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Electrochemical behavior and electrocatalytic activity of a zinc hexacyanoferrate film directly modified electrode

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Abstract

A thin film of zinc hexacyanoferrate (ZnHCF) was formed directly on a Zn electrode to prepare a chemically modified electrode. The electroactive film was strongly attached to the electrode surface and was stable against gradual dissolution during potential cycling and long-term usage. The voltammetric characteristics of the directly modified ZnHCF film electrode were also investigated in the presence of different alkali metal cations. In view of the fact that, unlike the other transition metal hexacyanoferrates, ZnHCF film can be generated only at a certain ratio of modifier species, the modification process has an essential role in the nature and properties of the generated electroactive film. Due to the mechanism of the direct modification process, concentrations of the modifier species including Zn^{2+} and $\text{Fe}(\text{CN})_6^{3-}$ have no effect on the nature of the generated electroactive film. Thus, by using direct modification, the film formation is not affected by the ratio of $\text{Zn}^{2+}/\text{Fe}(\text{CN})_6^{3-}$, as this ratio is kept at 1:1 for any possible case. This results from the fact that, by involving a mole of $\text{Fe}(\text{CN})_6^{3-}$ in the surface reaction (the reaction which occurs at the electrode surface and causes the formation of the ZnHCF film), only a mole of Zn^{2+} dissolves from the electrode surface to share in the surface reaction (plus a mole of K^+ from the supporting electrolyte). The electrocatalytic properties of the modified electrode for oxidation of thiosulfate were also investigated.

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1. Introduction

Modification of electrode surfaces with various electroactive materials is an interesting area of research in solid-state electrochemistry. Various organic and inorganic modifiers have been immobilized on conducting substrate electrodes to prepare chemically modified electrodes (CMEs) [1,2]. Among inorganic materials, transition metal hexacyanometalates are very interesting due to their electrochemical properties, which make them suitable for various applications such as electrocatalysts, sensors, etc. [3–21]. Since the work of Neff [3], which reported the deposition of a thin film of Prussian blue (PB) on an electrode surface, considerable attention has been paid to the deposition of PB and its analogues on conducting substrate electrodes. As electrochemical properties of PB analogues are of interest as well as PB,

the electrochemistry of different PB analogues has been extensively studied [3–21]. However, less attention has been given to zinc hexacyanoferrate (ZnHCF). Joseph et al. [22] have studied the formation of ZnHCF film on a carbon electrode. They have found that modification of ZnHCF is different from the other PB analogues, as it can be formed only in a certain ratio of the modification species. Out of this ratio, electrocrystallization phenomena are observed instead of stable surface modification.

Several methods have been utilized for the modification of electrode surfaces to prepare CMEs [17–21]. More recently [23–25], we have described direct modification of electrode surfaces, based on a classical method, for the preparation of highly stable modified electrodes. Direct modification of electrode surfaces is an effective method for the preparation of CMEs with many advantages including the simplicity of the procedure. Moreover, it provides higher stability for the immobilized film on the metallic surfaces. As a part of the development of direct modification of electrode

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surfaces, we have used it for the preparation of the ZnHCF film-based modified electrode [26]. In the present paper we aim to study the electrochemical behavior of a directly modified ZnHCF film electrode and its advantages in comparison with other electrochemical methods. The novelty of this research lies in three points. (i) A typical example for using the direct modification as a simple and effective method for the preparation of CMEs; (ii) preparing the ZnHCF film modified electrode by omitting the influence of the modifier species concentration; and (iii) fabricating a new modified electrode based on the ZnHCF film as a new modifier material. To our knowledge, reports on ZnHCF immobilized on electrode surfaces for the preparation of CMEs are restricted to a few preliminary papers in the literature [22,27,28].

