

Study of zinc hexacyanoferrate—modified platinum electrodes using electrochemical quartz crystal microbalance

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Abstract In this work, the electrochemical quartz crystal microbalance has been employed to monitor directly the in situ growth of the zinc hexacyanoferrate film during the electrodeposition. Mass changes of the platinum|crystal working electrode were correlated with cyclic voltammetry data. Effects of the sorption of counter-cations (K^+ , Na^+ , and NH_4^+ and anions (Cl^- and SO_4^{2-}) during redox reactions were studied. The electrocatalytic oxidation properties of procaine by the zinc hexacyanoferrate films were performed.

Keywords Electrochemical quartz crystal microbalance · Zinc hexacyanoferrate · Chemically modified electrode · Procaine

Introduction

The application of the metal hexacyanometallates, also known as complexes of mixed valence, such as Prussian blue and its analogues, have been widely studied for decades. Metal hexacyanoferrates films show interesting redox chemistry that is accompanied by changes in their electrochromic, ion change, and electrocatalytic properties.

Thus, modified electrodes with metal hexacyanoferrate films, such as: cobalt hexacyanoferrate [1–3], thallium hexacyanoferrate [3], nickel hexacyanoferrate [1, 4],

indium hexacyanoferrate [1, 5], copper hexacyanoferrate [6, 7], vanadium hexacyanoferrate [8], osmium hexacyanoferrate [9], among others, have attracted the attention of several systems and researchers as materials for the preparation and characterization in the study of electrocatalytic reactions, using an electrochemical quartz crystal microbalance technique.

Inside of the metal-substituted analogues of Prussian blue, we can give prominence for the zinc hexacyanoferrate (ZnHCF). Initially, it was used by Kolthoff and Furman [10], and it was confirmed by Gibalo and Byr'ko [11]. However, it became necessary to analyze the physicochemical [12–20] and electrochemical properties [21–24] of this compound. So, the formation of insoluble complex, in the presence of several sulfonamides and procaine, was studied by Fogg and Reynolds [25, 26] using the fine layer chromatography and co-precipitation analyses.

Thus, the use of modified electrodes with ZnHCF in various electrodic matrixes, including its application such as an ion-selective electrode for alkali-ion metal [27], for the determination of several compounds have been growing becoming necessary the study of their physicochemical properties.

Subsequently, the electrochemical behavior and electrocatalytic activity of the metallic aluminum electrode modified with ZnHCF was studied by Eftekhari [28]. The result showed that the film formed on the electrode surface is highly stable, being formed without the dependence of the ratio between the added species. Analyzing the influence of pH of the reaction medium, the author observed that the dissolution of the film formed in alkaline medium increases the concentration of Zn^{2+} ions in solution. Also, it examined the electrocatalytic oxidation of thiosulfate in the presence of the modified electrode with

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ZnHCF, which observed through the calibration curve, that the modified electrode is a good sensor for determining $S_2O_3^{2-}$, giving a sensitivity of $8.41 \mu A \text{ mM}^{-1}$.

Thin films of ZnHCF are typically fabricated by electrodeposition. The process that leads to the formation of the ZnHCF on the electrode surface needs to be carefully and easily controlled by using consecutive cyclic voltammetry as a synthetic procedure. Thus, a combination of the electrochemical quartz crystal microbalance (EQCM) and the cyclic voltammetric (CV) techniques has been considered by many researchers in the last two decades.

The EQCM comprises a thin vibrating AT-cut quartz wafer sandwiched between two metal excitation electrodes. When small amounts of mass are adsorbed at the quartz electrode surface, the frequency of the quartz is changed according to the Sauerbrey equation [29].

When the surface of a quartz crystal electrode is coated by a material capable of interaction with the environment of interest, a sensor sensitive to this component can be constructed. The performance characteristics of the QCM sensor (such as selectivity, response time, and reversibility) will depend on the chemical nature and physical properties of the coating material. There has been considerable interest in its usage to monitor mass changes at electrode surfaces and in thin films on electrodes. This in situ approach has provided an important experimental method for studying the sorption of ions and solvent molecules in surface films on electrodes.

Due an important advantage of EQCM in answering to small mass changes on the surface of the electrode, it can be ended that this technique is not a selective detector and responds to any mass change. At this, the surface modification of the EQCM with a chemically selective reagent can lead to a useful chemical sensor which works in aqueous systems in which the insoluble salt exhibits selective adsorption/desorption of its component ions. So, if EQCM were coated with a thin film containing an insoluble ion-pair complex, it would become a highly selective and sensitive sensor showing a wide range of response.

Besides the electrochemical behavior, it has also been highlighted in the literature, studies of the electrocatalytic activity of this hexacyanoferrate, associated with the analysis of the growth of the film using EQCM, in the detection of some important analytes such as guanine [30], epinephrine [30], dopamine [30], and L-cysteine [30].

