperostatic method using a current density of 8 mA cm^{-2} for 1–4 min. Then the derivatization of the deposited cobalt was carried out in 0.05 M $\text{K}_3[\text{Fe}(\text{CN})_6]$ plus 0.05 M KCl by both potentiostatic and amperostatic techniques. In the potentiostatic technique the applied potential was 1 V vs. the reference electrode (the derivatization time may be varied between 2 and 16 min, depending on the film thickness desired). In the amperostatic method, the current density was 8 mA cm^{-2} ($E = -0.5 \text{ V}$ vs. the reference electrode; the derivatization time was between 2 and 16 min).

In order to morphologically stabilize the crystal lattice of the films, the freshly prepared electrode was cycled between 0 and 1.0 V for about 20 cycles with scan rate of about 50 mV s^{-1} . The surface concentrations of the mediator in the film per unit surface area of the electrode, Γ , were determined from the area under the anodic part of the cyclic voltammograms (CVs) of the CoHCF-coated Al electrode.

Results and discussion

CoHCF/Al electrode prepared chemically

Electrode modification conditions

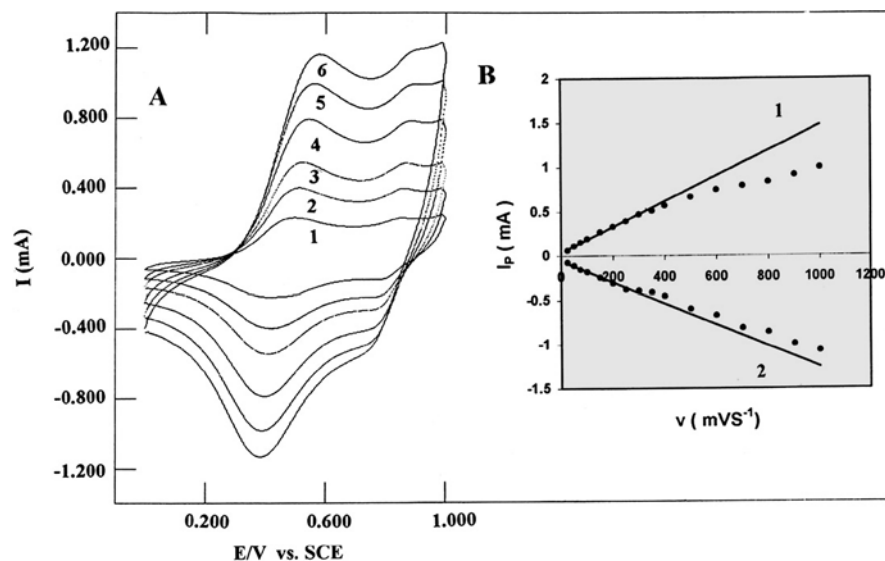
The electroless preparation of the CoHCF/Al modified electrode was carried out in two steps involving the deposition of metallic cobalt on the aluminum surface and then derivatization of the deposited cobalt to give CoHCF. Preliminary experiments showed that by dipping the aluminum surface in the Co^{2+} solution, no chemical

deposition of metallic cobalt on the aluminum surface is performed. We have found that the redox reaction between metallic aluminum and Co^{2+} can be performed in the presence of F^- ions. In fact, in the presence of F^- : (1) the apparent standard potential of the Al^{3+}/Al system (E_0') is decreased, which favors the redox reaction to form metallic cobalt on the electrode, and (2) the Al_2O_3 deposited on the electrode is dissolved by complexing the Al^{3+} ions as AlF_4^- to provide the surface conditions for the metallic cobalt deposition on the aluminum. The optimization of the CoCl_2 and NaF concentrations in the plating solution is very important in this step. An extensive study lead us to use a 2 M CoCl_2 solution, saturated with NaF (plating solution). On the other hand, preliminary experiments showed that the chemical derivatization of metallic cobalt to give CoHCF film on the electrode can be performed even in the absence of any deliberately added oxidizing agent. In this step the kind of electrolyte, its concentration, as well as the concentration of $\text{Fe}(\text{CN})_6^{3-}$, are important. We have found that a 0.25 M solution of $\text{Fe}(\text{CN})_6^{3-}$ containing 0.25 M KCl (derivatization solution) is suitable. The thickness of the CoHCF film depends on the immersing time of the electrode in the plating and derivatizing solutions. In the present work the plating time varied from 2 to 7 min and the derivatizing time from 2 to 30 min, respectively, depending on the desired film thickness. However, if both plating and derivatization times are maintained almost constant, the thickness of the film can be reproduced. We have found that the relative standard deviation of the anodic peak current for five CoHCF film preparations was 8%.

