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Electrochemical Behavior of Thin Ruthenium–Modified Cobalt-Hexacyanoferrate Films Immobilized on Self Assembled Monolayer Gold Electrodes

Valber A. Pedrosa, Mauro Bertotti*

Instituto de Química, USP, São Paulo, SP, Brazil
*E-mail address: valber.pedrosa@gmail.com

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The electrochemical behavior of a ruthenium-modified cobalt–hexacyanoferrate electrode grown electrochemically onto a gold surface previously coated with a monolayer of 3-Mercaptopropionic is reported. Studies on the incorporation of ruthenium centers into the hexacyanoferrate layer were performed and the procedure represented a very effective contribution to the maintenance of the electrode stability. The film exhibited sharp redox peaks at about 0.5V in the presence of K^+ and the peak potential shifted linearly with K^+ concentration over the range 1.0 mmol L^{-1} to 1.0 mol L^{-1}.

Keywords: Modified electrodes, self assembled monolayer, hexacyanoferrates.

1. INTRODUCTION

Self-assembly techniques are gaining importance in electrochemistry since they enable fine-tuning of interfacial structures which will ultimately find applications in diverse fields such as molecular electronics [1], molecular recognition [2] and sensors development [3-5]. Self assembled monolayer (SAM) of alkanethiols and disulfides deposited onto gold surfaces form organic interfaces with properties largely controlled by the end groups of the molecules comprising the film. SAMs provide a unique link between the science of organic surfaces and technologies that seek to exploit their adaptable character. These SAMs may serve as precise spacers with atomic resolution between the electrode and redox centers and provide a way to immobilize redox active groups onto the electrode. Some simple redox systems such as ferrocene [6] derivates and quinones [7] have been widely suited in this way. Moreover, these SAMs can be predesigned on molecule radicals to introduce specific interactions between the monolayer and the analyte for molecule recognition. The SAM surface has a highly organized molecular structure which represents a proper matrix to investigate the interdependence between molecular organization and recognition processes [8]. The modification of redox centers on electrode surfaces using the monolayer approach has been widely reported for investigations of facile electron transfer kinetics [9,10]. For instance, Wang *et al.* [11] reported investigations on mixed dodecanethiol-glutathinone self-assembled monolayers prepared on a gold electrode and further derivatization to form a monolayer of cupric hexacyanoferrate. This modified electrode showed selectivity to potassium ion and exhibited an ideal Nernstian response with a slope of 60 mV/decade in the 10^{-2} to 1.0 mol L^{-1} concentration range.

There has been a growing interest in the preparation and characterization of metal hexacyanoferrates (MHE) as electroactive materials [12,13] because they possess interesting properties such as capability to store counter ions [14], ion exchange selectivity [15] and ability to mediate electrochemical reactions [16]. These inorganic materials must offer high chemical and electrochemical stability along with a simple preparation method to gain acceptance in practical applications. Very often, a satisfactory stability for each MHE based on metal–hexacyanometalate is claimed, but the real applicability of such systems is actually poor and generally inadequate. The main drawback that afflicts MHE based on transition metal cyanides is the gradual dissolution during potential cycling. Among them, nickel hexacyanoferrate (NiHCF) shows good response to alkali metal cations, the electrochemical behavior depending selectively on the type and concentration of cations [17].

Quantitative detection of K^+ ion is considered important since it is the most essential intracellular action for maintaining osmotic pressure and electrodynamic cellular properties in living organisms. Electrodes modified with thin films of electroactive nickel hexacyanoferrate have been shown to act as effective potentiometric sensors for the determination of potassium ions [9,18,19] as the formal potential changes linearly with log $[K^+]$. Accordingly, this report is devoted to a description of a simple procedure that has been developed to produce stable, thin layers of RuCoHCF/SAM electrodes and to study their voltammetric behavior. Applications on the voltammetric determination of K^+ will also be addressed.

2. EXPERIMENTAL

2.1. Materials

3-Mercaptopropionic (3-MPA) (Aldrich 99%), $K_3Fe(CN)_6$, $CoCl_2{\cdot}6H_2O$, ruthenium(III)chloride hydrate, sodium chloride, potassium chloride and ammonium chloride were purchased from Sigma. All the solutions were prepared by dissolving the compounds or concentrated solutions in deionized water processed through a water purification system (Nanopure Infinity, Barnstead).

