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Electrocatalytic oxidation of hydrazine at cobalt hexacyanoferrate-modified glassy carbon, Pt and Au electrodes

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Abstract The electrocatalytic oxidation of hydrazine has been studied on glassy carbon, Pt and Au electrodes modified by cobalt hexacyanoferrate (CoHCF) using cyclic voltammetry and rotating disc techniques. It has been shown that the oxidation of hydrazine to nitrogen occurs at the potential coinciding with that of Co(II) to Co(III) transformation in a CoHCF film, where no oxidation signal is observed at a bare glassy carbon electrode. A Tafel plot, derived from RDE voltammograms, exhibits a slope of 150 mV, indicating a one-electron charge transfer process to be the rate-limiting step. The electrocatalytic efficiency of the modified electrode towards hydrazine oxidation depends on solution pH, and the optimum range was found to be located between pH 5 and pH 7. The kinetic behaviour and location of the electrocatalytic process were examined using the W.J. Albery diagnosis table, and it was concluded that the reaction has either a “surface” or a “layer” reaction mechanism. Pt- and Au-CoHCF-modified electrodes show no significant electrocatalytic activity towards hydrazine oxidation.

Key words Electrocatalysis · Hydrazine · Cobalt hexacyanoferrate · Modified electrodes · Glassy carbon

Introduction

The electrocatalysis of slow electron transfer reactions is perhaps the most important feature of chemically modified electrodes (CMEs). Such electrodes enhance the rate of electron transfer by reducing the overpotential associated with a reaction. Therefore, such electrocatalysis enables a high current density (i.e. increased sensitivity) to be obtained for a poor kinetic reaction at a

potential close to the equilibrium potential. The electrocatalytic properties of many modified electrodes have already been studied by different authors, and valuable reviews have been published [1–4]. Among the various compounds used as electrode surface modifiers, the hexacyanoferrates of transition elements are very important. This may be due to the presence of two sets of redox couples, i.e. $\text{Fe}(\text{CN})_6^{3-/4-}$ and $\text{M}_{\text{ox}}/\text{M}_{\text{r}}$ in some of the hexacyanoferrates which appear during the variation of potential. Such a characteristic favours the use of some hexacyanoferrates as electron transfer mediators in the preparation of CMEs. The first attempt in this domain was made when iron(III) hexacyanoferrate (Prussian Blue, PB)-coated electrodes were prepared by V.D. Neff [5]. Thereafter, electrodes modified by various hexacyanoferrates have been prepared by other workers [6–16]. In recent years, the efficiency of such electrodes in the electrocatalysis of some oxidable compounds such as ascorbic acid [16–18], ferrocene [19], hydrogen peroxide [20], nicotinamide adenine dinucleotide (NADH) [21] and hydrazine [22, 23] has been reported. The practical importance of the catalytic oxidation of hydrazine derives from the fact that this compound is the base product of an established fuel cell. The overpotential for this reaction depends on the electrode material [24] and type of pretreatment employed [25]. Consequently, it is to be expected that the change of electrocatalytic activity of the electrode with suitable modifying layers such as transition metal hexacyanoferrates will considerably affect the rate of this reaction. In this connection, A.B. Bocarsly et al. have been shown that $[\text{NiFe}(\text{CN})_6]^{2-/1-}$ -derivatized nickel electrode represents an electrocatalytic surface for the mediated oxidation of hydrazine [23]. Other authors have reported the use of cobalt protoporphyrin dimethyl ester, iron and cobalt sulfonated phthalocyanins, cobalt tetra-aza-annulenes, hemine, ruthenium cyanide and Prussian blue (PB) modified electrodes as electrocatalysts of hydrazine [24–29]. Although the preparation of cobalt hexacyanoferrate at a wax-impregnated graphite electrode (WIGE) and other solid electrodes has already been reported

[11, 30], its potential application as an electrocatalyst of hydrazine still remains unexplored. In this work, we will discuss the catalytic effect of a glassy carbon electrode modified by cobalt hexacyanoferrate on the electrooxidation of hydrazine.

Experimental

Cyclic voltammetric experiments were performed with a three-electrode system using a potentiostat (Polarecord E626 from Metrohm), a function generator (VA Scanner E612 from Metrohm) and a Hewlett-Packard model 3310A X-Y recorder. The glassy carbon, Pt or Au disc electrodes with a diameter of 3, 5 and 3 mm respectively (from Metrohm and Beckman) were used as working electrodes. Each of these working electrodes was cleaned by polishing with 0.5- μm alumina and washed thoroughly with sulfuric acid, acetone and water successively before electrodeposition of the CoHCF film. The modification of the electrode surface was implemented by potential recycling for 15 cycles between 0 and 1.00 V vs SCE at 100 mV s^{-1} for GC and Pt electrodes and between 0 and 0.80 V at 100 mV s^{-1} for the Au electrode in an aqueous solution of 0.5 M KCl containing 1 mM CoCl_2 and 0.5 mM $\text{K}_3\text{Fe}(\text{CN})_6$. A platinum wire electrode (model EA 120 from Metrohm) was used as auxiliary. The potentials were measured and reported versus a saturated calomel electrode (SCE) (model EA 404 from Metrohm).

