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Cobalt hexacyanoferrate based amperometric ascorbate sensor: attempts to increase its stability

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A cobalt hexacyanoferrate modified electrode has been prepared following an "insertion-substitution" mechanism based procedure and tested as an amperometric ascorbate sensor. The sensitivity of the sensor grows up with increasing pH of the solution from 5.5 to 7.3 and with increasing the operating potential from 0.1 to 0.3 V vs. Ag/AgCl. The decrease of the sensor response has been studied, and attempts have been made towards its stabilization.

Key words: sensor, ascorbate, cobalt hexacyanoferrate, Prussian blue, electrocatalysis

INTRODUCTION

Prussian blue and its analogues, metal hexacyanoferrates (MHCF), are finding increasing use as sensing materials for optical and electrochemical sensors and biosensors. Most research activities reported are directed towards electrochemical hydrogen peroxide sensors. These are often used as transducers for biosensors, based on peroxide generating oxidase type enzymes [1]. In a reaction sequence taking place at these sensors, hydrogen peroxide reacts with a reduced form of Prussian blue (i. e. Prussian white) turning it into its oxidised form that is electrochemically reduced to the initial form. As a result of this electrocatalytic conversion, the reduction (i. e. cathodic) current appears to be directly proportional to the concentration of hydrogen peroxide.

Apart from hydrogen peroxide, some other species are able to react with Prussian blue or other MHCF turning them into an appropriate redox form that could be continuously regenerated by electrochemical means yielding cathodic or anodic current as a response to these species [1, 2]. Some of these species present an analytical interest, thus, new sensors for important analytes could be developed based on MHCF electrocatalytic layers. Electrocatalytic oxidation of dopamine has been shown to proceed at a nickel hexacyanoferrate modified electrode, resulting in a linear dependence of anodic current on dopamine concentration within the range of $1 \cdot 10^{-4}$ to $1.5 \cdot 10^{-2}$ M [3]. A cobalt hexacyanoferrate modified glassy carbon electrode has been also used for the electrocatalytic oxidation of dopamine [4]. Later, the electrocatalytic action of a cobalt HCF layer on the oxidation of dopamine has been improved by inclusion of a cationic surfactant during the preparation of this layer [5]. Mechanistic studies on the electrocatalytic oxidation of hydrazine at electrodes, modified with cobalt HCF, have been provided [6], and electrocatalytic reactions of dopamine, epinephrine, norepinephrine and thiosulphate at an electrode modified with osmium HCF were reported [7].

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Among many species that undergo electrocatalytic transformations at MHCF electrodes, ascorbic acid (vitamin C) is of analytical significance [8]. Ascorbate is well known to interact with Prussian blue turning it into Prussian white, and some analytical spectrophotometric schemes based on this reaction have been proposed. Based on discoloration of Prussian blue in the presence of ascorbate, followed by the change in optical absorbance at 720 nm, disposable plastic cuvettes with an integrated Prussian blue sensor layer and similar analytical devices have been proposed for the assay of ascorbate in pharmaceutical products within the 0.1–10 mM range of concentration [9, 10]. Somewhat later, flow injection systems for ascorbate assay based on optical detection of ascorbate interaction with a Prussian blue layer have been proposed [11, 12].

When coupled with a continuous electrochemical regeneration of the oxidised form of Prussian blue from its reduced form Prussian white, formed in a chemical interaction with ascorbate, a continuous electrocatalytic oxidation of ascorbic acid could be realized. Electrocatalytic oxidation of ascorbate at a Prussian blue modified platinum microelectrode has been described [13]. When adopted to an analytical assay, a linear range of the response up to 4.5 mM of ascorbate has been reported for electrooxidation at a Prussian blue modified electrode [14]. For flow injection mode of operation, a linear range of the response for ascorbate from $5 \cdot 10^{-6}$ to $1 \cdot 10^{-3}$ M with the use of Prussian blue based amperometric detection has been reported [15].

Next to Prussian blue, other MHCF and related complexes have been involved in electrocatalytic oxidation of ascorbate. Copper heptacyanonitrosylferrate film-modified electrode showed a high stability in electrooxidation of ascorbate [16]. A thin film of nickel pentacyanonitrosylferrate has been obtained at an aluminum electrode, showing electrocatalytic activity towards ascorbate [17]. Cobalt HCF, either included into a polyethyleneglycol paste at a platinum microdisk electrode [18], or deposited at a glassy carbon electrode [19], is able to electrocatalyze the anodic oxidation of ascorbate. Analytical method for the determination of ascorbate in commercial samples has been proposed based on electrooxidation at a graphite electrode, containing mechanically immobilized copper hexacyanoferrate [20]. Lanthanum HCF particles, occluded within a gold film, were immobilized at a electrode, and showed a better stability in a catalytic electrooxidation of ascorbate compared to mechanical attachment of electroactive films [21].