2.2. Apparatus

Cyclic voltammetry was performed by using an EG&G (Princeton Applied Research, Princeton, NJ) Model 273A potentiostat/galvanostat. Data acquisition and potentiostat control were accomplished with a computer running the M270 electrochemical research software (EG&G) version 4.11. Cyclic voltammetry experiments were carried out at room temperature in a standard threeelectrode glass cell (10 ml) constituted of a gold disc electrode (geometric area = 10 mm^2) as working electrode, a platinum wire as auxiliary and Ag/AgCl (3.0 mol L^{-1} KCl solution) as reference electrode.

2.3. Preparation of the RuCoHCF/SAM modified electrode

The Au electrode surface was polished with 1 μm alumina powder before chemical modification. After the polishing treatment, the electrode was abundantly rinsed with deionized water and sonicated in water for 5 min. Then, the electrode was cleaned in a freshly prepared solution containing 1 part of 30 % H_2O_2 and 3 parts of concentrated H_2SO_4 for 5 min for further washing with deionized water. Finally, the electrode was electrochemically cleaned by cycling the potential between 0.0 and 1.65 V in a 0.5 mol L^{-1} H_2SO_4 solution at 1 V s^{-1} until a characteristic voltammogram of a clean Au electrode was obtained. Immediately after the cleaning step, a monolayer of 3-MPA was immobilized onto the gold surface by immersion in a 1.0 mmol L^{-1} 3-MPA ethanolic solution for 2 hours. The modified electrode was further rinsed with ethanol and water.

The electrochemical deposition of the CoHCF film onto the SAM surface was accomplished by cycling the potential of the SAM electrode between 0.0 and -0.9 V in a freshly prepared solution containing 1.0 mmol L^{-1} $CoCl_2$ and 1.0 mmol L^{-1} $K_3Fe(CN)_6$ in 0.5 mol L^{-1} KCl at pH 3 (20 potential cycles). Subsequently, the CoHCF/SAM electrode was placed in a freshly prepared acidic solution containing 2 mmol L^{-1} $RuCl_3$ and subjected to a potential scanning at 50 mV s^{-1} for 50 cycles. Supporting electrolyte and potential window were the same used for the film deposition. Then, the ruthenium-modified CoHCF/SAM (RuCoHCF/SAM) electrode was placed in the supporting electrolyte and a steady-state voltammetric profile was promptly observed. When not in use the modified electrode was left immersed in the supporting electrolyte.

3. RESULTS AND DISCUSSION

3.1 Electrochemical behavior of the modified electrode

Fig. 1 shows a typical voltammogram of a CoHCF modified electrode grown on a gold surface at two different experimental conditions. Curve a represents the response of the modified electrode in supporting electrolyte just after the electrodeposition procedure. The electrochemical processes associated with redox couples I and II can be written according to Eqs. (1) and (2), respectively [20]:

$$K_2Co^{II}Fe^{II}(CN)_6 \leftrightarrows KCo^{III}Fe^{II}(CN)_6 + K^+ + e^- \qquad (1)$$

$$K_2Co^{II}_3\,[Fe^{II}(CN)_6]_2 \leftrightarrows Co^{II}_3\,[Fe^{III}(CN)_6]_2 + 2K^+ + e^- \qquad (2)$$

A continuous loss of current is observed by repeating the experiment and almost no faradaic current is noticed after 500 potential scans (curve b). This behavior has already been reported in literature in studies on the electrodeposition of CoHCF films onto glassy carbon surfaces [21].

The usefulness of electrodepositing the CoHCF film onto surfaces previously modified by SAM films is shown in the inset of Fig. 1, where the stability of the modified electrode is evaluated by measuring the current decay upon repetitive potential scans. Five hundred potential cycles caused the current measured at the anodic peak at 0.55 V to drop successively to around 20% of its initial value as a consequence of the dissolution of CoHCF layers during the electrochemical process. On the other hand, films grown onto SAM surfaces are less influenced by the dissolution process probably because the immobilization of HCF anions is facilitated onto the SAM surface through electrostatic interactions. The above electrostatic interactions may also contribute to the stability of the modified film, as already reported in literature for deposition of metal hexacyanoferrates on SAM [22,23].