Electrochemical behavior of the modified electrode

The CoHCF film-modified Al electrode, prepared under optimum conditions, was characterized by cyclic voltammetry. The CVs obtained for the CoHCF film in 0.25 M phosphate buffer electrolyte (pH 7.2), containing no deliberately added electroactive material, are shown in Fig. 1A. We observed that these peaks were not affected by stirring of the electrolyte, offering proof that the material is well associated with the electrode surface under the solution conditions. We found that two sets of peaks, with $E_0 = (E_{\text{pa}} + E_{\text{pc}})/2$ of 0.45 V and 0.82 V, can be observed and at a scan rate of 25 mV s^{-1} the peak potential separations are 18 and 22 mV, respectively. At higher scan rates, a wider splitting (e.g. 126 mV for 1 V s^{-1}) appears, indicating the limitation arising from the charge transfer kinetics. The peak currents of the voltammograms are linearly proportional to the scan rate up to 300 mV s^{-1} (Fig. 1B) and the ratio of $i_{\text{pa}}/i_{\text{pc}}$ remains almost equal to unity, as expected for surface-type behavior. At scan rates higher than 300 mV s^{-1} , the anodic and cathodic peak currents are linearly proportional to the square root of the scan rate, which is expected for a diffusion-controlled electrode process.

Fig. 1. A CVs of the CoHCF/Al electrode ($A = 0.125 \text{ cm}^2$) prepared by the electroless method, in 0.25 M phosphate buffer solution as supporting electrolyte. Potential scan rates: (1) 100, (2) 200, (3) 300, (4) 500, (5) 700, (6) 900 mV s^{-1} . B Plot of anodic (1) and cathodic (2) peak currents vs. potential scan rate



Since the Co^{2+} cations in the modifying film are not expected to be electroactive in the potential range examined, 0.0–1.0 V, the two redox couples can be explained as proposed by Kulesza and co-workers [22] by assuming the existence of two possible stoichiometries for CoHCF, namely $\text{M}_2\text{Co}^{\text{II}}\text{Fe}^{\text{II}}(\text{CN})_6$ and $\text{MCo}^{\text{II}}_{1.5}\text{Fe}^{\text{II}}(\text{CN})_6$. Therefore it is likely that two redox couples, including $\text{Co}^{\text{II}}_{1.5}\text{Fe}^{\text{III}}(\text{CN})_6/\text{MCo}^{\text{II}}_{1.5}\text{Fe}^{\text{II}}(\text{CN})_6$ and $\text{MCo}^{\text{II}}\text{Fe}^{\text{III}}(\text{CN})_6/\text{M}_2\text{Co}^{\text{II}}\text{Fe}^{\text{II}}(\text{CN})_6$, are expected, respectively, where M denotes an alkali metal cation, which is necessary for doping of the film to provide charge neutrality within the film. Note that some other research workers reported a set of peaks observed at less positive potentials, assigned to $\text{MCo}^{\text{III}}\text{Fe}^{\text{II}}(\text{CN})_6/\text{M}_2\text{Co}^{\text{II}}\text{Fe}^{\text{II}}(\text{CN})_6$ [18].