In this paper, we describe an in situ preparation and the ion exchange properties of the hybrid film of ZnHCF based on the use of the cyclic EQCM technique. The electrocatalytic oxidation behavior of the procaine in the presence this hexacyanoferrate also was studied.

Experimental

Apparatus

Electrochemical measurements were made by means of cyclic voltammetry. CV was performed using a typical three-electrode cell where a platinum electrode of the piezoelectric quartz crystal (5 MHz AT-cut; Maxtek Inc.) of 1.37 cm^2 was the working electrode, a platinum wire was the counter electrode, and a $\text{Ag}/\text{AgCl}/\text{KCl}_{\text{sat}}$ was the reference electrode. All experiments were carried out by using the electrochemical quartz crystal microbalance PM-700 Series Plating Monitors (Maxtek Inc.) and the AUTOLAB PGSTAT 30 (Ecochemie) potentiostat controlled by a personal computer using the GPES 4.9 software. In the previous studies, the EQCM was calibrated by means of a galvanostatic Cu electrodeposition using CuSO_4 0.5 mol L^{-1} , H_2SO_4 0.1 mol L^{-1} , pH 1.92, and T 297.15 K. Thus, the experimental Sauerbrey constant is $5.60 \times 10^7 \text{ Hz g}^{-1} \text{ cm}^2$.

With relationship of the cleaning, the electrodes were polished, mechanically, after each experiment and washed with water from a Millipore Milli-Q system.

Reagents and solutions

All solutions were prepared using water from a Millipore Milli-Q system. The procaine hydrochloride (Sigma–Aldrich), potassium ferricyanide (Carlo Erba Reagents), zinc chloride (Mallinckrodt), and potassium chloride (Mallinckrodt), which was of analytical reagent grade, were used without further purification. The supporting electrolyte used for all experiments was a 1.0 mol L^{-1} potassium chloride solution without the adjustment in the value of the pH. A $1.0 \times 10^{-3} \text{ mol L}^{-1}$ procaine stock solution was prepared daily by dissolving a certain mass of the analyte (Sigma–Aldrich) in a small volume of concentrated HCl (Merck) until its complete dissolution and soon after diluting it in water purified by the system Milli-Q of Milipore®.

Procedure

The electrochemical formation of the zinc hexacyanoferrate was prepared using ZnCl_2 0.1 mol L^{-1} , $\text{K}_3\text{Fe}(\text{CN})_6$ 0.05 mol L^{-1} , KCl 0.5 mol L^{-1} , and HCl 0.1 mol L^{-1} solutions in $\text{pH} \approx 2.0$ where the formation of an orange precipitated was observed. The thin film were performed, on the surface of piezoelectric quartz crystal, by continuous cycling in a defined potential range between 0.0 and +1.2 V at scan rate of 5 mV s^{-1} and room temperature. The resulting modified electrode was rinsed with water purified by the system Milli-Q of Milipore®. After modification

procedure was completed, the modified electrode was immersed in a series of standard or sample solutions of the procaine and then the electrochemical behavior and massograms were recorded.

Results and discussion

Electrodeposition of the ZnHCF film

The transition metal hexacyanoferrate can be electrochemically grown on conducting substrates either during reduction steps (potential cycles) in colloidal solutions (containing hexacyanoferrate(III), a metal cation, and potassium electrolyte) or via generation of surface precipitates during oxidation of a metal film (which was previously deposited onto the substrate) in the presence of hexacyanoferrate(II).

Figure 1a and b shows typical current (cyclic voltammetry) and mass (EQCM) responses recorded during five consecutive potential cycles in zinc hexacyanoferrate modification solution according to the procedure described in the “Experimental” section. Both the increase of voltammetric peak currents in Fig. 1a and the mass increase in Fig. 1b are consistent with the steady growth of ZnHCF film on the electrode substrate (Pt). The voltammetric response of the crystal of quartz covered with film of ZnHCF, after several successive cycles, presents a defined redox pair in +0.95/+0.75 V in whose potential range, only the hexacyanoferrate is electroactive. Previous tests showed that the efficiency of growth of the film decreases, abruptly, with the increase of the number of cycles or of the scan rate during the deposition process. This behavior can be explained by the formation of very thick films and of bad adherence in the electrodic surface.

Observing the Fig. 1a, the reactional process can be explained when the species $\text{Fe}^{\text{III}}(\text{CN})_6^{3-}$ is reduced in $\text{Fe}^{\text{II}}(\text{CN})_6^{4-}$ followed, instantly, for the reaction with Zn^{2+} ion producing the ZnHCF film on the surface of the electrode. The growth of the film happens in the reduction could be confirmed by the increase of the mass. The zinc hexacyanoferrate film showed a chemically reversible redox couple in 0.5 mol L^{-1} aqueous KCl pH 5.5 solution when cyclic voltammetry was performed.