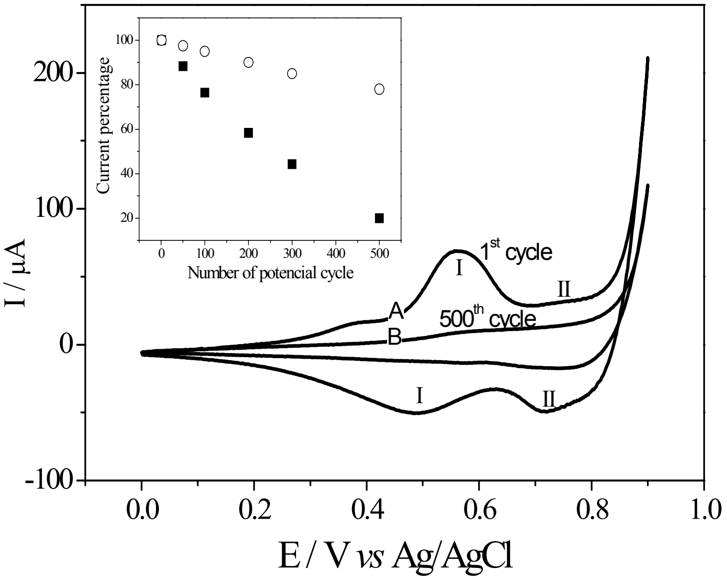

Figure 1. Voltammograms of the CoHCF film grown onto a gold electrode in a 0.5 mol L^{-1} KCl solution. The inset shows the percentage of anodic peak current (measured in comparison to the value obtained in the first potential scan) of CoHCF (■) and CoHCF/SAM (○) modified electrodes as a function of the number of redox cycles. Scan rate = 50 mV s^{-1}.

In order for a modified electrode to operate as an effective and practical sensor, the evaluation of the long-term stability is a crucial issue. Accordingly, Fig. 2A shows results on such an investigation where the CoHCF/SAM film stability was assessed by recording voltammograms over a large period of time. It should be pointed out that in this period the modified electrode was used for approximately one hour and when not in use it was stored in supporting electrolyte solution. By looking at these voltammograms and the plot shown in Fig. 2C, a relatively small but continuous current decrease is observed after 5 days. Hence, even though in a less significant extent in comparison with films prepared in the absence of the SAM layer, a leaching of the immobilized material from the electrode surface is noticed.

The beneficial effect of the incorporation of ruthenium (III) centers in CoHCF films to the enhancement of the chemical stability has been proposed in literature [24] and confirmed by our group [12,21]. Cataldi *et al.* [25] have attributed the increased stability of such films to the formation of mixed-valent dinuclear [Ru, Fe] oxo-bridges. Hence, further experiments were carried out with the attempt to incorporate ruthenium centers to CoHCF/SAM films electrodeposited onto gold surfaces. This was accomplished by potential cycling in a 2.0 mmol L^{-1} Ru(III)–chloride solution, thus obtaining RuCoHCF/SAM modified electrodes. Unlike the CoHCF film, the corresponding one containing Ru(III) exhibited very high stability (voltammograms in Fig. 2B). The significant improvement in stability can also be observed by noticing that the percentage of activity is retained even after 5 days