Effect of solution pH

Based on our previous work, the bare aluminum electrodes in phosphate buffer solution over the pH range 5–10 are electrochemically stable [7]. The voltammetric behavior of the CoHCF film-modified Al electrode was characterized at various pH values by cyclic voltammetry. This study showed that the peak heights of the set of peaks observed at 0.34 V in 0.25 M phosphate buffer solution of pH 5–10 exhibit negligible variations, while between pH 7 and 5 the peak potential shifted toward the more positive values. On the other hand, the peak currents of the set of peaks that appeared at 0.82 V were enhanced at pH values higher than 7, but decreased at pH values lower than 7. Not that both the two sets of peak disappeared at pH values lower than 4. This behavior leads us to suggest that: (1) the permeability of the CoHCF film toward the H^+ ions is weak or (2) the set of peaks that appeared at 0.82 V may be attributed to a $\text{Co}^{\text{III}}(\text{oxide})/\text{Co}^{\text{II}}(\text{oxide})$ system, which are enhanced at alkaline solutions and depressed at acidic media when the electrode potential is scanned between 0 and 1.0 V. The latter assumption will be investigated

when the CoHCF film is prepared by the electrochemical method. On the basis of the results obtained from this study, a suitable pH range 5–9 (preferably 7.2) was chosen for further electrochemical experiments.

Effect of alkali metal cation of the supporting electrolyte

In order to maintain the electroneutrality of the modified film during the electrochemical process, ions usually enter into or escape from the immobilized film. So ions have a considerable effect on the electrochemical behavior of the modified electrodes. The effect of ions on the voltammetric behavior of the CoHCF film was studied by cyclic voltammetry. Figure 2 shows the CVs of the CoHCF/Al modified electrode recorded in different alkali metal cation-phosphate buffer solutions for Li^+ , Na^+ , K^+ , and Cs^+ , at the same concentration. As seen in Fig. 2, the CoHCF/Al electrode showed two sets of well-defined redox peaks in the presence Na^+ phosphate buffer, whereas in the presence of K^+ only one set of broadened peaks was observed, and the peak height drastically decreased. In the presence of Li^+ - and Cs^+ -containing phosphate buffer solutions, no obvious redox peaks can be observed. The results obtained from this study lead us to conclude that, unlike nickel cyanoferrates, among the alkali metal cations only Na^+ can freely penetrate into the CoHCF crystal lattice. The CVs recorded for a CoHCF/Al electrode in four different concentrations of phosphate buffer (pH 7.2) showed that the voltammetric response of the modified electrode was not affected by the supporting electrolyte concentration.

Effect of anions

Experimental investigation showed that the voltammetric characteristics of the CoHCF/Al electrode were

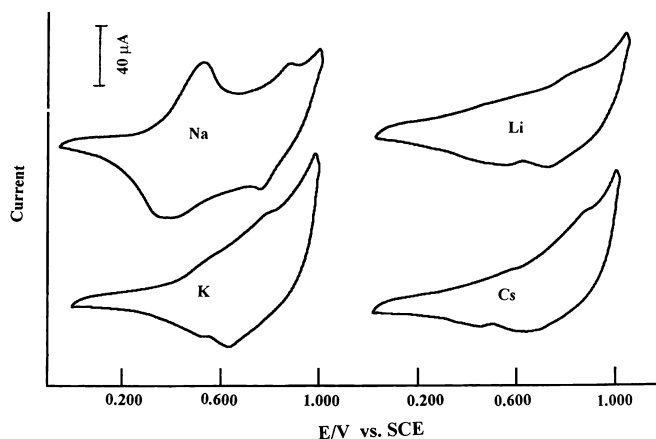


Fig. 2. CVs of the CoHCF/Al electrode ($A=0.125\text{ cm}^2$) in the presence of different alkali metal ion-phosphate buffer solutions as supporting electrolytes at the same concentration (0.25 M); scan rate 100 mV s^{-1}