The present study has been aimed to study a cobalt HCF modified electrode as an amperometric ascorbate sensor, and to improve its stability.

EXPERIMENTAL

A P-5848 model potentiostat, arranged with a PDA-1 model *X-Y-t* plotter and a G6-28 model function generator, was used throughout the work. A one-volume 25 ml three-electrode electrochemical cell, arranged with a magnetic stirrer, was used in all experiments. As a working electrode, a glassy carbon rod of 3 mm in diameter (Sigradur K, HTW, Germany), press-fitted into a plastic tube in order to expose its circular surface into the electrolyte and polished with 1 µm alumina (Struers, Denmark), was used. A glassy carbon rod, 3 mm in diameter and 10 mm in length, press-fitted into a plastic tube, served as a counter electrode. A saturated Ag/AgCl electrode was used as a reference electrode. All potential values reported below refer to this electrode.

A layer of cobalt hexacyanoferrate was deposited at the electrode following a two step procedure. First, a layer of Prussian blue was electrodeposited following the known procedure [22]. For this, a controlled potential of 0.4 V was applied for 1 min to the electrode, immersed into a solution containing 0.1 M of KCl, 0.1 M of HCl, 2.5 mM of potassium ferricyanide, and 2.5 mM of $FeCl_3$. After that, Prussian blue was converted into cobalt hexacyanoferrate by electrode potential cycling within the limits of –0.4 to 1.2 V for 7 min in a solution of 0.1 M $CoCl_2$ at a sweep rate of 50 mV/s, as described previously [23–25].

The response of a cobalt HCF modified electrode to ascorbate was studied in 0.05 M phosphate buffer solution, pH 5.5 or 7.3, containing additionally 0.1 M of KCl. Aliquots of ascorbate solution were added into a stirred buffer solution at the time intervals of 10 s, and anodic current responses were recorded at a controlled electrode potential, ranging from 0.1 to 0.3 V. In all experiments, the responses were recorded repeatedly for three runs with the same freshly prepared modified electrode.

RESULTS AND DISCUSSION

Prussian blue is probably the only hexacyanoferrate that can be electrodeposited at an inert electrode surface as a thin compact layer, following a simple electrochemical step. The preparation of other metal hexacyanoferrate complexes at the surface meets experimental difficulties. In the present work, we adopted a known procedure based on the "insertion-substitution mechanism" [24, 25] to convert an electrodeposited film of Prussian blue to a layer of cobalt HCF. The procedure consists of electrochemical cycling of a freshly prepared Prussian blue modified electrode in a solution containing cobalt ions. Under the conditions used, stable and reproducible CVs were obtained after the potential cycling for approx. 6 min, resulting in deposition of a thin well adherent layer of cobalt HCF.

The electrode thus prepared shows an anodic current response to ascorbate added (Fig. 1). The sensitivity to ascorbate depends on both pH of the solution and the operating potential applied (Table). The lowest sensitivity of ca. $25\ \mu A \cdot mM^{-1} \cdot cm^{-2}$, obtained in both pH 5.5 and pH 7.3 solutions tested at the lowest operating potential of 0.1 V, grows up to 4 and 11 times for pH 5.5 and pH 7.3 solutions, respectively, with increasing operation potential up to 0.3 V.

Table. **Initial sensitivity of freshly prepared and treated cobalt hexacyanoferrate modified electrodes to ascorbic acid**

pH	Operating potential, V	Sensitivity (freshly prepared electrode), $\mu A \cdot mM^{-1} \cdot cm^{-2}$	Sensitivity (treated electrode), $\mu A \cdot mM^{-1} \cdot cm^{-2}$ (1st to 3rd run)
5.5	0.1	27.6	
	0.2	63.2	55
	0.3	101	
7.3	0.1	23.9	
	0.2	141	69–83
	0.3	279	186–231