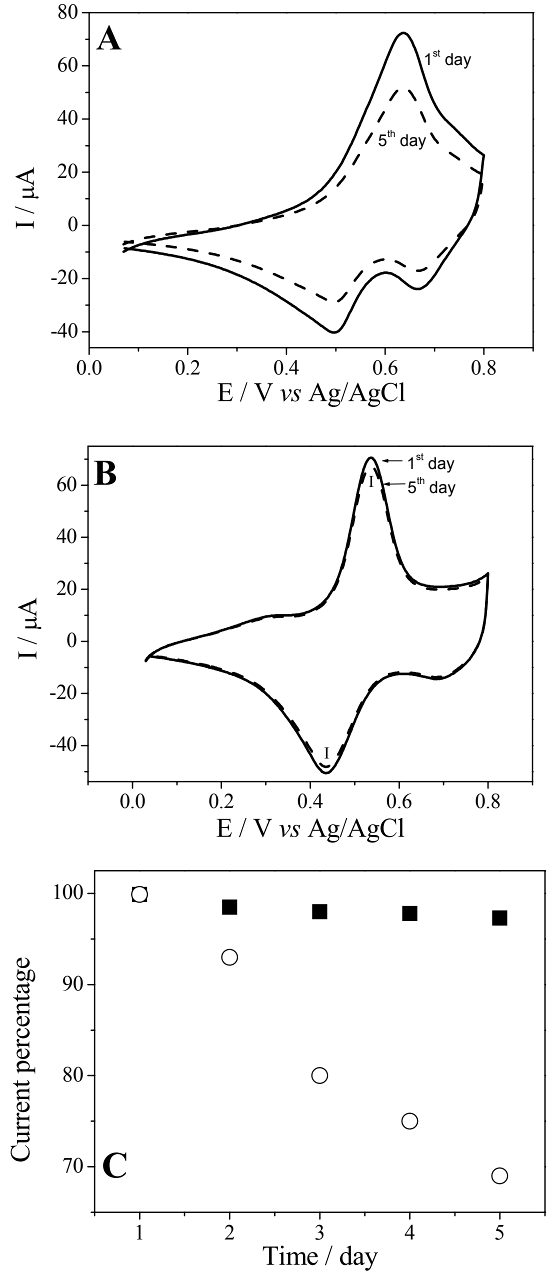

Figure 2. Voltammograms of the CoHCF/SAM (A) and RuCoHCF/SAM (B) modified electrodes in 0.5 mol L^{-1} KCl solutions at a scan rate of 50 mV s^{-1}. Panel C shows the relative current reduction for the anodic peak current as a function of time for CoHCF/SAM (○) and RuCoHCF/SAM (■) modified electrodes.

(around 95%, Fig. 2C), confirming the ability of Ru(III) to form more insoluble deposits with hexacyanoferrates.

The effect of scan rate on the electrochemical behavior of RuCoHCF/SAM in 0.5 mol L^{-1} KCl aqueous solutions is shown in Fig. 3A. The formal potential of the anodic redox couple I shifts slightly to the positive direction by increasing the scan rate, whereas a less significant change is observed for the cathodic redox couple I. Both anodic and cathodic peak current values increase linearly with scan rates at least up to 150 mV s^{-1} (Fig. 3B), as expected for surface controlled electrochemical reactions. At higher sweep rates the peak current vs. sweep rate plot deviates from linearity and the peak current became proportional to the square root of the sweep rate, indicating diffusional behavior in charge transport at short time windows.

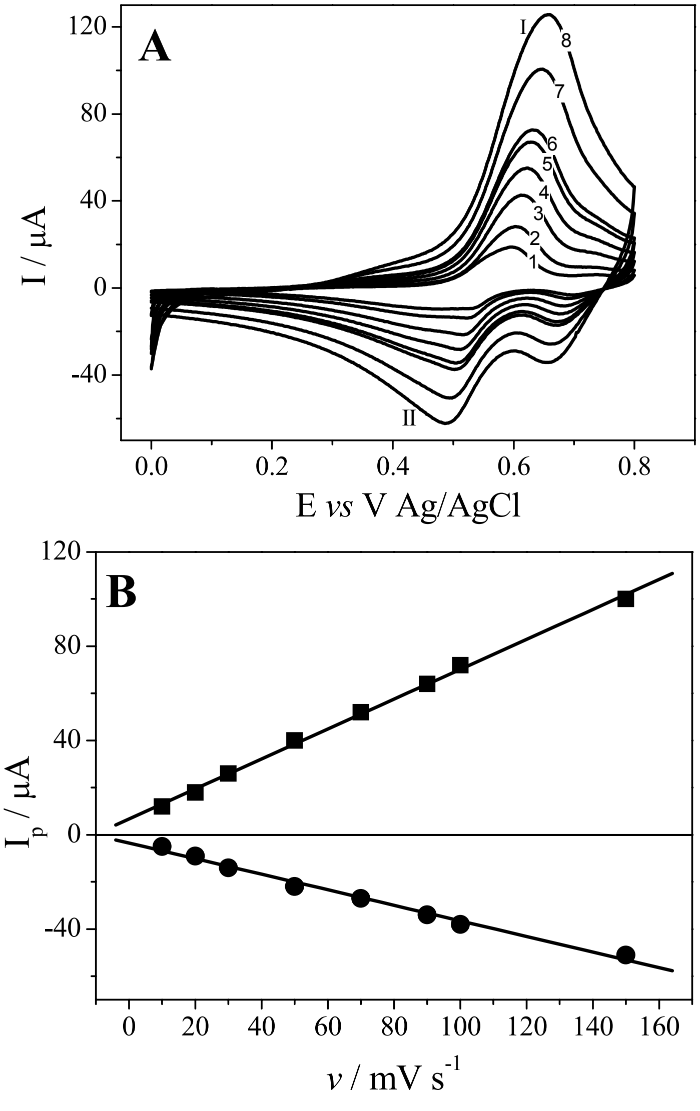

Figure 3. A) Voltammograms of the RuCoHCF/SAM electrode in 0.5 mol L^{-1} KCl solution as a function of the potential scan rate: (1) 20, (2) 30, (3) 50, (4) 70, (5) 90, (6) 100 and (7) 150 mV s^{-1}. B) Plot of anodic I (■) and cathodic II (●) peak currents *vs*. scan rate.