firmly affected by the anions present in the solution. In the presence of phosphate buffer media, a well-defined and reproducible CV was obtained. In the presence of some other anion supporting electrolytes (as sodium salts), the characteristic peaks of the film were depressed and the order of the depressing effect was $\text{ClO}_4^- > \text{Cl}^- > \text{NO}_3^- > \text{SO}_4^{2-} > \text{HCO}_3^-$. Note that the characteristic peaks of the film observed in the NaH_2PO_4 supporting electrolyte alone remain unchanged by the addition of other sodium salts of moderate concentration to the solution. This improved behavior of the modified electrode in the presence of phosphate anions may be attributed to the formation of cobalt-substituted aluminophosphate [26] stabilizing the CoHCF film on the aluminum substrate. Figure 3 shows typical CVs of CoHCF/Al in 0.25 M Na_3PO_4 buffer solution in the presence of 0.1 M Na_2SO_4 , KNO_3 , or NaNO_3 , and 0.05 M NaCl or KCl .

CoHCF/Al electrode prepared electrochemically

Electrode modification conditions

The CoHCF film preparation was carried out in two different steps, namely deposition of metallic cobalt on the aluminum substrate and then derivatization of the cobalt-plated surface to give the CoHCF film. The plating step may be achieved by an amperostatic procedure using optimized conditions (CoCl_2 concentration, current density, and plating time). Preliminary experiments showed that a low current density and a prolonged plating time were most convenient. We chose a 0.1 M CoCl_2 solution, a current density of 4 mA cm^{-2} , and a plating duration time of 1–4 min. The derivatization step was also carried out with both amperostatic and potentiostatic methods. A repetitive study showed that the modified electrode prepared in 0.05 M $\text{K}_3[\text{Fe}(\text{CN})_6]$ plus 0.05 M

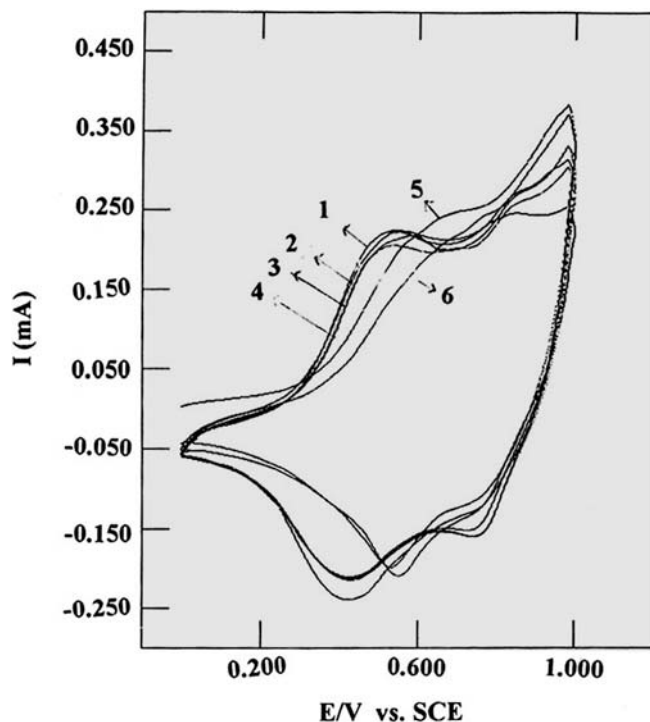


Fig. 3. CVs of the CoHCF/Al electrode ($A=0.125\text{ cm}^2$) in (1) 0.25 M phosphate buffer solution of pH 7.2, (2) as (1)+0.05 M NaCl , (3) as (1)+0.1 M NaNO_3 , (4) as (1)+0.1 M Na_2SO_4 , (5) as (1)+0.05 M KCl , and (6) as (1)+0.1 M KNO_3 . Potential scan rate 100 mV s^{-1}

