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Iron triad-mate hexacyanoferrates as Prussian Blue stabilizers: Toward the advanced hydrogen peroxide transducer

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ABSTRACT

Iron triad-mate hexacyanoferrates (Ni- and Co-hexacyanoferrates) are investigated as stabilizers for Prussian Blue (Fe-hexacyanoferrate) known to be the most advantageous hydrogen peroxide transducer. Both diffusion coefficients of potassium ions and the electron transfer rate constants for transition metal hexacyanoferrates as well as for their composites were determined. Being isostructural to Prussian Blue (PB) on the one hand, and much less suffering from drying–washing cycles compared to polymeric materials on the other hand, triad-mate hexacyanoferrates (HCFs) provide synthesis of the electrocatalyst with the dramatically improved operational stability. Composite films synthesized via layer-by-layer deposition of the catalytic and the stabilizing layers, demonstrate stable response under continuous flow of 1 mM hydrogen peroxide during one (PB/CoHCF) and two even hours (PB/NiHCF). Despite the lower sensitivity of PB/NiHCF-based sensor compared to the PB-based one, the decreased noise allows to maintain linear calibration range from 5×10^{-8} M to 5×10^{-4} M of H_2O_2.

1. Introduction

Monitoring of hydrogen peroxide is of great importance for modern medicine, environmental control, and various branches of industry. The major amount of hydrogen peroxide found in the atmosphere is the photochemical reaction product of organic compounds [1]. More than 50% of world production of hydrogen peroxide is due to pulp and paper industry [2]. H_2O_2 is a chemical threat agent; its excessive concentration affects the environment and it is necessary to control hydrogen peroxide content in wastewater and atmospheric presipitations [3,4]. In food industry hydrogen peroxide is used for the disinfection of equipment and packages, which have direct contact with food products [5]. Therefore, it is necessary to measure its residual contents in water used for the packages washing.

On the other hand, H_2O_2 is the most valuable marker for oxidative stress, recognized as one of the major risk factors in progression of disease-related pathophysiological complications in diabetes, atherosclerosis, renal disease, cancer, aging, and other conditions [6–10]. This causes the requirements to use sensors for peroxide in clinical diagnostics and in vivo monitoring. Additionally, hydrogen peroxide is a side-product of oxidases and effective hydrogen peroxide transducers is essential for the first generation biosensors constructing [11].

Amperometric detection of hydrogen peroxide with Prussian Blue (PB) modified electrodes is now the most advantageous analytical approach. PB is the most effective catalyst for hydrogen peroxide electroreduction known [12]. Its applicability for selective determination of H_2O_2 in the presence of oxygen was first shown in our laboratory in 1994 [13]; the sensor for hydrogen peroxide based on PB nanostructures with record analytical characteristics has been developed [14]. However, for long term continuous monitoring of H_2O_2 especially in its high concentration the operational stability of PB is not sufficient. Such tasks appear in industrial production control, in environmental control, and in vivo monitoring as well.

The ways to stabilize ferric hexacyanoferrate films are: (1) immobilization by sol–gel [15–17] or polymer matrixes [18–20]; (2) layer-by-layer deposition with polymers [21–24]. The main disadvantage of all these approaches is the possibility of matrix degradation upon drying–swelling. Therefore, a search for inorganic materials as stabilizers of the catalyst is an actual task. From this point of view, other transition metal hexacyanoferrates, iron triad-mate HCFs in particular, are of great interest. They are (i) isostructural to PB [25,26]; (ii) forms chemically and mechanically stable films on electrodes [27,28]. This makes iron triad mate hexacyanoferrates attractive for the stabilization of Prussian Blue, the advanced hydrogen peroxide transducer.

The aims of this work were to stabilize PB based electrocatalyst with nickel and cobalt hexacyanoferrates toward the development

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of sensor with improved analytical characteristics suitable for continuous hydrogen peroxide monitoring.

2. Experimental

2.1. Materials

Experiments were carried out with Milli-Q water from a Millipore Milli-Q system. All inorganic salts and hydrogen peroxide (30% solution) were obtained at the highest purity from Reachim (Moscow, Russia) and used as received. Glassy carbon disk electrodes (2 mm in diameter) used as working electrodes were made by pressing glassy carbon rods (Su-2500) in Teflon. Prior to use, glassy carbon electrodes were mechanically polished in air and then in water suspension of alumina powder (Al_2O_3, 0.05 μm, Sigma) until a mirror surface was observed.

2.2. Instrumentation

Deposition of transition metal hexacyanoferrates as well as their characterization by cyclic voltammetry was made in a three-compartment electrochemical cell containing a platinum net auxiliary electrode and Ag|AgCl reference electrode in 1 M KCl. Cell construction allowed deaeration of the working electrode space. The Metrohm-μAutolab III or PalmSens interfaces were used.