3.2 Ion Effect

In order to maintain the electroneutrality of the coating during the electrochemical process, ions penetrate into or escape from the immobilized film and, therefore, have an influence on the electrode process. The effect of ions on the voltammetric behavior of the RuCoHCF/SAM film was studied by cyclic voltammetry. Fig. 4 shows the cyclic voltammograms of the RuCoHCF/SAM modified electrode recorded in different cations in chloride solutions containing separately Na^+, NH_4^+ and K^+ at the same concentration. When Na^+ (Fig. 4, curve b) or NH_4^+ (Fig. 4, curve c) containing electrolyte solutions were used, broad and ill-defined redox peaks were observed. Moreover, the peak current values decreased drastically in Na^+ and NH_4^+ when compared with K^+ containing electrolyte solution. The results obtained from this study lead us to conclude that among the alkali metal cations only K^+ can freely penetrate into RuCoHCF/SAM crystal lattice probably because its hydration radius fits the holes in the metalocyanoferrate film (hydration radius for these cations are 0.36, 0.24 e 0.24 nm [26] for Na^+, K^+, NH_4^+, respectively). It should be pointed out that although both radii of NH_4^+ and K^+ are similar, the permeability of the film through the diffusion of K^+ ions seems to be more effective. A likely explanation for these results is based on the assumption that the incorporation of hydrated cations into the reduced structures is not only dependent on the size but also on some interaction of NH_4^+ with the film. A similar conclusion has already been reported in spectroelectrochemical investigations on indium hexacyanoferrates and the permeability through the penetration of alkali metal countercations [27].

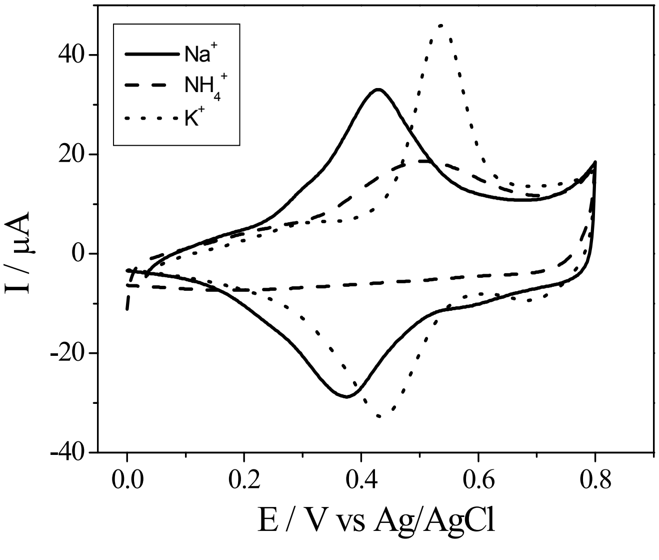

Figure 4. Cyclic voltammograms of the RuCoHCF/SAM electrode in the presence of different ion solutions at the same concentration (0.5 mol L^{-1}) at a scan rate of 50 mV s^{-1}.

3.3 Dependence of the voltammetric response on the K^+ concentration

Fig. 5A shows voltammetric responses of the RuCoHCF/SAM modified electrode to potassium ions in the range of 1.0 mmol L^{-1} to 1.0 mol L^{-1}. Peak potential separation values are almost unchanged at different K^+ concentrations, but both the anodic and cathodic peaks shift to more positive potentials with increase of K^+ concentration. Fig. 5B shows the linear relationship between the anodic peak potential and the logarithm of K^+ concentration with a slope (60 mV per decade) near to the expected Nernstian behavior. Experiments performed during five consecutive days involving the determination of the slope of the analytical curve by using the same modified electrode attest the response stability as a deviation not greater than 5% was observed. The use of the RuCoHCF/SAM modified electrode as a K^+ potentiometric sensor was not investigated owing to the already reported high response time of hexacyanoferrate sensors for potentiometric measurements [28].