The chemicals used for surface modification and buffer preparation and the hydrazine (as hydrazinium dichloride) were reagent grade from Merck or Fluka. Doubly distilled water was used for making the solutions, and deaeration was carried out by bubbling with nitrogen with a purity of 99.999% for 15 min.

Results and discussion

Electrochemical characteristics of cobalt hexacyanoferrate (CoHCF) modified glassy carbon electrode

Our previous paper [30] deals in some detail with the electrochemical properties of some solid electrodes modified by CoHCF. However, we noted that the cyclic voltammogram of a modified GC electrode exhibits at least two sets of main surface redox peaks with $E_m = [(E_{p,a} + E_{p,c})/2]$ values of about 0.43 and 0.85 V/SCE respectively. These peaks correspond, by analogy with the case of the PB-modified electrode [31], to the $\text{Co}^{2+} \rightleftharpoons \text{Co}^{3+}$ and $\text{Fe}(\text{CN})_6^{4-} \rightleftharpoons \text{Fe}(\text{CN})_6^{3-}$ transitions in the CoHCF layer. Moreover, such an assumption seems to be reasonable in view of the results reported for cobalt protoporphyrin [26] and cobalt phthalocyanine [27] modified electrodes. Finally, a similar assumption was made by other workers for the CoHCF-modified electrode [13]. The number and the position of these peaks depend strongly on the thickness of the modifying layer as well as the nature of the supporting electrolyte. Consequently, the surface of all the electrodes used in this study was modified by 15 cycles of potential between 0 and 1 V versus SCE at a scan rate of 100 mV s^{-1} . The surface coverage of such electrodes was estimated as

$(5.07 \pm 0.16) \times 10^{-9} \text{ mol/cm}^2$ from the charge under the oxidation peak at 0.43 V (Fig. 1B, curve a), assuming the involvement of one electron in the process [32]. The stability of the CoHCF film deposited on Au, Pt and GC electrodes towards various influences was also examined and was found satisfactory. The cyclic voltammetric patterns of modified electrodes remain unchanged after storage for 48 h in air or 0.5 M NaCl solution, but their stability towards repeated potential cycling in KCl solution is better than that in NaCl solution, which is probably explained by their higher affinity for the K^+ ion [30]. For the GC matrix, extension of the electrode potential range to 1.1 V and down to -1.3 V versus SCE does not result in degradation of the film. In the case of the Au and Pt matrix, the CoHCF film remains intact if the potential is swept only within the electroactivity range of the bare electrodes. For a coated GC electrode in 0.5 M NaCl solution, the cycling of potential in the range from 0 to 1 V/SCE at a scan rate of 100 mV s^{-1} shows only a 10% decrease in peak current after 100 cycles of potential. The effect of hydrazine on the voltammetric response of CoHCF-modified electrodes was also verified. The cyclic voltammogram of a modified GC electrode, previously stored in hydrazine solution, exhibits an increase in the first anodic peak current in 0.5 M NaCl solution, most likely due to penetration of the hydrazine inside the CoHCF layer. However, the cyclic voltammogram regains its initial appearance after a few more cyclings of potential, which can be considered as evidence for the stability of the catalyst in hydrazine solutions. Accordingly, a 0.5 M solution of NaCl was mainly used as the electrolyte except for the cases where the effect of a supporting electrolyte cation was studied.

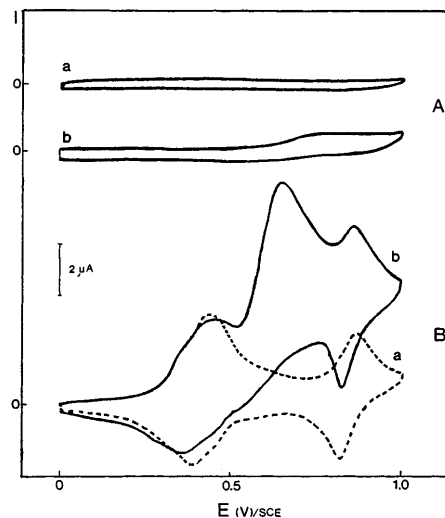


Fig. 1 Cyclic voltammograms of **A** bare GC disc electrode in *a* 0.5 M NaCl solution, *b* as *a* + 1 mM N_2H_4 ; **B** CoHCF-modified GC disc electrode in *a* 0.5 M NaCl solution, *b* as *a* + 1 mM N_2H_4 . Scan rate: 20 mV s^{-1}