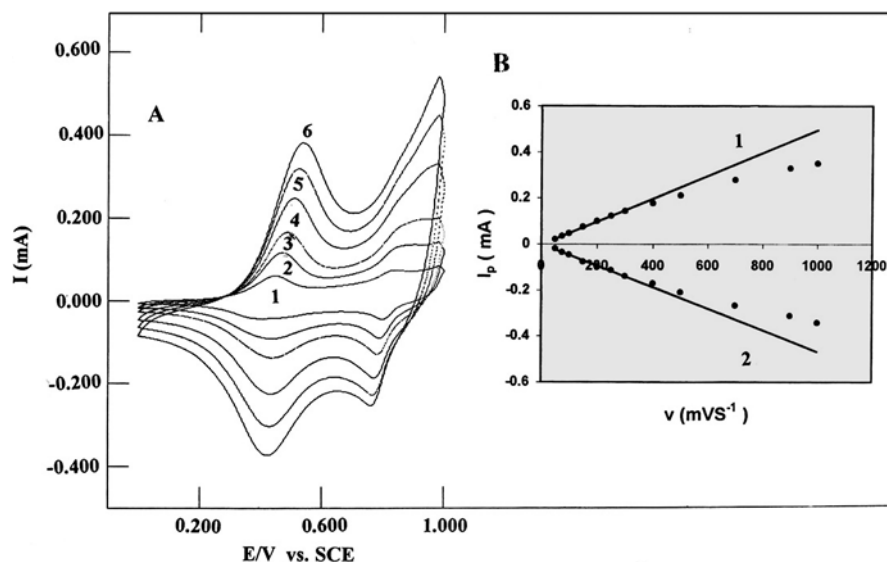
KCl solution, using an amperostatic method with a low current density of 2 mA cm^{-2} ($E \sim -0.5\text{ V}$), always exhibited two set of peaks similar to those observed in the case of the chemical preparation. We have found that the set of peaks that appeared at 0.82 V were depressed with increasing the current density and disappeared for 80 mA cm^{-2} . Similarly, for the modified electrode prepared by the potentiostatic method, at a negative potential ranging from -0.5 to 0 V , two set of peaks were observed, whereas the second pair (0.82 V) tended to disappear with increasing the potential applied to the electrode. Only one set of peaks with a formal potential of 0.45 V was observed at positive potentials higher than 0.5 V (current density higher than 25 mA cm^{-2}).

Electrochemical behavior of the modified electrode

The CVs obtained for CoHCF film in a 0.25 M phosphate buffer electrolyte solution of pH 7.2 are shown in Fig. 4. The formal potentials for the two redox couples are 0.45 and 0.82 V, respectively, very close to those obtained for the films prepared chemically.

The dependence of the CoHCF film voltammetric behavior on the solution pH and the electrolyte cations and anions in the present case is similar to that observed in the case of chemical preparation. The effect of the potential scan rate on the currents of the CVs on the modified electrode are shown in Fig. 4B.

Fig. 4. A Cyclic voltammograms of the CoHCF/Al electrode ($A = 0.125 \text{ cm}^2$) prepared by the electrochemical method, in 0.25 M phosphate buffer solution as supporting electrolyte. Potential scan rates: (1) 100, (2) 200, (3) 300, (4) 500, (5) 700, and (6) 900 mV s^{-1} . **B** Plot of anodic (1) and cathodic (2) peak currents vs. potential scan rates (ν)



On the basis of some experimental observations described above, the following experiments were carried out to confirm whether or not a set of peaks observed at 0.82 V could be associated with the $\text{Co}^{\text{III}}(\text{oxide})/\text{Co}^{\text{II}}(\text{oxide})$ system. A cobalt-plated aluminum electrode was placed in a 0.25 M phosphate buffer solution of pH 7 or 10 and the potential of the electrode was scanned between 0 and 1 V for several cycles. The CV recorded after 20 cycles showed that in the presence of non-deliberately added $\text{K}_3[\text{Fe}(\text{CN})_6]$, only one anodic peak appeared at about 0.89 V, not close to those obtained for CoHCF films. These findings disprove our assumption suggesting that the second set of peaks for the CoHCF film should be assigned to the $\text{Co}^{\text{III}}(\text{oxide})/\text{Co}^{\text{II}}(\text{oxide})$ system.