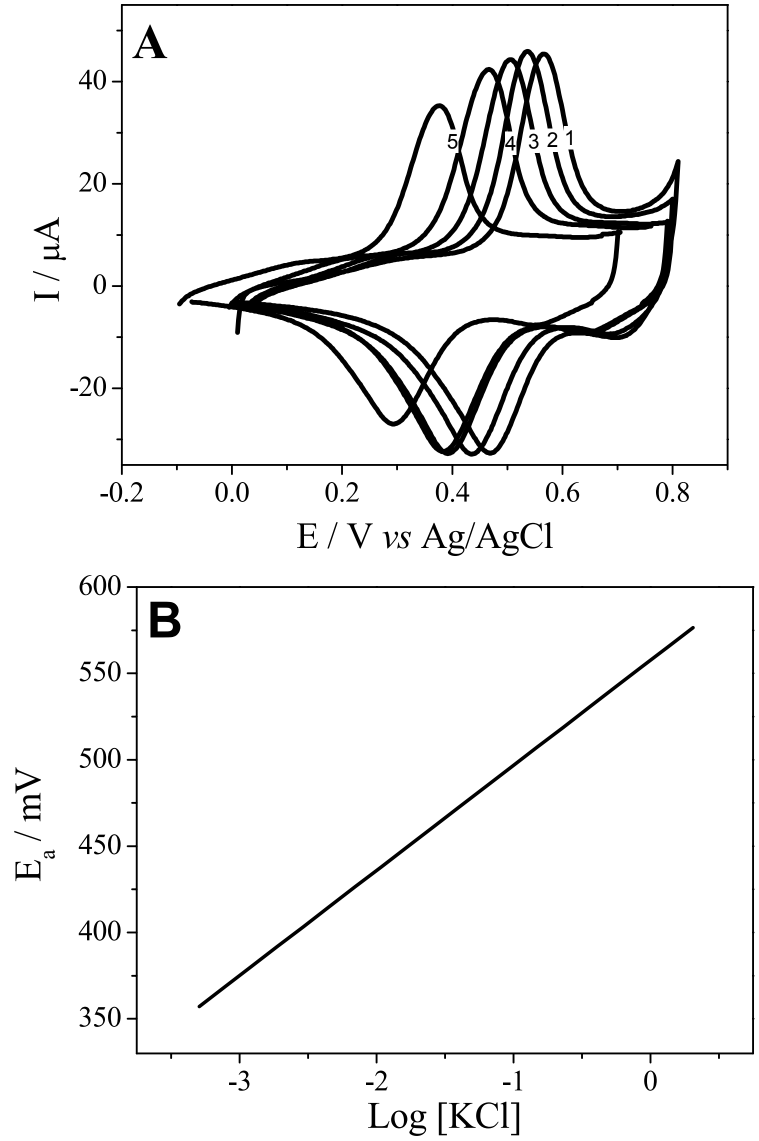

Figure 5. A) Cyclic voltammograms of RuCoHCF/SAM in KCl solutions at different concentrations: 1) 1.0; 2) 0.5; 3) 0.1; 4) 0.05 and 5) 0.001 mol L^{-1} at a scan rate of 50 mV s^{-1}. B) Anodic peak potential vs. Log [KCl] plot.

4. CONCLUSION

We have demonstrated the possibility of preparing thin films of ruthenium and cobalt hexacyanoferrate on a self assembled monolayer surface. The electrochemical properties of this modified electrode have been investigated in detail. The nature of the alkaline cation has considerable influence on the electrochemical behavior of the film. Taking into account the use of the device as a long-term sensor, the deposition of the hexacyanoferrate film onto a self-assembled monolayer was shown to be an efficient strategy as the stability of the electrochemical response was greatly enhanced. Increased stability was achieved by incorporating ruthenium centers to the CoHCF/SAM film. The prepared modified electrode was stable for a week in KCl solutions (pH 3) whereas a continuous loss of sensitivity was noticed for similar sensors prepared in absence of the SAM layer or without insertion of Ru(III). The suggested conditioning steps for the electrodeposition of hexacyanoferrate films with remarkable stability constitute a significant contribution to their use both in electrochemical and in solid state applications. The RuCoHCF/SAM modified electrode showed selectivity toward potassium ion in the range of 1.0 mmol L^{-1} to 1.0 mol L^{-1}. This is important taking into consideration that the selectivity of most of hexacyanoferrate modified electrodes is restricted in the presence of alkaline cations. The results of this work will be useful to evaluate the best experimental conditions to anchor enzymes onto the modified electrode in the fabrication of biosensors.

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