According to the theoretical concepts presented in the literature [31] for a surface covered with species redox, the peak-to-peak separation, ΔE_{peak} ($E_{\text{cathodic peak}} - E_{\text{anodic peak}}$), for chemically modified electrode, is equal to zero; even so the experimental value found, for the redox couple in the cyclic voltammograms, was non-zero ($\Delta E_{\text{peak}} = 120 \text{ mV}$) at a scan rate of 10 mV s^{-1} , indicating that the redox couple might involve an ion exchange or proton transfer, a smaller rate in the electronic transfer and/or an increase of the resistance of the formed film. The reversibility of the

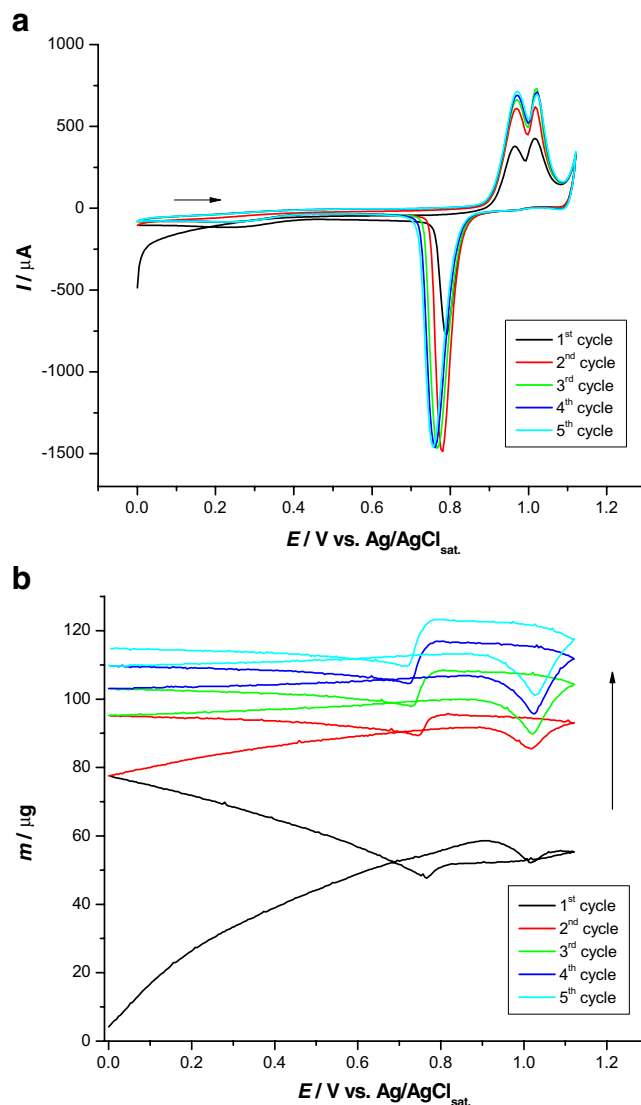


Fig. 1 a Cyclic voltammograms during the electrochemical formation of a ZnHCF film. Scan rate, 5 mV s^{-1} ; solution, ZnCl_2 0.1 mol L^{-1} ; $\text{K}_3\text{Fe}(\text{CN})_6$ 0.05 mol L^{-1} ; KCl 0.5 mol L^{-1} ; HCl 0.1 mol L^{-1} ; $\text{pH} \approx 2.0$. b EQCM mass response obtained simultaneously with the cyclic voltammograms of Fig. 2a

electron transfer process can be analyzed through the relationship between the anodic and cathodic peak currents, determined by Nicholson–Shain equation, that for redox reactions, it is the same to 1. For the hexacyanometallate in subject, the found ratio of $I_{\text{anodic peak}}/I_{\text{cathodic peak}}$ was 0.47 for a scan rate of 10 mV s^{-1} , showing that the system stands back of the reversibility.

In the potential +0.95 V, the present anodic peak, possibly, can be attributed an intermediate compound in the reactional stage of the formation of the film and with the washing of the electrode, this compound soluble itself.

The superficial excess of the deposited film can be expressed by the integration of the area through the

equation: under the voltammetry wave, for the obtention of the charge Q and applied in the relation $\Gamma = Q/nFA$ in which Γ is the concentration or superficial excess (cm), n is the number, A the area of the electrode (cm²), and F is the constant of Faraday (96,500 C mol⁻¹). Therefore, using the equation above mentioned, the value of the superficial excess of the film of zinc hexacyanoferrate was determined deposited in the piezoelectric quartz crystal with platinum surface whose found value, for ten voltammetric cycles, was $(1.82 \pm 0.76) \times 10^{-4}$ mol cm⁻².