2. Experimental

All chemicals were of analytical grade, used without further purification, and doubly distilled water was used for preparing all solutions. Buffer solutions were prepared from $\text{H}_2\text{SO}_4 + \text{KHP}$ (potassium hydrogen phosphate) as phosphate buffer for the pH range 0–14 unless otherwise noted. All experiments were done using a conventional three-electrode cell at room temperature. The working electrode was prepared from a zinc rod 1 mm in diameter, which was polished before each experiment. The purity of the zinc was better than 99.99%. A Pt rod and a saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. All electrochemical measurements were performed using a low-noise homemade potentiostat connected to a microcomputer running CorrView software.

Direct modification of the zinc electrode was carried out by immersing the electrode for a certain period of time into a solution of 2 mM $\text{K}_3\text{Fe}(\text{CN})_6$ containing 0.1 M KCl as supporting electrolyte. A time of 5 min was applied for the modification process in the present investigation. The ZnHCF film formed directly on the Zn electrode surface is insoluble in both aqueous and organic solvents. The modification process is as simple as transformation of a metal in an active chemical medium. A possible chemical reaction for this process is given below in Eq. (1).

3. Results and discussion

3.1. Electrochemical characteristics of the directly modified ZnHCF film electrode

Fig. 1 shows a typical cyclic voltammogram of the directly modified ZnHCF film electrode. A pair of peaks

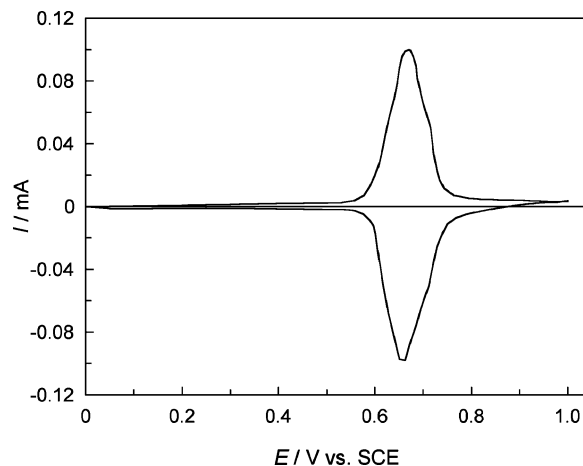
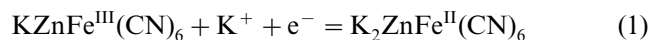


Fig. 1. Typical cyclic voltammogram of the directly modified ZnHCF film electrode in 0.1 M KCl supporting electrolyte with scan rate $\nu = 100 \text{ mV s}^{-1}$.

is observed due to the redox reaction of the surface-confined iron centers ($\text{Fe}^{\text{II/III}}$). The formal potential $E_f = 0.666 \text{ V}$ (vs. SCE) was evaluated from the average of the oxidation and reduction peak potentials. The difference of the anodic and cathodic peak potentials is approximately zero, indicating a reversible behavior for the redox system. The surface coverage of the film deposited on the electrode, Γ , was determined from the area under the anodic voltammogram of the directly modified ZnHCF film electrode. In the present case, Γ is $1.0 \times 10^{-8} \text{ mol cm}^{-2}$. The value obtained is close to those reported in the literature for other transition metal hexacyanoferrates. The half peak width is about 92 mV indicating the theoretical value of a one-electron reaction mechanism process [29]. The redox couple is related to the oxidation and reduction of the center atom by the following equation:



In addition, both the anodic and the cathodic peak currents showed a linear relationship with potential scan rate up to 100 mV s^{-1} (Fig. 2(a)), indicating a surface reaction during the time scale of the experiment. At higher scan rates, the peak currents are proportional to the square root of the scan rate, indicating that the reaction is diffusion-limited (Fig. 2(b)). As expected, the cation of the supporting electrolyte is also involved in the redox couple. Based on the thermodynamic behavior discussed by Itaya et al. [7] for PB, a general formula can be formulated for the Nernstian equation of the solid films:

$$E = E^\circ + \frac{RT}{F} \ln \left[\frac{a_{\text{ZF}} a_{\text{K}^+}}{a_{\text{KZF}}} \right] \quad (2)$$

where a_{ZF} and a_{KZF} denote the activities of ZnHCF and its potassium salt, respectively. According to the above-mentioned equation, the directly modified ZnHCF film electrode exhibits a Nernstian response to the potassium