Repeating of stepwise additions of ascorbate results in a drop of anodic response, more pronounced for a higher operating potential (Fig. 1). A drop of ca. 17% and 31% was observed in the 3rd run, as compared to the 1st one, at the operating potential of 0.3 and 0.1 V, respectively (Fig. 2). The results obtained show the instability of cobalt hexacyanoferrate modified electrodes as amperometric sensors for ascorbate assay. It is well known that Prussian blue, as well as cobalt HCF modified sensors, gradually loss their current output when used as hydrogen peroxide sensors [23]. The reason for this is a gradual deterioration of a catalyst layer by hydroxyl ions, formed in the course of cathodic reduction of peroxide, i. e. an increase of a local pH at the electrode surface [22]:

$$H_2O_2 + 2e^- \rightarrow 2OH^-.$$

Therefore, higher stability is observed in slightly acidic supporting solutions than in neutral ones [23]. In opposite to the cathodic reduction of hydrogen peroxide, the anodic oxidation of analyte species like ascorbate does not produce hydroxyl ions, thus, no local increase of pH at the electrode surface should proceed. Therefore, other possible processes should be responsible for the decrease of sensor output.

In an experimental set with a prolonged controlled-potential electrolysis of ascorbate solution, a gradual decrease of anodic current has been observed (Fig. 3). A fast decrease of anodic current proceeds during the first 20–30 min up to 0.4–0.5 of its initial level. After that, a slow decrease occurs during a few hours of electrolysis. Most probably, two processes are taking place during the controlled-potential electrolysis, proceeding at different rate. The corresponding rate constants can be obtained by fitting the data of

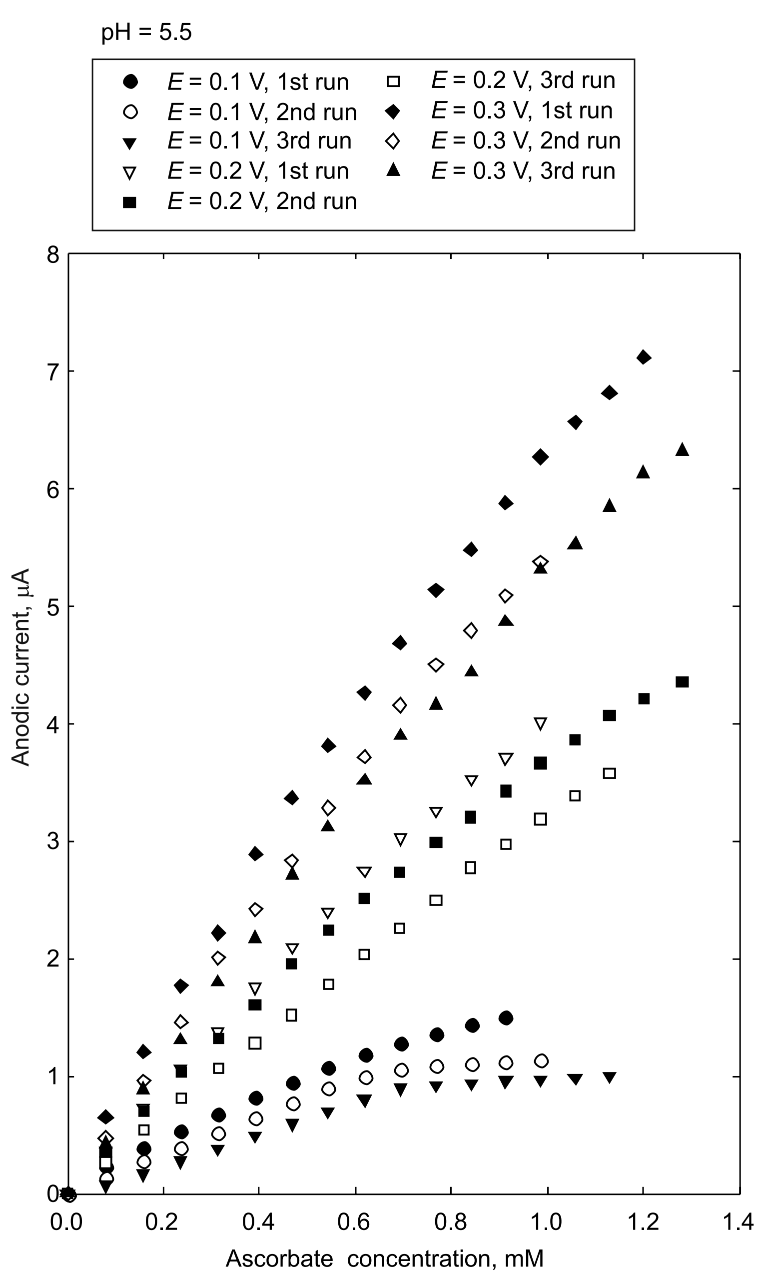

Fig. 1. Dependence of anodic current for cobalt hexacyanoferrate modified electrode on the concentration of ascorbate added, as obtained in 0.05 M pH 5.5 phosphate buffer solution containing 0.1 M of KCl at different electrode potential values (as indicated). In all cases, three runs have been done repeatedly with the same electrode

Fig. 3 according to a double, 4-parameter exponential decay equation:

$$I = a \cdot \exp(-bt) + c \cdot \exp(-dt),$$

where I is a relative current, t is time, a, b, c and d are empirical coefficients.