Also, it is necessary to verify the viscoelastic changes in the structure of the film deposited on the electrodic surface for the evaluation of the correct use of the EQCM [32]. So, the viscoelastic behavior of the film was analyzed through the relation between the mass variation (Δm) and the charge Q (Fig. 2), where the linear profile, represented by the equation $\Delta m(\text{g}) = 46.03 + 7.91 \times 10^{-2}Q(\text{C cm}^{-2})$ with a linear correlation coefficient of 0.9943 and a relative standard deviation (RSD) of 1.80%, showing the tendency of the rigid behavior of this formed film.

Monitoring cation effects

According to the theoretical concepts presented in the literature, there is a relationship of dependence between the electrochemical behavior of zinc hexacyanoferrate with the scan rate. Thus, there was the study of the influence of scan rate in KCl 0.50 mol L⁻¹. A typical electrodeposited ZnHCF film (as in Fig. 3a and b) was further subjected to cyclic voltammetric and EQCM diagnostic experiments.

The results, presented by the Fig. 3a and b, showed the increase of the mass until the 4th cycle and the constant variation of the peak currents, at low scan rates (for example, 10 mV s⁻¹), whose behavior is caused by the

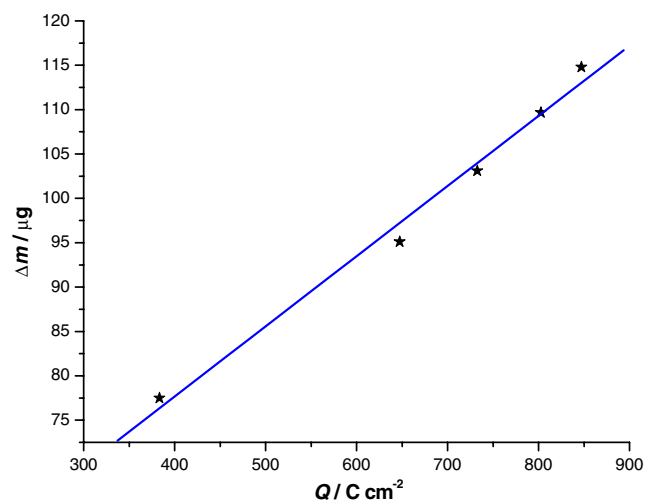


Fig. 2 Variation of the mass in function of the charge for the electrodeposition of zinc hexacyanoferrate

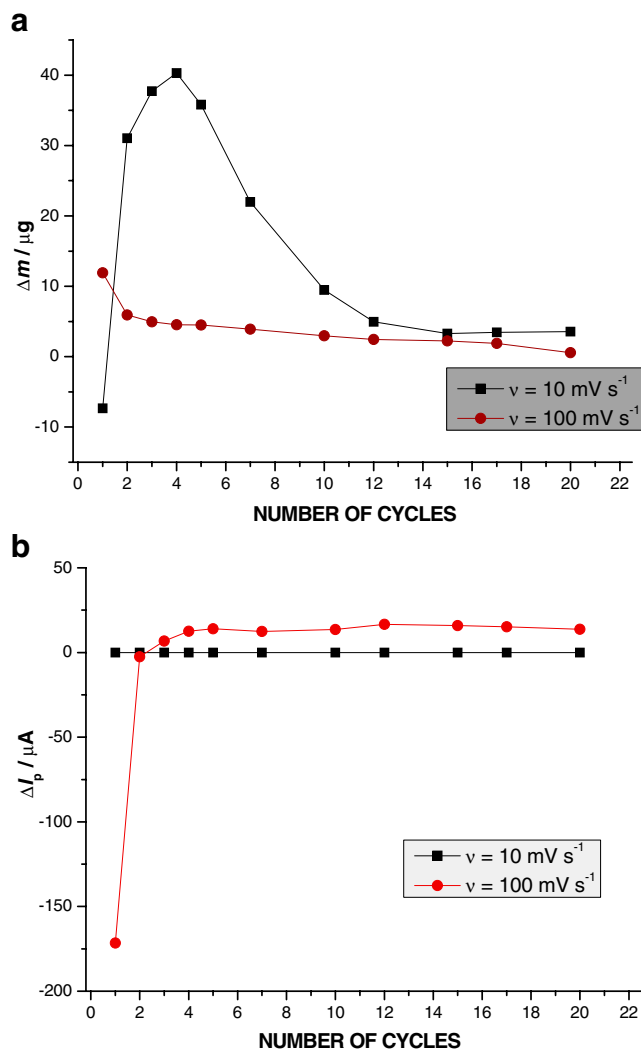


Fig. 3 Influence of the scan rate in the **a** mass variation and of the **b** peak currents for the piezoelectric quartz crystal modified with zinc hexacyanoferrate in the following scan rates of 10 and 100 mV s⁻¹ (KCl 0.5 mol L⁻¹)

diffusion of the K⁺ ions into the structure of the film. At higher scan rates (in this scan range of 100 mV s⁻¹), this behavior cannot be observed because the ionic flux is not complete. So, we observed that the film presented better stability and adherence in the electrodic surface when studied by cyclic voltammetry at low scan rates.