Electrocatalytic oxidation of hydrazine

In order to elucidate the catalytic function of CoHCF in the oxidation of hydrazine, we first investigated the voltammetric behaviour of hydrazine at the surface of both free and CoHCF-covered GC electrodes under identical conditions. Figure 1 shows the cyclic voltammograms obtained for a bare (A) and a CoHCF-covered (B) GC electrode, each immersed in (a) 0.5 M NaCl blank solution and (b) 0.5 M NaCl solution containing 1 mM hydrazinium dichloride.

The cyclic voltammogram of hydrazine at a bare electrode in the potential range of 0 to 1 V/SCE shows a small anodic current associated with the oxidation of N_2H_4 , but no oxidation peak is found indicating sluggish heterogeneous charge transfer in this system, whereas a well-defined oxidation peak with a peak potential of ~ 0.65 V/SCE was observed with the modified electrode, which is an indication of a decrease in the oxidation overpotential of N_2H_4 compared with that at the bare GC electrode. In addition, there is a significant increase in the oxidation current of hydrazine and in the sharpness of the peak current. These results suggest that the electrochemical process at the modified electrode occurs by mediation of the surface-modifying layer. Figure 1B (curve b) also shows that the hydrazine oxidation peak is located before the $Fe(CN)_6^{4-/3-}$ peaks and in the proximity of the Co^{III}/Co^{II} peaks of the CoHCF layer. Moreover, in the presence of hydrazine, $Fe(CN)_6^{4-/3-}$ peaks remain unchanged, while the height of the first cathodic peak, relative to the reduction of Co^{III} to Co^{II} , begins to decrease with increase of the hydrazine concentration in the solution. Accordingly, we assume that the catalytic oxidation of hydrazine is mediated by a surface Co^{III}/Co^{II} couple, and consequently the anodic sweep of electrode potential just before the transformation of $Fe(CN)_6^{4-}$ to $Fe(CN)_6^{3-}$ will be sufficient for the hydrazine catalytic oxidation peak to be observed (Fig. 3C). These results are in good agreement with the ideas of C.P. Andrieux and J.M. Saveant concerning the condition required for heterogeneous catalysis of an oxidation reaction using electrodes coated with redox polymers [33].

On the other hand, as will be seen below, the mediated oxidation of hydrazine is pH dependent and the optimum results are obtained for pHs around 6. In this condition, the peak currents relative to the anodic oxidation of hydrazine are proportional to the square root of scan rate in 0.5 M NaCl and/or KCl buffered solutions, indicating that the oxidation processes are always diffusion-controlled. The slope of the I_p versus $v^{1/2}$ plot for a 1 mM solution of hydrazinium dichloride in 0.5 M NaCl buffered solution (pH = 6) is $7.7 \mu A/(mV s^{-1})^{1/2}$. The peak currents are also directly proportional to the hydrazine concentration in NaCl and KCl solutions over the ranges up to 3 mM and 1 μM respectively. We assume that this catalytic process is a four-electron oxidation of hydrazine to nitrogen gas, as it appears at about the same potential as that already reported for a

prussian blue (PB) modified GC electrode [36]. The peak current ($I_{p,a}$) approach can therefore be used for the estimation of the total number of electrons involved in the anodic oxidation of hydrazine. Assuming the electrode reaction to be a totally irreversible diffusion-controlled process, n is calculated from the following equation [28]:

$$n = (I_{p,a}/v^{1/2})/\{3.01 \times 10^5[(1-\alpha)n]^{1/2}AD^{1/2}C^*\}$$

where, $(I_{p,a}/v^{1/2})$ is the slope of the $I_{p,a}$ versus $v^{1/2}$ plot. Assuming that $(1-\alpha)n = 0.6$, $A = 0.07 \text{ cm}^2$ ($r = 0.15 \text{ cm}$), $D = 1.39 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ [34], $C^* = 1 \text{ mM}$ and $I_{p,a}/v^{1/2} = 7.7 \mu A/(mV s^{-1})^{1/2}$, it is calculated that $n = 4$.

Information about the rate-determining step was obtained from a Tafel plot derived from data of the rising part of the current-voltage curves (see Fig. 5B). A slope of $145 \pm 5 \text{ mV/decade}$ is obtained, which indicates the involvement of one electron in the rate-determining step, assuming a transfer coefficient of $\alpha \approx 0.40$.