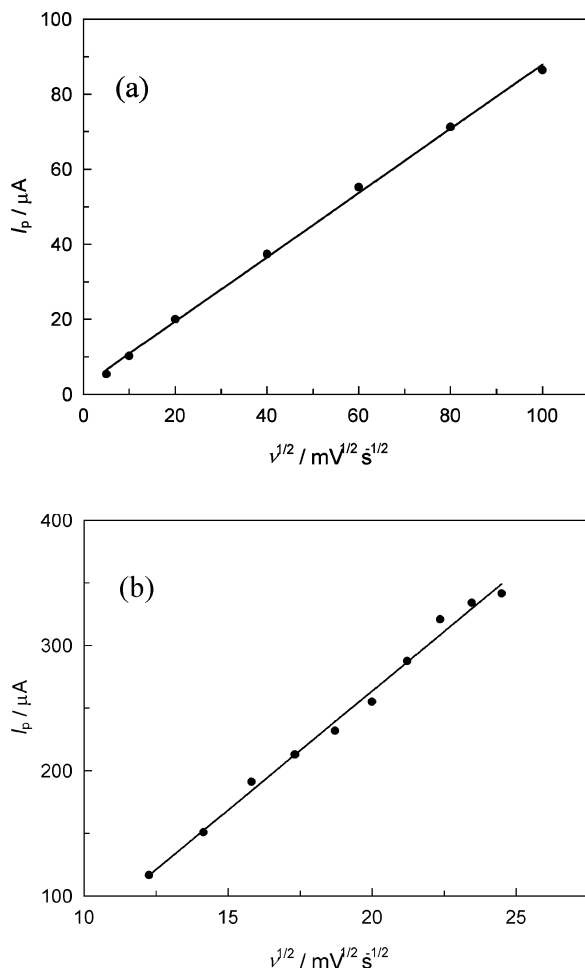


Fig. 2. Dependence of the anodic peak current on scan rate. Plots of I_p vs. v for slow scans (a), and I_p vs. $v^{1/2}$ for fast scans (b).

ion activity, which is in agreement with similar redox systems (PB and its analogues). In addition, as expected, the electrode response is related to potassium ion activity instead of potassium ion concentration, which is an important problem in the preparation of potassium-selective electrodes based on such solid films [14]. The activities for potassium ions in dilute solutions were calculated according to the Debye–Huckel approximation, in the usual manner in this context [14]. The strong evidence for this behavior is that the formal potentials of the cyclic voltammograms recorded at different K^+ activities show a Nernstian response. The dependence of the formal potential of the directly modified ZnHCF film electrode to the potassium ion activity is shown in Fig. 3. The curve has a slope of 55 mV per decade, which is close to the theoretical slope of 59 mV per decade. As expected potassium ion activity of the supporting electrolyte also has an effect on the peak current, which is usual for this type of redox system [29].

In addition, the effects of various supporting electrolytes containing different cations (alkali metals) were investigated. For this purpose, voltammetric studies of

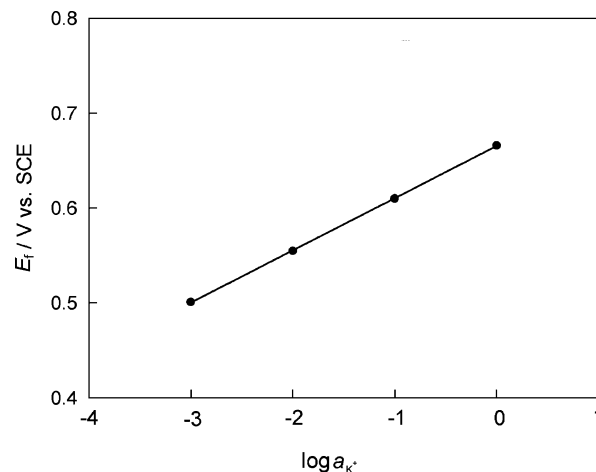


Fig. 3. Relationship of the formal potential of the directly modified ZnHCF film electrode to potassium ion activity.