The pH is a very important parameter for the stability of the film formed as the same as the stability decreases in alkaline medium, where there is a decrease of the anodic and cathodic currents caused by the degradation of the film.

Therefore, based in this information, we studied the effect of the pH on the electrochemistry response and on the stability of the chemically modified electrode with zinc hexacyanoferrate in the KCl 0.5 mol L⁻¹ solution, with different levels of acidity. The results of these experiments are shown in the Table 1.

Table 1 Variation of the mass and current of the zinc hexacyanoferrate film after ten cycles, in 0.5 mol L⁻¹ solution of KCl, under different pHs

pH	$\Delta m/\mu\text{g}$	$\Delta I/\times 10^{-4} \text{ A}$
2.0	8.94	-4.43
4.0	6.53	-4.43
6.0	-50.86	-4.36
8.0	-8.90	-4.00
10.0	-0.05	-4.59

It was observed that, in the whole range of studied pH, the film did not show the electrochemical signal. This behavior was observed because all the sites of the Zn²⁺ or Fe³⁺ ions present in the zeolitic structure are busy other than the occurrence of the charge transfer in the maximum value of the peak current for each studied pH. With relationship to the study of the mass variation, for the pH range between 4.0 and 2.0, there is an increase in mass caused by the diffusion and incorporation of the cations in the crystalline lattice until it has stabilized even so without causing the dissolution of the film. That behavior can be explained by the competition between the H⁺ and K⁺ ions during the process of electrodic transfer. Already, at higher pHs (above pH 6), the film deposited on a platinum substrate undergoes profound chemical and structural alterations in which it occurs the dissolution of the film electrodeposited on the electrode surface because the complex is influenced by the hydrolysis of Zn(II) in alkaline medium. So, we opted for using the KCl supporting electrolyte without pH adjustment in order to facilitate the experimental procedure used.

It is known that the zeolites as hexacyanoferrates are known by reversible insertion of the cations of alkaline metals during the electrochemical redox process in which the inserted cations move, freely, among the sites of the crystalline grip of the hexacyanoferrate where the movement in the ion channel of the hexacyanoferrates are not accompanied by any dissolution of the solid compositions.

Simultaneous cyclic voltammetric and mass responses are done for a ZnHCF film exposed to 0.5 mol L⁻¹ potassium, sodium, and ammonium (chloride) electrolytes, respectively. The increase of mass is seen during reduction of ZnHCF in all these electrolytes and an opposite effect can be observed during oxidation. In general, a flux of cations accompanies electron transfer: cations are incorporated into the ZnHCF film during reduction and expelled from this phase during oxidation.

Analyzing the experimental responses, it can be observed that the behavior was similar for all tested electrolytes in other words; there is a progressive decrease of the electrochemical signal and an increase of the mass during the successive scans.

Also, it has been established that metal hexacyanoferrates show selective permeability towards the cations in the supporting electrolyte, such as alkali metal ions and other

monovalent and divalent cations, due to their intrinsic zeolitic structure. Only those cations with hydrated radii smaller than that of the ion channel of hexacyanoferrates can be easily accommodated. So, in this case, these permeability orders are in accord with the order of hydrated ionic radius where the voltammetric cycle of the K⁺ ion, whose hydration diameter is 2.4 Å, showed a great ability in penetrating easily into the interior of the interstitial zeolitic structure, replacing the H⁺ ion of the hydrated part of the complex, allowing the generation of Faraday's currents during the electrodeposition process. This easiness incorporation has as purpose the maintenance of the electroneutrality of the system during the reactional process. For the NH₄⁺ and Na⁺ ions, where the hydration radii of the ions are larger than the diameter of the zeolitic cage, there was a distortion of this profile attributed that is to say the highly hydrated lithium or ammonium ions move slowly, while the least hydrated potassium has the fastest transport rates that generates the difficulty of mobility and incorporation within the crystalline structure of the hexacyanoferrate resulting to a bad definition and less stability of the redox behavior of the ZnHCF film.

So, the order of mobility in the zeolitic structure of the complex formed is K⁺ > Na⁺ > NH₄⁺, indicating that the film possesses a prior selectivity for K⁺ ion as a counter-ion among the above three cations.