In order to elucidate the optimum conditions for mediated oxidation of hydrazine, the effect of some variables such as solution pH and supporting electrolyte cation on electrode process were also investigated.

The effect of solution pH

The electrocatalytic efficiency of CoHCF in the oxidation of hydrazine has been studied as a function of solution pH, and a series of voltammograms were recorded at various pH values (Fig. 2). The variation of the anodic peak current as a function of solution pH is presented in the inset of Fig. 2. As can be seen, the catalytic current is pH dependent. A decrease in pH causes the heights of all the voltammetric peaks to decrease. This can be the result of the relatively difficult penetration of protons into the film during the electrochemical process [30]. On the other hand, with increasing pH, the peak potential of hydrazine oxidation is shifted negatively, and the peak current also increases. At pH values greater than about 5, the E_p values are fixed and are also independent of pH. A regular increase in the peak current of hydrazine oxidation as a function of solution pH (see the inset of Fig. 2) suggests that only the deprotonated form of hydrazine, i.e. N_2H_4 , acts as an electrocatalytic substrate. Similar behaviour is also reported for hydrazine oxidation at a nickel ferricyanide modified electrode [23]. At higher pH values the electrochemical process is blocked, which is shown by the considerable decrease in the height of the peaks. Such behaviour can result from a provisional and reversible slackening of the electrode process in the presence of OH^- ions or other anions of the buffer used without any deteriorating effect on the modifying layer, since by transferring the blocked electrode into a 0.5 M NaCl solution it regains its initial behaviour [30]. Thus, it can be concluded that the optimum pH values are situated between 5 and 7, and the utility of a CoHCF-modified electrode is limited for this

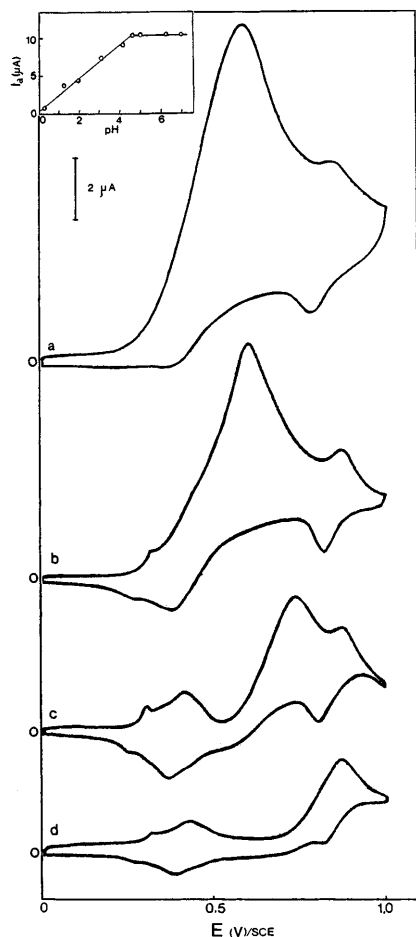


Fig. 2 Cyclic voltammograms of 1 mM solution of N_2H_4 at CoHCF-modified GC electrode in 0.5 M NaCl solution with pH *a* 6.10 [0.1 M $\text{NaH}_2\text{PO}_4 + \text{NaOH}$], *b* 5.00 [0.1 M $\text{CH}_3\text{COOH} + \text{NaOH}$], *c* 2.03 [0.1 M $\text{H}_3\text{PO}_4 + \text{NaOH}$] and *d* 0.22 [HCl 1 M + NaOH]. Scan rate: 20 mV s^{-1} . The inset shows the variation of anodic peak current of hydrazine against solution pH

pH range. Therefore, the experiments described below were performed at a pH of about 6.

Figure 3 shows the cyclic voltammograms of a CoHCF-GC electrode in 0.5 M sodium phosphate buffer solution (pH 6.1) in the absence (curve A) and in the presence (curves B and C) of hydrazine. Comparison of the N_2H_4 oxidation peak potential at the CoHCF modified electrode with those of a CoHCF film in hydrazine-free solution (curve A) indicates the crucial role of electrochemically generated Co(III) species in the film on the oxidation of N_2H_4 . The fact that the presence of N_2H_4 attenuates the Co(III) reduction peak supports this hypothesis. On the other hand, there is a large increase in current in the anodic region corresponding to the oxidation of Co(II) to Co(III) in the CoHCF film in parallel with a decrease in the cathodic current corresponding to the reduction of Co(III) to Co(II) in the CoHCF film itself when hydrazine was added to 0.5 M sodium phosphate buffer solution (pH 6.1). Obviously,