Charge transfer rate in the film

For an Al electrode having a surface coverage of about $10^{-8} \text{ mol cm}^{-2}$, the peak-to-peak separation potential ($\Delta E_p = E_{\text{pa}} - E_{\text{pc}}$) observed for scan rates up to 100 mV s^{-1} was less than 60 mV in the presence of phosphate buffer as supporting electrolyte. At higher scan rates this value was increased (to 126 mV for 1 V s^{-1}), indicating the limitation arising from charge transfer kinetics.

Laviron [27] has derived general expressions for the linear potential sweep voltammetric response for the case of surface-confined electroactive species. These expressions are as follows:

$$E_{\text{pa}} = E_0 + A \ln(1 - \alpha)/m \quad (1)$$

$$E_{\text{pc}} = E_0 + B \ln(\alpha/m) \quad (2)$$

and for $\Delta E_p = E_{\text{pa}} - E_{\text{pc}} > 200/n \text{ mV}$:

$$\log k_s = \alpha \log(1 - \alpha) + (1 - \alpha) \log \alpha - \log(RT/nFv) - \alpha(1 - \alpha)nF\Delta E_p/2.3RT \quad (3)$$

where $A = RT/(1 - \alpha)nF$, $B = RT/\alpha nF$, and $m = (RT/F)(k_s/nv)$.

From these expressions it is possible to determine the transfer rate constant (α) by measuring the variation of the peak potentials with scan rate ν , as well as the apparent charge transfer rate constant (k_s) for electron transfer between the electrode and surface deposited layer. According to Eqs. 1 and 2, a plot of $E_p - E_0$ versus $\log \nu$ yields two straight lines with a slope equal to $2.3RT/\alpha nF$ for the cathodic peak and $2.3RT/(1 - \alpha)nF$ for the anodic peak. A typical example of these plots is shown in Fig. 5 for a CoHCF film for scan rates of 1–2 V, in the presence of 0.25 M Na_2HPO_4 . Using such a plot and Eq. 3, the values of α and k_s were found to be 0.5 and 5.6, respectively. Note that the surface coverage Γ evaluated from the relation $\Gamma = Q_H/nFA$ was $\sim 5 \times 10^{-8} \text{ mol cm}^{-2}$. Further experiments showed that the values obtained for α and k_s remained almost unchanged for Γ values in the range 10^{-8} – $10^{-9} \text{ mol cm}^{-2}$.

Diffusion coefficient of Na^+ in the film

The height of the CV peaks obtained for scan rates $> 300 \text{ mV s}^{-1}$ is an important criterion, which can be related to the facility of cation diffusion in the modifier film [28]. The peak current of the CVs obtained for scan rates higher than 300 mV s^{-1} in the presence of sodium cations is proportional to the square root of the scan rate, $\nu^{1/2}$, indicating its diffusion nature. We could calculate the diffusion coefficient of the cations in the modifier film exhibiting an irreversible behavior at high scan rates using Eq. 4 [29]:

$$i_p = 2.99 \times 10^5 n^{3/2} \alpha^{1/2} A D^{1/2} C v^{1/2} \quad (4)$$

where D is diffusion coefficient of cations in the film ($\text{cm}^2 \text{ s}^{-1}$), A is the electrode area (0.125 cm^2), ν is the potential scan rate (V s^{-1}), and i_p is the peak current (A). Since, at high scan rates, all redox sites, including mixed valance iron in the film, are not electroactive due to the presence of an insufficient amount of counterions in the