the modified electrode were carried out using different supporting electrolytes with cations of alkali metals. The formal potentials of the ZnHCF modified electrode in the presence of different supporting electrolytes were determined from voltammetric experiments as $E_f = (E_{p,a} + E_{p,c})/2$, where $E_{p,a}$ and $E_{p,c}$ are the anodic and cathodic peak potentials, respectively. The calculated values for the formal potentials of the ZnHCF film in the presence of different cations are presented in Table 1.

The ZnHCF film can be cycled in the presence of sodium ion. This is in contrast to what is observed for PB, though it has been reported for NiHCF and some other transition metal hexacyanoferrates [13,15,30]. In the case of rubidium and cesium ions, a gradual deterioration is observed. It is clear that the shape of voltammogram changes as the formal potential of the modified electrode varies in the presence of different cations. The main reason for this behavior is due to an enthalpy term included in the Gibbs energy of mixing, as has been discussed by Scholz and Dostal for different solid metal hexacyanometalates [16]. The channel diameter is approximately constant for different transition metal hexacyanoferrates (ca. 320 pm) [16]. The diameters of alkali-metal ions are shown in Table 1. This explains why smaller ions can easily be exchanged into

Table 1
Effect of the supporting electrolyte (0.1 M concentration) on the voltammetric characteristics of the directly modified ZnHCF film electrode

	Cation diameter/pm	E_f^0/V vs. SCE	$\Delta G_{it}/kJ\ mol^{-1}$
Li ⁺	148	0.621	−114.6
Na ⁺	204	0.574	−89.7
K ⁺	276	0.666	−73.5
Rb ⁺	298	0.759	−67.5
Cs ⁺	340	0.556	−60.8

the solid film, and also the special behavior of rubidium and cesium (gradual deterioration). In addition, the Gibbs energies of different cations are presented in Table 1, which similarly explains the behavior for lithium [16].

3.2. Stability of the directly modified ZnHCF film electrode

The stability of the ZnHCF film immobilized on the electrode surface was studied during potential cycling and long-term usage. As has been reported [31], the main drawback for CMEs based on transition metal cyanide complexes is gradual dissolution of the electroactive films during potential cycling. The effect of potential cycling on the directly modified ZnHCF film electrode is shown in Fig. 4(a). For this purpose, the repetitive cyclic voltammograms were recorded as the potential was scanned between 0.0 and 0.9 V (vs. SCE) with a scan rate of 50 mV s⁻¹. It is noticeable that the deposited film is stable for more potential cycles.