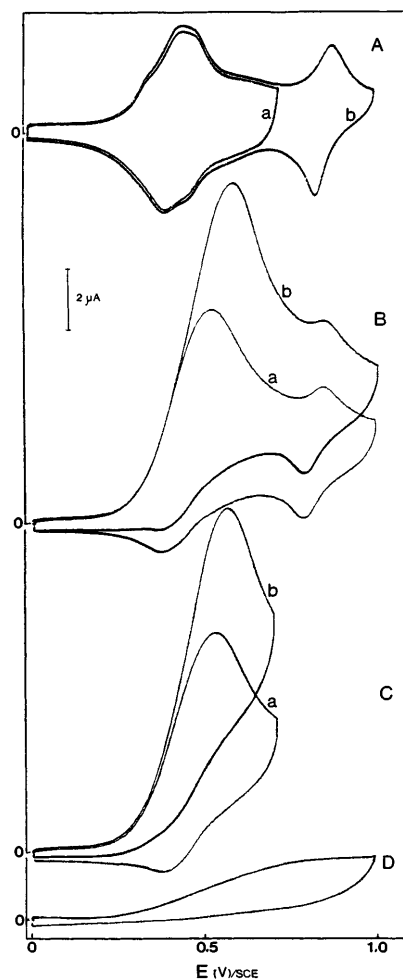


Fig. 3 Cyclic voltammograms of CoHCF-modified GC electrode at potential sweep range of *a* 0–0.7, *b* 0–1.0 V/SCE; **A** in hydrazine-free solution; **B** in solution with *a* 0.5 mM, *b* 1 mM of hydrazine; **C** as **B** at potential sweep range of 0–0.7 V/SCE; **D** bare GC electrode. Supporting electrolyte 0.5 M sodium phosphate buffer of pH 6.1. Scan rate: 20 mV s^{-1}

the increased current in the anodic region is due to the fact that the hydrazine present in solution diffuses toward the electrode and reduces the Co(III) produced electrochemically. As Co(II) is regenerated by N_2H_4 during the potential sweep, there is a resultant increase in the anodic current. Similarly, the cathodic current is smaller in the presence of N_2H_4 and decreases with increase of the hydrazine concentration in solution (curves *a* and *b* in Figs. 3B and 3C). Thus, it can be concluded that the overall reaction proceeds according to an EC' catalytic mechanism [35].

A further debatable point is the permeability of the COHCF film to hydrazine molecules as indicated for other hexacyanoferrates [23, 36]. Therefore, one can suppose that the oxidation process of hydrazine occurs not only at the film-solution interface, but also in the part of the CoHCF film adjacent to the solution. The latter case leads to the release of a considerable amount of protons inside the film, which must diffuse into the

solution in order to keep the process running. It seems that part of the released protons can be neutralised by buffer solution which penetrates inside the film and another part of these protons is transferred by diffusion outside the film. Consequently, any process slackening the facile diffusion of buffer ions or protons across the film-solution interface will lead to the inhibition of the catalytic reaction to some extent. In practice, it is easily seen that on increasing the scan rate (a shortest time window), the peak potential of the hydrazine oxidation is largely shifted towards more positive potentials, and the peak current function ($I_{p,a}/v^{1/2}$) is gradually decreased. Such behaviour is particularly enhanced in unbuffered electrolytes. Therefore, it can be concluded that any perturbation in mass transfer between the CoHCF film and the adjacent solution will lead to slackening of the electrode process. Accordingly, the best results for the electrocatalytic oxidation of hydrazine are obtained in less acidic solutions ($7 > \text{pH} > 5$) and at low scan rates ($10\text{--}20 \text{ mV s}^{-1}$).

The effect of the composition of the supporting electrolyte

As mentioned in section 1, the shape and the potential of the surface peaks of the CoHCF film are dependent on the choice of the cation of the supporting electrolyte [30]. For example, the voltammetric feature of such an electrode is substantially changed by passing from 0.5 M NaCl to 0.5 M KCl solution (Fig. 4A). However, a further change is observed when a 0.5 M solution of potassium phosphate buffer (pH = 5) is used as supporting electrolyte (Fig. 4B). Obviously, such an evolution can be assigned to the presence of mono- and