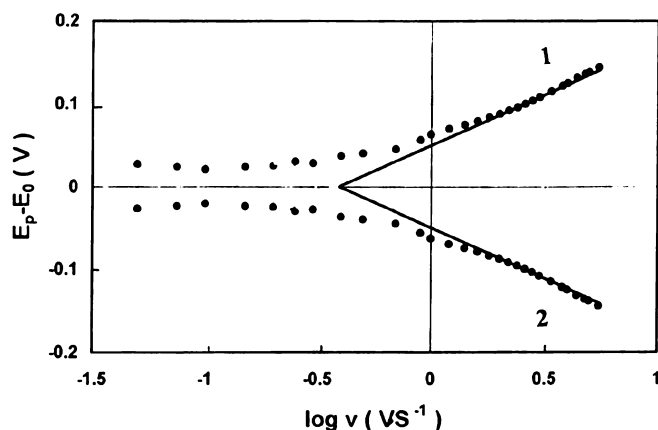


Fig. 5. Plot of $E_p - E_0'$ vs. $\log v$ for CVs recorded for a CoHCF/Al electrode ($A = 0.125 \text{ cm}^2$) in the presence of 0.25 M phosphate buffer solution at scan rates (v) of 1–10 V s^{-1} : (1) for anodic peaks and (2) for cathodic peaks

film, in Eq. 4 the symbol C represents the concentration of alkali metal cation in the film (mol cm^{-3}). The value of C varies with the scan rate and was calculated by means of the total moles of cations in the film, obtained from Q_H (the area under the CVs recorded at scan rates higher than 300 mV s^{-1}) and the total volume of the film obtained from Q_L (the area under the CVs recorded for a scan rate of 50 mV s^{-1}), the molecular weight and density of CoHCF (assumed to be 1.79 g cm^{-3}). Using the peak currents i_p measured from the baselines and C for each scan rate higher than 400 mV s^{-1} , and a plot of i_p versus $Cv^{1/2}$, the diffusion coefficient was calculated as $2.5 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$. A typical example of these plots is shown in Fig. 6 for the CV peaks recorded in the presence of Na^+ . The value of D is relatively small and may be due to the rigid microstructure of the CoHCF interface formed; presumably a low porous interface would reduce ion diffusion rates through the layer. However, this value is comparable with the D values obtained for Na^+ in NiPCNF film [8] and in electroactive poly(N,N -dialkylaniline) films with which multiply-charged anionic metal complexes such as $\text{Fe}(\text{CN})_6^{3-/4-}$, $\text{Mo}(\text{CN})_6^{3-/4-}$, $\text{W}(\text{CN})_6^{3-/4-}$, and $\text{Ru}(\text{CN})_6^{3-/4-}$ are electrostatically combined [30].

Stability study

In the phosphate-based electrolytes

The stability of the CoHCF/Al electrode was examined by repetitive scanning at a scan rate of 50 mV s^{-1} . The potential of the CoHCF/Al electrode prepared with both methods was scanned between 0 and 1 V in 0.25 M phosphate buffer solutions (pH 7). After 20 cycles continuous scanning, well-defined CVs with one or two sets of peaks, depending on the preparation procedure, were obtained. The peak currents decreased on continuous scanning and remained at 94% of the first cycle after 100 cycles scanning; then almost no change in height was

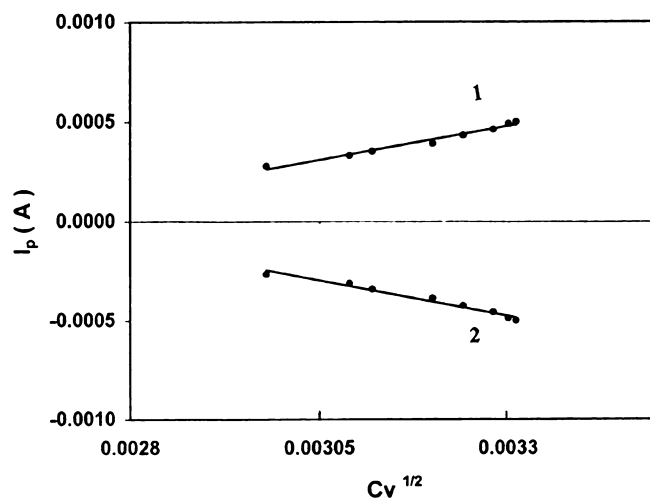


Fig. 6. Plot of I_p vs. $Cv^{1/2}$ for CVs recorded for a CoHCF/Al electrode ($A = 0.125 \text{ cm}^2$) in the presence 0.25 M phosphate buffer solution at scan rates of 400–1000 mV s^{-1} : (1) for anodic peaks and (2) for cathodic peaks

observed. In addition, the CoHCF/Al electrode can withstand being exposed to air (for at least 4 weeks) and the peak height and the separation of the peak potentials remain unchanged.