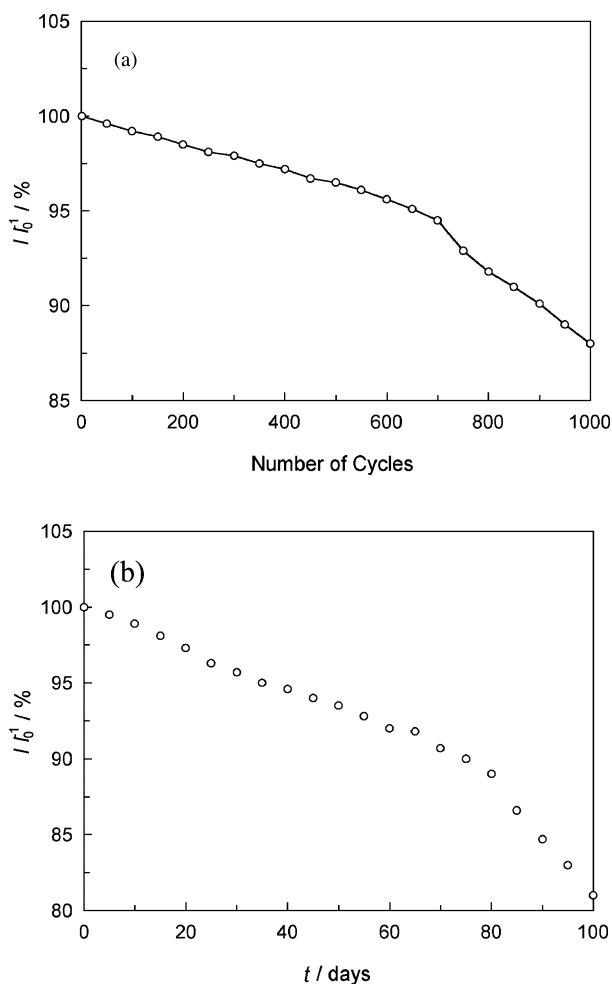


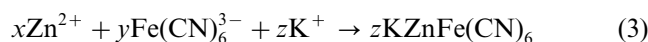
Fig. 4. Stability of the ZnHCF film formed directly on the Zn substrate electrode: (a) during potential cycling; and (b) in long-term usage.

However, the first 1000 cycles are presented as a typical behavior. The electroactive film shows only a 10% decrease in the peak current during 1000 potential cycles, indicating a high stability of the ZnHCF film formed on the Zn electrode surface. This enhanced stability of the deposited film can be concluded by comparison of the results obtained with those reported in the literature such as a 90% decrease in stability during the same number of potential cycles for CoHCF, NiHCF and InHCF [31–33].

In addition, the long-term stability of the modified electrode was also examined. The voltammetric response of the directly modified ZnHCF electrode was investigated during 100 days of usage (Fig. 4(b)). It shows a high stability of the ZnHCF film formed directly on the Zn electrode surface during long-term usage as well as the stability during potential cycling. This enhanced stability of the ZnHCF film modified electrode is related to the simple modification process, as the electroactive film is formed directly on the electrode surface and the electrode has one interface of the substrate electrode | electroactive film. This effect is simple and has been described previously [25]. Another important reason for the enhanced stability of the directly modified electrode is the occurrence of a self-passivation process. Formation of a passive layer on the substrate electrode creates more suitable sites for the deposition of the electroactive film. This phenomenon has been examined for the deposition of various transition metal hexacyanometalates [34–36].

3.3. Effect of experimental conditions during modification process

As a part of our investigation, the effect of the experimental conditions during the modification process on the electrochemical behavior of the directly modified ZnHCF film electrode was investigated and compared with the results reported in the literature. It has been reported that ZnHCF film can be prepared electrochemically only at an equal ratio of zinc and ferricyanide ion concentrations [22]. For example, in a ratio of 1:2 for Zn²⁺/Fe(CN)₆³⁻, the cathodic peak disappears in the voltammetric characterization and similar behavior is observed for the anodic peak for a 2:1 ratio [22]. The general reaction for the formation of ZnHCF film can be written as:



where z is equal to the lower concentration (x or y). According to the results obtained from experimental studies of the formation of the ZnHCF film on glassy carbon from an aqueous solution of zinc and hexacyanoferrate, the reaction occurs to form a well-defined electroactive film only where $x = y$.

To study this effect, we have investigated the effect of the modification species on the electrochemical behavior of the electrode. Due to the type of modification, it is not possible to change the value of x (in Eq. (3)), as there is no Zn ion in the modification solution. Thus, the effect of the concentration of ferricyanide ion and supporting electrolyte (potassium chloride) was examined. Both species had little effects on the nature of the electroactive film. The effect of potassium ion concentration is similar to the effects reported in the literature for PB analogues as a usual effect of the supporting electrolyte. The concentration of $\text{Fe}(\text{CN})_6^{3-}$ has no effect on the type of electroactive film produced. This means that the nature of the electroactive film formed directly on the Zn electrode is independent of the ferricyanide concentration in the modification solution. The modification time increases with decreasing ferricyanide ion concentration but the prepared films have similar voltammetric characteristics. The results are indicative of the fact that, unlike the previous report [22], the ZnHCF film formed directly on the Zn electrode surface is not affected by the concentration of the modification species. It is due to the type of modification process as will be described briefly below.