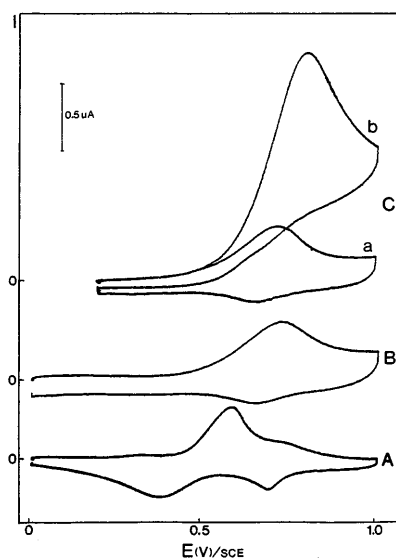


Fig. 4 Cyclic voltammograms of **A** CoHCF-modified GC electrode in 0.5 M KCl solution; **B** as **A** in 0.5 M potassium phosphate buffer (pH 5); **C** as **B**, **b** as **B** + 1 mM hydrazine. Scan rate: 20 mV s^{-1}

dihydrogenphosphate anions as well as to the effect of a buffered pH medium. It seems that in this condition the first redox peaks are shifted towards more positive potentials and merge into the second couple, so that only one broadened anodic peak is observed. In this case, the anodic oxidation of hydrazine appears essentially at the same potential as that of the CoHCF film itself (Fig. 4, curve c). This potential, 0.80 V/SCE, is more positive than that observed in 0.5 M sodium phosphate buffer (see Fig. 3). Thus, the catalytic oxidation of hydrazine at a CoHCF film modified GC electrode is affected by the composition of the supporting electrolyte and particularly the nature of the cations. Such behaviour has also been reported for the electrocatalytic response of a nickel hexacyanoferrate modified electrode [37]. Additionally, the anodic peak currents in the presence of Na^+ are significantly higher than those observed in the presence of K^+ ions. In supporting electrolyte containing K^+ cation, the current is again enhanced compared with that at a bare electrode and the cathodic peak of the film is suppressed to some extent and proportional to the N_2H_4 bulk concentration. Consequently, a 0.5 M solution of supporting electrolyte with Na^+ or K^+ ions was found to be a suitable medium for the electrocatalytic oxidation of hydrazine, but the first medium was used for mechanistic investigations of hydrazine oxidation because of the higher peak current densities that are observed in this medium.

Kinetic analysis

The catalysis of slow reactions at the surface of redox film modified electrodes is affected by four key factors: the intrinsic reactivity of the catalyst (CoHCF in this case) or the rate of the catalytic reaction between the catalyst and substrate (hydrazine), the rate of permeation of substrate into the film, the rate of electron transport through the film, and the rate of diffusion of the substrate from the bulk of the solution to the film-solution interface [38, 39]. C.P. Andrieux et al. have indicated the first three of these rate-limiting factors by the letters R, S and E respectively. Moreover, a series of cases are considered at which two or more of these factors act simultaneously. Soon after, W.J. Albery et al. identified ten different kinetic cases for faradaic reactions at the redox-modified electrodes, considering the location of reaction as well as the rate-limiting processes [40]. They have also presented a diagnosis table for elucidation of the reaction mechanism at modified electrodes. In order to evaluate the effects of these parameters on the kinetics of the electrooxidation of hydrazine, the rotating-disc electrode, RDE, approach was employed and the voltammograms of hydrazine oxidation at a CoHCF-modified rotating-disc electrode in three different concentrations and as a function of the electrode rotation rate ($\omega^{1/2}$) were recorded (Fig. 5A). On the basis of the Albery diagnosis table, we consider first the relationships between the limiting currents, i_L , and

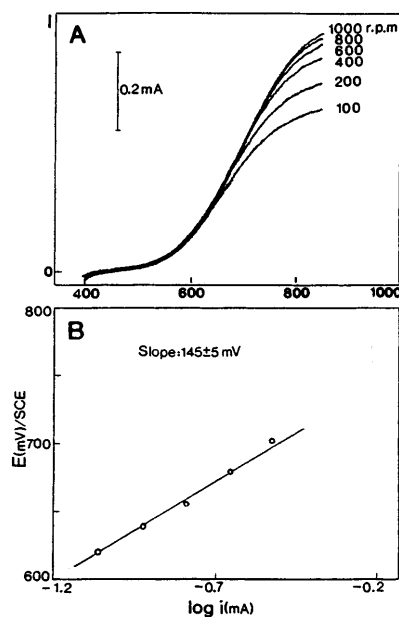


Fig. 5 **A** Voltammograms of a CoHCF-modified GC rotating disc electrode in 5 mM solution of hydrazine in 0.5 M sodium phosphate buffer (pH 6.1) at rotation rates indicated for each voltammogram, **B** Tafel plot derived from voltammograms shown in **A**. Sweep rate: 5 mV s^{-1}