In the absence of phosphate

The stability of the CoHCF/Al electrode was drastically affected in the NO_3^- , Cl^- , ClO_4^- , and SO_4^{2-} containing electrolyte solutions in the absence of deliberately added phosphate ions. Indeed, under these solution conditions, in the first few scans the peaks current of the pre-conditioned CoHCF/Al electrode in phosphate buffer decreased and then quickly disappeared.

In the presence of ruthenium(III)

Recently, a ruthenium-modified CoHCF thin film electrode on a GC substrate with enhanced stability was described [31]. In order to enhance the stability of the CoHCF film on the Al electrode, the CoHCF/Al electrode was placed in RuCl_3 solutions of various concentrations and scanned over 0–1.0 V by different scan rates, ranging from 50 to 200 mV s^{-1} . The results obtained showed that the most stable modified CoHCF film was obtained by cycling the electrode in a fresh solution of 2 mM RuCl_3 for 100 cycles at a scan rate of 50 mV s^{-1} . Typical CVs recorded before and after scanning in RuCl_3 solution are shown in Fig. 7. As seen in this figure, unlike the CoHCF film, the ruthenium-modified CoHCF film shows good stability and electrochemical behavior in the NaNO_3 electrolyte solution.

The enhanced stability of the Ru-modified CoHCF/Al electrode is thought to correspond to the inclusion of $-\text{O}-\text{Ru}$ species and their ability to form very stable

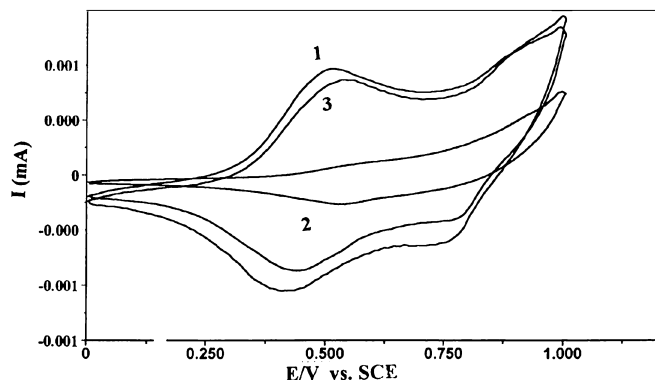


Fig. 7. CVs of a CoHCF/Al electrode ($A=0.125\text{ cm}^2$): (1) in 0.25 M phosphate buffer solution, (2) in 0.5 M NaNO_3 after preparation, and (3) after 100 cycles, cycling the electrode potential between 0 and 1.0 V, in RuCl_3 solution; scan rate 100 mV s^{-1}

mixed-valent binuclear (Ru, Fe) oxo bridges. The inclusion of such species is beneficial because a layered network of bridging oxo species of intra- and interparticles are formed [32, 33, 34].

Conclusion

We have demonstrated the possibility of preparing thin films of cobalt hexacyanoferrate on an aluminum surface. The film can be formed by chemical or electrochemical methods. The pH and alkali metal cation and the nature of the anion of the supporting electrolyte have considerable effects on the stability and electrochemical behavior of the film. Only Na^+ can freely enter the CoHCF crystal lattice. An electrolyte solution containing phosphate ions provides good stability and electrochemical characteristics for the modified electrode. The prepared modified electrode is stable for several weeks in air as well as in sodium phosphate buffer solutions (pH 5–10). The stability of the film can be enhanced when the electrode is cycled in fresh RuCl_3 solution for at least 100 cycles.

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