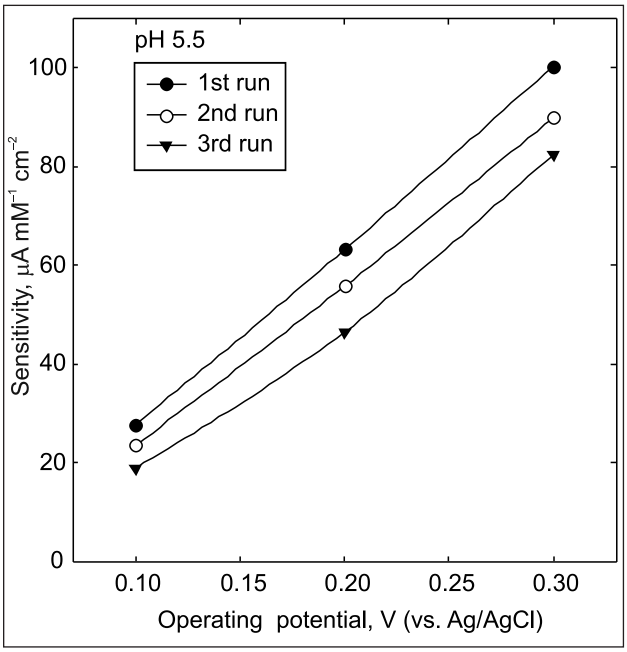

Fig. 2. Dependence of sensitivity to ascorbate on operating potential, as obtained for cobalt hexacyanoferrate modified electrode in pH 5.5 buffer solution for the 1st, 2nd, and 3rd runs (as indicated)

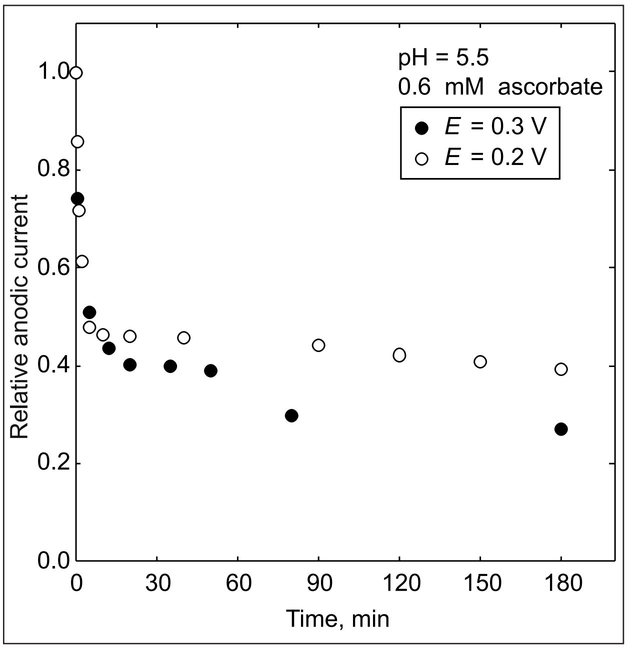

Fig. 3. Time-dependence of anodic current for cobalt hexacyanoferrate modified electrode during a prolonged electrolysis of 0.6 mM of ascorbate in pH 5.5 solution, performed at different electrode potential values (as indicated)

Fitting of the data obtained according to this equation yields first-order rate constants for the two processes. For the fast process (i. e. an initial fast decrease), the current decay rate constants of $(1.20 \pm 0.07) \cdot 10^{-2}$ s^{-1} and $(2.15 \pm 0.51) \cdot 10^{-2}$ s^{-1} were obtained for the operating potential of 0.2 and 0.3 V, respectively. For the slow process (i.e. a slow decrease after a relative stabilisation), first-order rate constants of $(1.61 \pm 0.26) \cdot 10^{-5}$ s^{-1} and $(6.17 \pm 1.46) \cdot 10^{-5}$ s^{-1} for operation potentials of 0.2 and 0.3 V, respectively, have been estimated.