To investigate the influence of the experimental conditions during the modification process on the electrochemical behavior of the deposited film, different modified electrodes were prepared using modification solutions at various pHs (Table 2). According to the data presented, the ZnHCF film can be obtained only at near-neutral pHs. At both basic and acidic pHs, the voltammetric characteristics of the electroactive film do not show reversible behavior. By further attention to the results obtained, it can be recognized that this behavior is similar to that reported for a high ratio of zinc ion in the modification solution [22]. This is completely in agreement with our knowledge about the electrochemical behavior of Zn in basic and acidic media. In these media, dissolution of zinc causes the generation of zinc ion and an increase in its concentration in the solution (particularly around the electrode surface). This is similar to a high ratio of zinc in the modification solution. In fact, the active dissolution of zinc in acidic or basic media causes an increase of the zinc ion concentration at the electrode surface.

Table 2
Effect of solution pH in the modification process on the voltammetric behavior of the modified electrode

Solution pH	$\Delta E/\text{mV}$ vs. SCE
2	77
4	12
6	8
8	15
10	50

In addition to the effect of solution pH, the electrochemical behavior of the modified electrode is affected by the nature of the buffer solution. It was found that the voltammetric characteristics of the ZnHCF film modified electrode are different in the presence of various buffers. Of course, this effect is not very strong and changes in the voltammogram shape are not noticeable. The effect is mainly obvious by the peak current of the voltammogram. The results obtained from voltammetric measurements of the modified electrode in different buffer solutions are presented in Table 3. This behavior is due to the electrochemical properties of the electroactive film and has been observed for other hexacyanoferrate film-based modified electrodes [36].

Out of the near-neutral pH range, in acidic or basic solutions, high peak currents with large values of the peak-to-peak separation are observed due to the appearance of electrocrystallization phenomena as the result of an excess concentration of Zn^{2+} in bulk solution and at the electrode surface. Consequently, the results obtained from experimental measurements presented in Tables 2 and 3 suggest near-neutral pHs as the optimum medium for the modification process. However, it should also be emphasized that the nature of the solution buffers has no effect on the most favorable film formation or the appearance of electrocrystallization phenomena. The proposed dependence of the ZnHCF formation on concentration of the modifier species is true only for values of the solution pH, not the type of buffer.

Although, the above statement is simple, it is very useful to obtain a well-defined ZnHCF film. It is assumed that for the case of near-neutral pHs, no active dissolution occurs. This allows the zinc electrode to react with the modification species with a one-electron reaction to form the ZnHCF film according to Reaction (3) in the case of $x = y$. However, this is the main reason for the independency of the ZnHCF film prepared by direct modification from the concentration of the modification species. During the direct modification at near-neutral solution, there is no noticeable dissolution

Table 3
Effect of the buffer solution used during the modification process on the voltammetric characteristics of the ZnHCF film modified electrode

Buffer	pH	$I_p/\mu\text{A}$
Phosphate	4	79.1
Succinic acid	4	83
Acetate	4	77.7
Phosphate	5	92.1
Succinic acid	5	101.4
Acetate	5	98.9
Phosphate	6	105.1
Succinic acid	6	111.8
Acetate	6	109.9

of the zinc electrode and modification occurs by a chemical ion-exchange reaction of ferricyanide ion on the electrode surface. To compare the results with those obtained for the formation of a ZnHCF film on glassy carbon, we turn our attention to Reaction (3). As the ZnHCF formation occurs at the electrode surface, the surface concentration of the modification species is important in attaining the aforementioned ratio. To balance the charge in the electrode surface solution, for every ferricyanide ion reaching the electrode surface, a zinc ion dissolves. Thus, over the time of the modification process, the concentration of ferricyanide is equal to that of zinc ion, indicating the necessary condition of $x = y$ for the formation of the well-defined ZnHCF film described for Reaction (3).