Monitoring anion effects

In the above discussion, we assume that alkali metal cations are the only mobile counter-cations that provide charge balance during ZnHCF redox reactions. In the majority of literature reports, the anion effect is neglected although some differences in the cyclic voltammetric responses have been reported which it was showing contradictory results concerning the general role of anions in the electrochemistry of metal hexacyanoferrate films. Therefore, in order to clarify the importance of these anions in the electrochemical behavior of ZnHCF, the influence of the Cl⁻ and SO₄²⁻ ions were analyzed, in the present study, in supporting electrolyte solutions, containing the K⁺ ion in the concentration 0,5 mol L⁻¹.

The effect of anions is clearly seen in Fig. 4a and b which shows the cyclic voltammetric and simultaneously obtained EQCM curves for a ZnHCF film in contact with the electrolytes mentioned above. Analyzing the results, it can be observed that the voltammetric behavior of ZnHCF is almost independent of the choice of the anion in the electrolyte containing K⁺ ions. Although, there is no significant change in the values of the peak potentials, the differences in the kinetic behavior are evident. In both cases, there was a decrease of the anodic and cathodic peak currents whose characteristic is, possibly, of the electro-

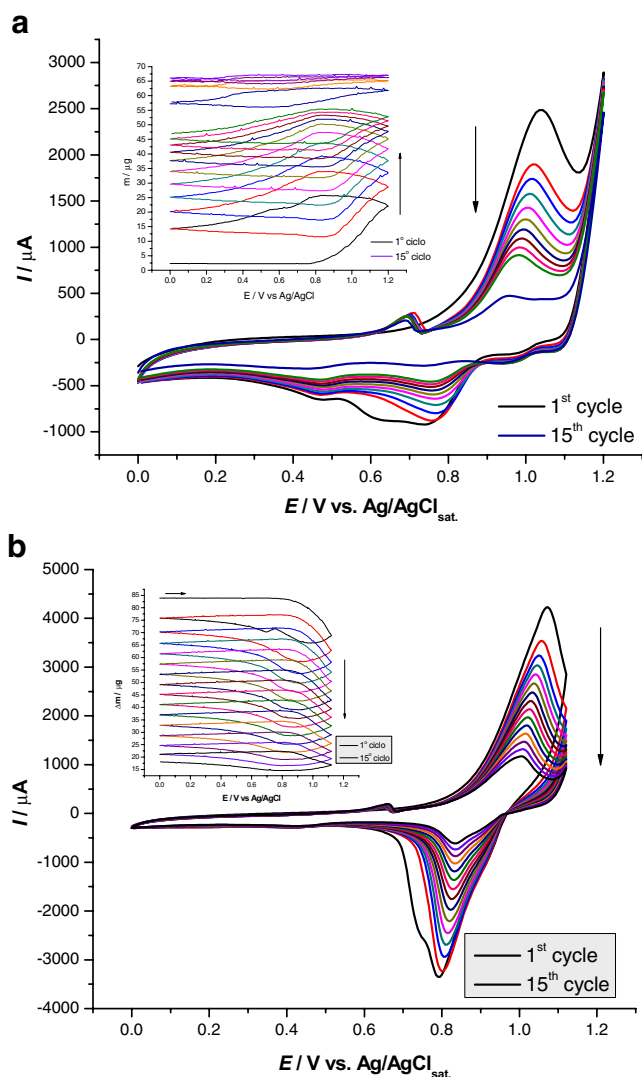


Fig. 4 Cyclic voltammograms and inserted EQCM responses of a platinum electrode of the piezoelectric quartz crystal modified with zinc hexacyanoferrate in the electrolytes solutions: **a** KCl 0.5 mol L⁻¹ and **b** K₂SO₄ 0.5 mol L⁻¹ (Scan rate: 10 mV s⁻¹)

inactivity of the compound and/or increased resistance of the film formed on the electrodic surface.

In the presence of the Cl⁻ anions, the transport of the charge is easier and there is an increase of the deposited mass due to the incorporation of these anions, for example, under the form of the ionic pairs where an oxygen from the water molecule, present in the vacancy of the formed complex, is replaced by Cl⁻ ion without affecting the balance of the system in subject. As for the SO₄²⁻ ions, an antagonistic behavior was observed with respect to the mass, possibly, caused by the difficulty of incorporation of these anions in the crystalline lattice of this compound leading to the dissolution of the film.