It follows from the data obtained that a relative stabilization of electrode output could be probably attained by avoiding of the first (fast) degradation process. For this purpose, a freshly prepared cobalt HCF modified electrode has been subjected to a continuous electrolysis for 30 min at 0.2 V in a solution containing a high concentration of ascorbate (5.7 mM), and then tested for its stability. Hopefully, the reasons responsible for a fast initial decay process should be avoided by applying of these harsh treatment conditions. After the treatment, again, calibration graphs for ascorbate have been obtained for a variety of experimental conditions, as shown in Fig. 4.

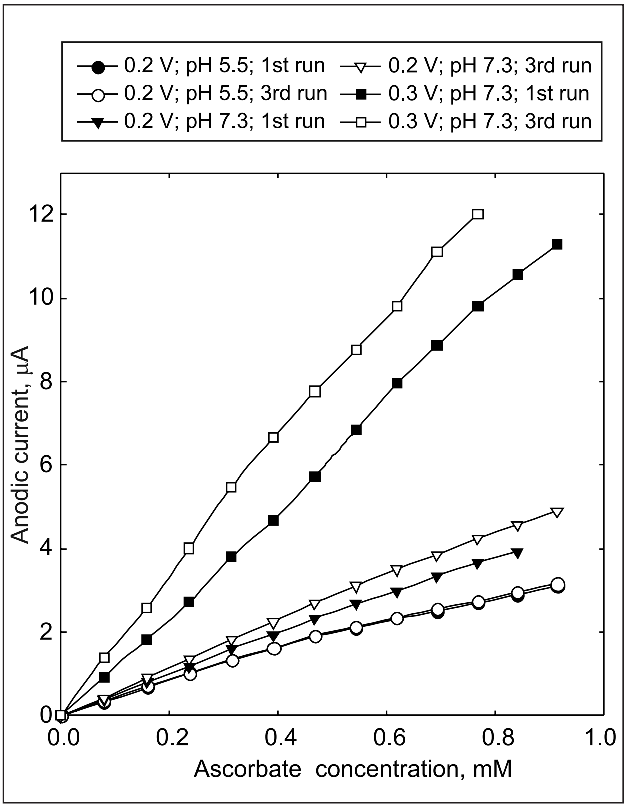

Fig. 4. Dependence of anodic current for cobalt hexacyanoferrate modified electrode on the concentration of ascorbate added, as obtained in pH 5.5 buffer solution at different electrode potential values (as indicated), shown for the 1st and 3rd runs (as indicated). The electrode has been pretreated by keeping it at a controlled potential (same as that used later in obtaining current-concentration dependencies) for 30 min in pH 5.5 buffer solution containing 5.6 mM of ascorbate

In a pH 5.5 solution, nearly coinciding graphs have been obtained for the 1st, 2nd, and 3rd repeating experimental runs. As expected, the sensitivity for the treated electrode appears to be some lower than for the freshly prepared electrode. For operating potential of 0.2 V, a small drop of sensitivity of ca. 15% has been obtained in pH 5.5 solution (Table). For pH 7.3 solution, an increase of sensitivity has been observed for the first three runs. Turning from the 1st to the 3rd run, an increase in sensitivity of ca. 20 and 24% was observed in pH 7.3 solution for operating potentials of 0.2 and 0.3 V, respectively (Table). After that, the sensitivity tends to stabilize at an appropriate level.

CONCLUSIONS

Cobalt hexacyanoferrate modified electrode can be prepared following a known procedure, based on the "insertion-substitution" mechanism. When operated at the controlled potential ranging from 0.1 to 0.3 V vs. Ag/AgCl, the resulting modified electrode shows the anodic current response to ascorbate. The sensitivity of the sensor prepared grows up with increasing pH of the solution from 5.5 to 7.3 and with increasing the operating potential from 0.1 to 0.3 V. Under continuous operation conditions, a relatively fast decay of the electrode response proceeds. The stability of the electrode can be improved by its conditioning, consisting of a controlled potential electrolysis of ascorbate solution.

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AMPEROMETRINIO ASKORBATO JUTIKLIO, SUKURTO KOBALTO HEKSACIANOFERATO PAGRINDU, STABILUMO PADIDINIMAS

Santrauka

Elektrodas, modifikuotas kobalto heksacianoferato sluoksniu, panaudotas kaip amperometrinis jutiklis, jautrus askorbatui. Jutiklio jautris didėja didinant tirpalo pH nuo 5,5 iki 7,3 ir didinant jutiklio darbinį potencialą nuo 0,1 iki 0,3 V pagal Ag/AgCl palyginamąjį elektrodą. Buvo tirtas jutiklio atsako mažėjimas, bandyta jį stabilizuoti.