It should be noted that the pH of the supporting electrolyte has an effect on the formation of an

electroactive film only during the modification process. The acidic or basic medium causes the dissolution of the bare zinc electrode, whereas, after modification of the electrode surface, the constructed electrode can be used in relatively acidic and basic media, as the deposited film protects the zinc substrate against corrosion.

3.4. Electrocatalytic oxidation of thiosulfate at the directly modified ZnHCF film electrode

The electrocatalytic activity of the ZnHCF film directly modified electrode was examined for the electrocatalytic oxidation of thiosulfate. Electrocatalytic oxidation of thiosulfate is of interest from both the chemical and biological points of view [37]. Therefore, it is the subject of much research and different electrodes including hexacyanoferrate-based modified electrodes

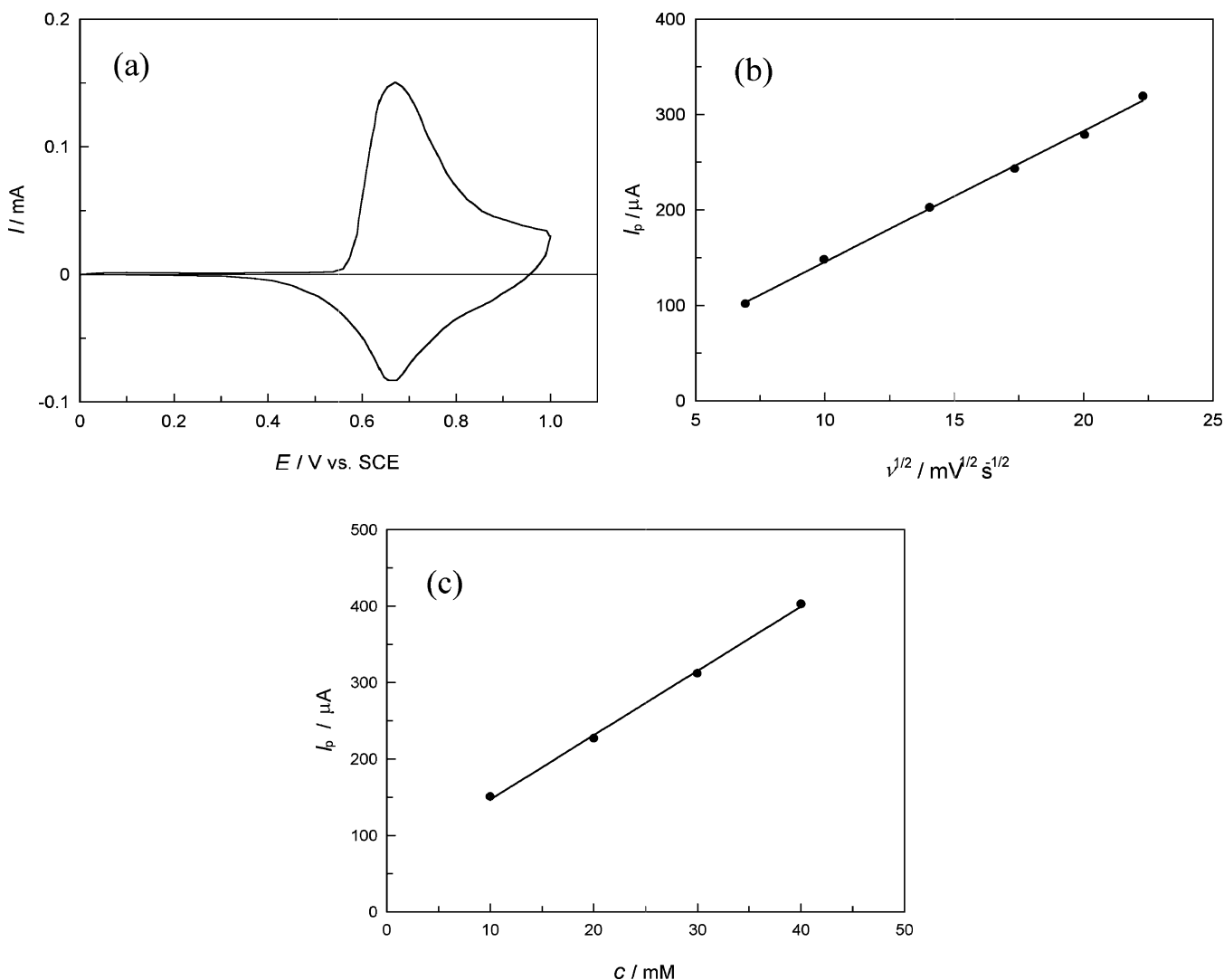
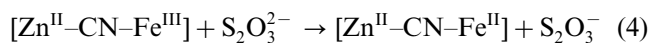