rotation speeds, $\omega^{1/2}$, (Levich equation). According to this equation, the plot of the limiting current as a function of $\omega^{1/2}$ should be a straight line passing through the origin. From Fig. 6A, this is true for low concentrations of N_2H_4 and for low electrode rotation speeds, and the straight lines have slopes reasonably proportional to the inverse of the hydrazine bulk concentration but have non-zero intercepts. These small intercepts on the ordinate was attributed to the contribution of N_2 bubbling, produced as electrode reaction product, to the mass transfer of substrate [41]. However, we assume such behaviour to be due to the penetration of N_2H_4 into the CoHCF film [23]. Indeed, as Fig. 6A shows, the intercepts of Levich plots increase linearly with increasing N_2H_4 concentration in solution, and a CoHCF-modified electrode previously immersed in N_2H_4 solution and subsequently transferred to 0.5 M NaCl solution regains its initial features only after some cycling of potential, which are signs of the facile and reversible penetration of substrate through the film. Thus, for low concentrations of hydrazine and low rotation rates of the disc electrode, one can assume that the rate of the electrode process is limited only by (a) the rate of the catalytic reaction between N_2H_4 in solution and the redox centers in the film and (b) the diffusion of substrate to the electrode. In order to elucidate the kinetics of the hydrazine oxidation at CoHCF-modified GC electrode, the Koutecky-Levich plot was performed using the values obtained for limiting current with different rotation speeds and various concentrations of hydrazine in solution (Fig. 6B). It can be seen that the

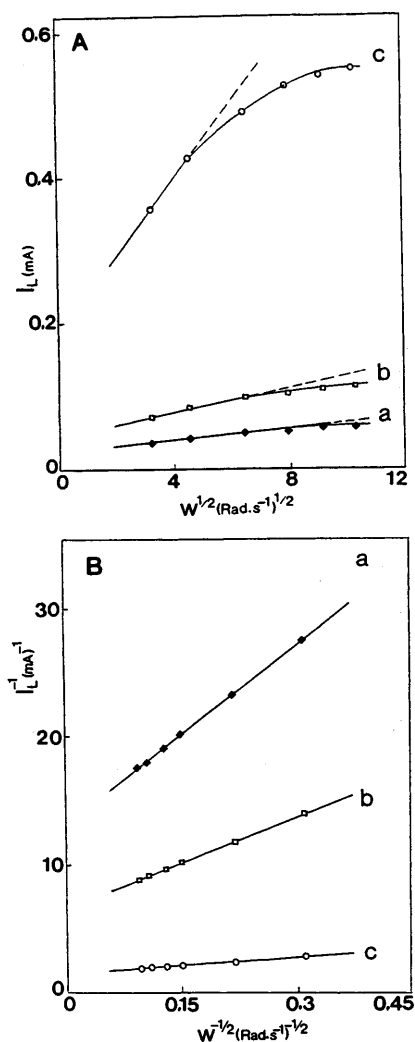


Fig. 6 **A** Levich plots derived from RDE voltammograms of a CoHCF-modified GC electrode in *a* 0.5 mM, *b* 1 mM, *c* 5 mM hydrazine. Supporting electrolyte 0.5 M sodium phosphate buffer (pH 6.1), **B** Koutecky-Levich plots corresponding to Levich plots shown in **A**

intercepts of all linear plots are positive, clearly indicating the kinetic limitation of the electrode process. In addition, within experimental error, the slopes and intercepts are inversely proportional to the bulk concentration of hydrazine, suggesting that the current is not limited by the rate of electron transport within the film. Following the diagnosis table in [40], it is necessary to calculate the value of the Levich constant, Lev , from the gradient of the linear Koutecky-Levich plots presented in Fig. 6B. We have obtained a mean value of $(1.82 \pm 0.10)10^{-3} \text{ cm s}^{-1/2}$ for Lev , which is in good agreement with the value of $1.93 \times 10^{-3} \text{ cm s}^{-1/2}$ calculated by using the following equation:

$$Lev = 1.55D^{2/3}\nu^{-1/6} \quad [40]$$

where D is the diffusion coefficient of hydrazine in solution ($1.39 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ [34]) and ν is the kinematic viscosity of the medium ($\sim 0.01 \text{ cm}^2 \text{ s}^{-1}$ [42]). Afterwards,

we examine the value of the heterogeneous rate constant for the modified electrode, K'_{ME} , [43], using the intercepts of the Koutecky-Levich plots which correspond to infinite rotation speed with negligible concentration polarisation in the electrolyte phase. The Koutecky-Levich equation [44] for limiting current, i_L , at a rotating modified disc electrode is written as follows:

$$\begin{aligned} 1/i_L &= 1/1.55nFAD^{2/3}\nu^{-1/6}\omega^{1/2}C^* + 1/nFAK'_{ME}C^* \\ &= 1/nFAC^*[(1/Lev \cdot \omega^{1/2}) + (1/K'_{ME})] \end{aligned}$$