Some attention was paid to the influence of a counterion concentration on the voltammetric characteristics of

ZnHCF. These films are highly stable in aqueous solutions of KCl. The combination between EQCM and cyclic voltammetry allows the obtaining of an estimate for the mass molar of the species involved in the electronic transfer. Therefore, in order to extract information more meaningful about the data presented by the EQCM technique, it is useful to report the changes in the mass with the transmitted electric charge. The mass/charge ratio gives the information about the nature of the species or the mechanism of a chemical reaction involving changes in mass on the surface of the electrode, in which it is shown by the relation $W_{\text{dep}} = F \frac{\Delta m}{\Delta Q}$ where W_{dep} is the mass/charge relationship ($\mu\text{g mol}^{-1}$), F the Faraday constant (C mol^{-1}), Δm the mass change ($\mu\text{g cm}^{-2}$), and ΔQ the charge change (C cm^{-2}). These functions are negative for the increase in mass during the cathodic processes ($\Delta m > 0$; $\Delta Q < 0$) or for the decrease in mass during the anodic processes ($\Delta m < 0$; $\Delta Q > 0$) and are positive for the increase in mass during the anodic processes ($\Delta m > 0$; $\Delta Q > 0$) and the decrease in mass during the cathodic processes ($\Delta m < 0$; $\Delta Q < 0$). This relationship, also, gives idea about the species involved in the compensation reaction of the charge in different potentials during the successive scans in which it is valuable information for elucidating the kinetics of the electrodic processes.

Therefore, we studied the mass/charge ratio for the ZnHCF film electrodeposited on the piezoelectric quartz crystal with platinum surface, in the electrolytic solutions of KCl 0.5 and 1 mol L⁻¹. The observed results showed certain linearity between ΔQ and Δm in the 1 mol L⁻¹ KCl solution in which indicates that the composition of the deposit is quite uniform throughout.

In the conditions mentioned above, the film of ZnHCF presented a better voltammetric response and experimental reproducibility besides the present redox couple in this film is responsible by the proton transfer in the oxidation and reduction processes. Through the slope, the value of the mass/charge ratio (W_{dep}), defined as the mass variation by 1 mol of electrons, was determined whose the average experimental value found was of $(2.70 \pm 0.28) \times 10^4 \text{ g mol}^{-1}$, respectively.

The electrocatalytic oxidation of procaine

The procaine, or procaine hydrochloride, discovered by Alfred Einhorn, is one of the oldest and effective local anesthetics being also named as novocaine or neocaine. This composition is a derived tertiary aminic of the p-aminobenzoic acid [2-(diethylamino)ethyl ester of the 4-aminobenzoic acid]. In the presence of zinc hexacyanoferrate, this analyte reacts to form an insoluble compound which the precipitation is in the order of 90%, according to the literature [26].

The precipitation reaction of this substituted aniline, after the addition of an amount equivalent to the concentration of $1 \times 10^{-3} \text{ mol L}^{-1}$, with the zinc hexacyanoferrate film, previously electrodeposited on the platinum surface of the piezoelectric quartz crystal, in 1 mol L^{-1} KCl supporting electrolyte, using the cyclic voltammetric and the EQCM techniques is shown in Fig. 5a and b.

In the cyclic voltammograms showed in the Fig. 5a, it can be observed that there is an abrupt decrease of the anodic and cathodic peak currents, during the subsequent cycling, until the complete dissolution of the film. The same behavior was observed in the EQCM technique in which the variation of the mass is abrupt during the first successive scans. The variation of the mass in function of the number of cycles is described well in the Fig. 5b in