Fig. 5. (a) Electrocatalytic oxidation of thiosulfate at the directly modified ZnHCF film electrode in 0.1 M KCl supporting electrolyte with scan rate, $v = 100 \text{ mV s}^{-1}$ in the presence of 10 mM $\text{S}_2\text{O}_3^{2-}$. (b) The variation of the anodic peak current as a function of square root of scan rate. (c) The dependence of the anodic peak current on the thiosulfate concentration.

have been applied for this purpose [38–42]. Electro-catalytic oxidation of thiosulfate at the directly modified ZnHCF film electrode is presented in Fig. 5(a). As is seen, the electrocatalytic reaction occurs at the same potential of the ZnHCF redox for the oxidation of $[\text{Fe}(\text{CN})_6]^{4-}$ (Fig. 1). This indicates that the electrochemically generated $[\text{Fe}(\text{CN})_6]^{3-}$ in the film is responsible for the oxidation of thiosulfate ($2\text{S}_2\text{O}_3^{2-} = \text{S}_4\text{O}_6^{2-} + 2\text{e}^-$, $E^\circ = -0.08 \text{ V}$ [43]). The overall process can be expressed as:



As presented in Fig. 5(b), the anodic peak current of the thiosulfate oxidation process is proportional to the square root of the scan rate, which is indicative of the fact that the reaction is mass transfer controlled. Moreover, the peak potential shifts towards more positive potentials by increasing the scan rate, suggesting a kinetic limitation in the reaction between the redox sites of the electroactive film (ZnHCF) and thiosulfate.

The results obtained from electrocatalytic oxidation of thiosulfate at different concentrations showed that the cathodic peak current is proportional to the $\text{S}_2\text{O}_3^{2-}$ concentration. The peak current increases with increasing $\text{S}_2\text{O}_3^{2-}$ concentration (Fig. 5(c)). This indicates that the electrocatalytic activity of the modified electrode towards thiosulfate can be used for analytical purposes. The results are satisfactory for the determination of $\text{S}_2\text{O}_3^{2-}$, as the calibration plot (Fig. 5(c)) has a correlation coefficient of 0.0998 and a sensitivity of $8.41 \mu\text{A mM}^{-1}$.

4. Conclusion

A thin solid film of ZnHCF was chemically deposited onto a zinc electrode. The electroactive film formed on the electrode surface has high stability during potential cycling and long-term usage. In contrast to the available method reported in the literature for the formation of a favorable film with well-defined electrochemical behavior, the ZnHCF film was formed on the electrode surface without dependence on the concentration of the modification species. This is due to the direct modification process whereby the film formation occurs by a simple chemical reaction on the electrode surface. It occurs with a constant stoichiometric ratio of modifier species during the modification process. In addition, it was shown that in acidic or basic media, dissolution of zinc causes an increase of Zn^{2+} and unity of the aforementioned ratio is not necessary for favorable formation of the ZnHCF film.

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