where A is the area of the electrode, C^* is the bulk concentration of the substrate, ω is the rotation speed, K'_{ME} is the heterogeneous rate constant for the modified electrode, and other terms have their usual meanings. The calculated value for K'_{ME} was $(5.61 \pm 0.08)10^{-3} \text{ cm s}^{-1}$. Recently, we have shown that a thin film of CoHCF behave as an analogue of prussian blue [30], and thus we can expect to have a CoHCF film thickness-independent value for K'_{ME} similar to that already reported for the PB-modified electrode [41]. Moreover, the same K'_{ME} values were acquired at different C^* levels, confirming that the catalytic reaction is first order with respect to the bulk concentration of hydrazine. Consequently, from the diagnosis table of W.J. Albery, the mechanism is either SK'' or LSK. In other words, the reaction is located either at the interface of the electrolyte and the CoHCF film or the reaction layer is located close to the electrolyte-film interface. In the frame of the Saveant-Andrieux model, the latter behaviour corresponds to the case SR, which is also reported for electrocatalytic oxidation of hydrazine at a PB-modified glassy carbon electrode [36].

Electrocatalytic oxidation of hydrazine at CoHCF-modified Pt and Au electrodes

Electrocatalytic behaviour of Pt- and Au-CoHCF modified electrodes with respect to N_2H_4 oxidation were also investigated. At a Pt-CoHCF electrode (Fig. 7, curve a), the oxidation of hydrazine occurs at the same potential as that of the bare Pt electrode (curves c and d). This behaviour indicates that the N_2H_4 molecules can easily penetrate into the film and participate in the oxidation process at the bare electrode. Thus, the CoHCF film deposited at a Pt electrode is not active for catalytic oxidation of hydrazine.

At an Au-CoHCF-modified electrode, the peak potential of N_2H_4 oxidation appears at 0.590 V/SCE, whereas at the bare Au electrode the anodic peak is observed at 0.620 V/SCE. It is seen that the peak potential difference between modified and bare Au electrodes is not large and could even be attributed to some extent to experimental error. Consequently, we consider that the modification of an Au electrode by CoHCF is unable to reduce effectively the activation energy of hydrazine oxidation in comparison with that observed with an unmodified electrode.

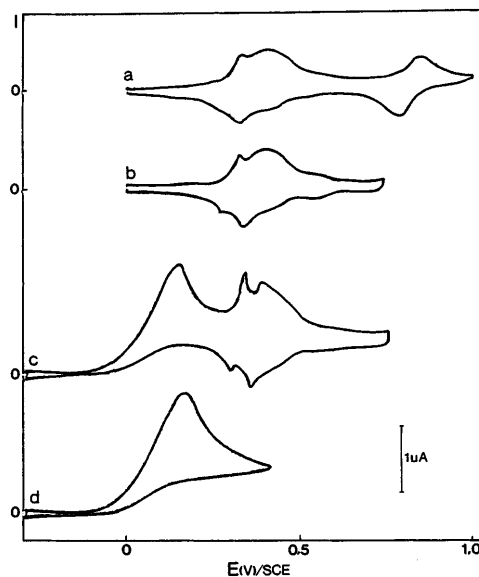


Fig. 7 Cyclic voltammograms of Pt-CoHCF-modified electrode, a in 0.5 M sodium phosphate buffer (pH 6.1) at potential range of 0–1.0 V/SCE, b as a, at 0–0.8 V/SCE, c b + 1 mM hydrazine, d as c for bare Pt electrode. Scan rate: 20 mV s^{-1}

Conclusions

Cobalt hexacyanoferrate (CoHCF) film deposited at a glassy carbon electrode acts as an electrocatalyst for the oxidation of hydrazine. The process is pH dependent and a higher catalytic current is observed at pHs ranging from 5 to 7 at a potential close to that of the transformation of Co(II) to Co(III) in the CoHCF film. The catalytic current is also affected by the nature of the cation present in solution, sodium ion being found to be the best. On the base of a Tafel plot, the charge transfer step of the rate-limiting reaction is suggested to be a one-electron process with a transfer coefficient of ~ 0.4 . The reaction is proved to be first order with respect to the concentration of hydrazine. According to the W.J. Albery kinetic diagnosis table [40], it is concluded that the reaction mechanism is either of the “surface” or “layer” reaction type at a CoHCF-modified GC electrode. The Au and Pt CoHCF-modified electrodes show no significant electrocatalytic activity towards hydrazine oxidation, most probably because of film permeability arising from the nature of the substrate and electrode matrix.

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