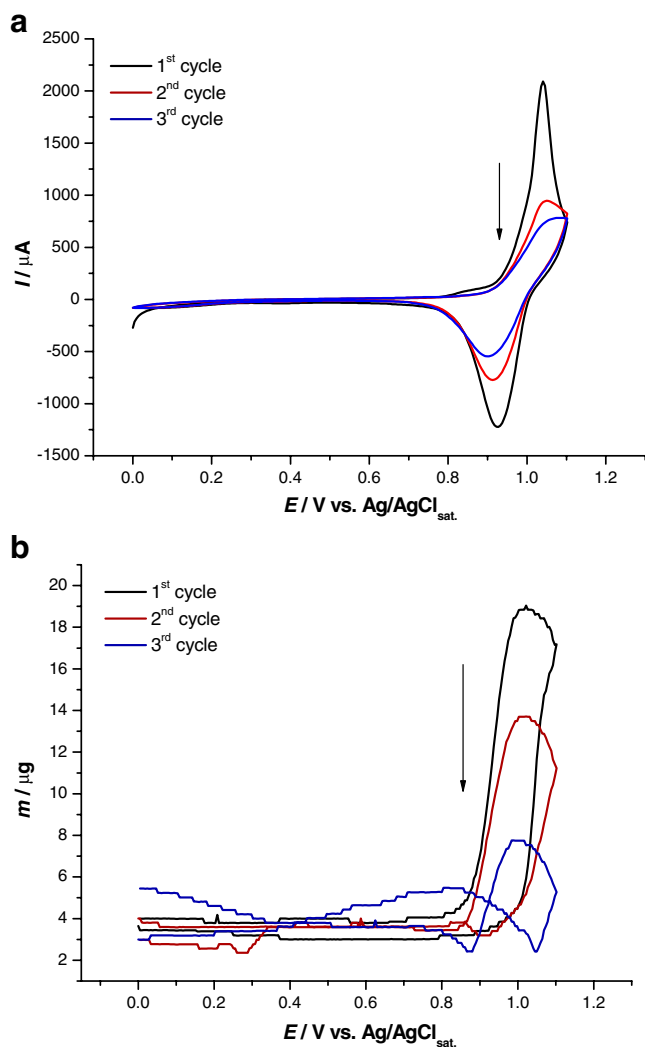


Fig. 5 Behavior of the piezoelectric quartz crystal modified with ZnHCF film after successive scans in the $1 \times 10^{-3} \text{ mol L}^{-1}$ procaine solution: **a** cyclic voltammograms and **b** EQCM responses (KCl 1 mol L^{-1} supporting electrolyte; scan rate, -10 mV s^{-1})

which, after the third cycle, there was complete removal of the film on the electrodic surface. Therefore, based on the chemical structure of the procaine, we supposed that, probably, the reaction of the complex formed occurs when the procaine links itself in the molecule of zinc hexacyanoferrate, causing the exit of the two K^+ ions. Therefore, as there was an expressive decline in the experimental values of the peak currents and in the mass deposited on the electrodic surface, we opted for accomplishing the analyses using just a single scan after the addition of the analyte.

As mentioned earlier, the mass/charge ratio gives us the information about the nature of the species or the mechanism of chemical reaction involving changes in mass on the electrodic surface. Then, Table 2 shows the mass/charge ratio for the concentration range of procaine, at the reaction between the film electrodeposited on the electrodic surface and the analyte in subject. It can be observed that there was a decrease in the value of this ratio as there was a decrease in the concentration of the analyte.

Conclusions

EQCM and cyclic voltammetry are powerful tools for the characterization of the in situ growth of ZnHCF films. Mechanistically, the preparation methods are based on distinct principles: reduction of the $\text{Fe}^{\text{III}}(\text{CN})_6^{3-}$ to $\text{Fe}^{\text{II}}(\text{CN})_6^{4-}$ and reaction with Zn^{2+} ion with $\text{Fe}^{\text{II}}(\text{CN})_6^{4-}$ to produce the ZnHCF film. During potential cycling, this film exhibited a pair of well-defined redox peaks with the formal potentials of $+0.95/+0.75 \text{ V}$ (versus Ag/AgCl), at scan rate of 5 in 1 mol L^{-1} KCl supporting electrolyte and with the superficial excess after ten voltammetric cycles around of $(1.82 \pm 0.76) \times 10^{-4} \text{ mol cm}^{-2}$. So, an inherent advantage of the electrodeposition method is the possibility of easy control (during voltammetric potential cycling) of the film growth.

For diagnosing the counter-ion flux during redox reactions, simultaneous sorption of alkali metal cations takes place. The transport behavior of K^+ , Na^+ and NH_4^+ ions through the channel of ZnHCF were studied. The voltammetric results showed an irregular permeability for the counter-cation in the

Table 2 Mass/charge ratio of the zinc hexacyanoferrate film in the presence of various concentrations of procaine performed in triplicate

$C_{\text{procaine}}/(\text{mol L}^{-1})$	$W_{\text{dep}}/(\text{g mol}^{-1})$
1.0×10^{-3}	$6.70 \pm 0.27 \times 10^5$
1.0×10^{-4}	$5.13 \pm 0.57 \times 10^5$
1.0×10^{-5}	$4.19 \pm 0.17 \times 10^5$
1.0×10^{-6}	$2.09 \pm 0.48 \times 10^5$

order of $K^+ > Na^+ > NH_4^+$ and K^+ ion matched the ion channel of ZnHCF the most closely. The behavior of the ZnHCF film in the presence of the anions showed the facilitated transport of the charge and an increase of the deposited mass for the Cl^- anions but an antagonistic behavior was observed with relationship to the mass for the SO_4^{2-} ions. The pH of the electrolytic solution, also, has a considerable effect in the ionic stability of the film indicating that the acid range is ideal for it analyzing this complex. Therefore, the experiments reported here lead to a better understanding of the charge propagation mechanism in ZnHCF films.

The electrochemical behavior of procaine with the zinc hexacyanoferrate film was investigated using cyclic voltammetry and EQCM techniques in which for the concentration range examined, there was a decrease in peak currents that are directly associated with the mass reduction of the film adheres on the electroodic surface and clearly reflected by the ratio mass/charge.

Thus, these modified quartz crystals have shown great potential for the development of sensors due to their chemical stability, ease of preparation, and possible quantitative application in various areas of chemical–pharmaceutical industry.

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