Both catalytic and analytical performances were investigated in a flow-through mode. The setup consisted of a Cole Parmer (Vernon Hills, IL) peristaltic pump (7519-10), homemade flow-through wall-jet cell with 0.5-mm nozzle positioned at 1.5 mm distance from the surface of disk electrode, the above reference, and a homemade injector. Flow rates used were in the range from 0.5 to 4 mL/min. The working electrode potential was 0.00 V. The carrier solution in FIA experiments was 0.05 M phosphate buffer pH 6.0 or 7.0 containing 0.1 M KCl as the supporting electrolyte.

The morphology of the films was investigated with the help of SPM microscope NT-MDT NTEGRA – Aura (NT-MDT, Russia). Images have been obtained in semicontact mode. We use silica cantilevers NSC15/AlBS with elasticity constant 40 N/m (Mikromasch, Estonya).

The concentration of hydrogen peroxide in stock solutions was controlled by optical density at 230 nm with an LKB-Ultraspec UII spectrophotometer (Broma, Sweden).

2.3. Electrodeposition of metal hexacyanoferrates

Electrodeposition of Prussian Blue was carried out in cyclic voltammetric conditions by cycling in the range from 0.7–0.8 V to 0.4 V at a sweep rate of 0.04 V/s. The growing solution contained 0.5–4 mM $K_3[Fe(CN)_6]$ and 0.5–4 mM $FeCl_3$. A solution of 0.1 M HCl and 0.1 M KCl was used as supporting electrolyte. After deposition, Prussian Blue films were electrochemically activated in the same supporting electrolyte by cycling in the range from 0.35 V to −0.05 V at a rate of 0.04 V/s until a stable voltammogram was obtained. Then, the electrodes were heated at 100 °C for an hour.

Electrodeposition of nickel and cobalt hexacyanoferrates from noncolloid solutions became possible due to stabilization of the diluted solution of Ni^{2+} (Co^{2+}) and $[Fe(CN)_6]^{3-}$ ions in aqueous media with the excessive amount of supporting electrolyte (KCl) [29]. It was carried out from 0.5 to 1 mM solutions of precursors (Ni^{2+} or Co^{2+} and $[Fe(CN)_6]^{3-}$ ions). The potential was cycled between 0 V and 0.7–0.8 V in a case of NiHCF or 1 V in a case of CoHCF with the sweep rate 0.1 V/s. After the deposition, films were electrochemically activated in 0.1 M HCl and 0.1 M KCl supporting electrolyte by cycling in the range from −0.05 to 1 V at a rate of 0.04–0.1 V/s. Then the electrodes were heated at 100 °C for an hour.

Layer-by-layer deposition of Prussian Blue–metal hexacyanoferrates composites was made in different three-compartment electrochemical cells: one was with the solution of precursors for PB electrosynthesis, another contained mixture for NiHCF or CoHCF electrodepositing. After the deposition of one layer, electrode was intensively rinsed with Milli-Q water and moved to another cell.

After the deposition, all films were electrochemically activated in 0.1 M HCl and 0.1 M KCl supporting electrolyte by cycling in the range from −0.05 to 1 V at a rate of 0.04–0.1 V/s. Then the electrodes were heated at 100 °C for an hour.

3. Results and discussion

3.1. Layer-by-layer stabilization of Prussian Blue with nickel and cobalt hexacyanoferrates

As mentioned, transition metal hexacyanoferrates, iron triad-mate HCFs in particular possess attractive properties for Prussian Blue electrocatalyst stabilization. Here we discuss the layer-by-layer deposition of Prussian Blue and other transition metal hexacyanoferrates to synthesize the electrocatalyst with improved stability.

Iron triad mates represent minor electrocatalytic activity toward hydrogen peroxide reduction when compared with Prussian Blue [30]. However as mentioned, they are (i) isostructural to PB [25,26]; (ii) forms chemically and mechanically stable films on electrodes [27,28]. This makes iron triad mate hexacyanoferrates attractive for the stabilization of Prussian Blue, the advanced hydrogen peroxide transducer.

For development of the sensor with optimal analytical characteristics both operational stability (response wear over time under continuous flow of hydrogen peroxide) and sensitivity are important. Accordingly, we have chosen the ratio of the response toward 1×10^{-3} M of H_2O_2 to inactivation constant (determined as a slope of semilogarithmic plots) as the optimization parameter.

Fig. 1 represents typical cyclic voltammogram of the film synthesized via deposition of the stabilizing coating (example for nickel hexacyanoferrate) on the top of the so-called conventional Prussian Blue film, which covers the entire surface of the electrode. [14]. NiHCF deposition onto the modified electrode was carried out similarly to its growth on blank surfaces. The presence of NiHCF in the film is confirmed by the increase of the anodic response of the low-spin iron $[Fe_{ls}(CN)_6]^{3-/4-}$ in comparison with conventional PB and the appearance of cathodic peak, which is not observed on cyclic voltammogram of Prussian Blue [30]. It is known, that the value of formal potential $E^{\circ\prime}$ in metal cyanides depends on the ion

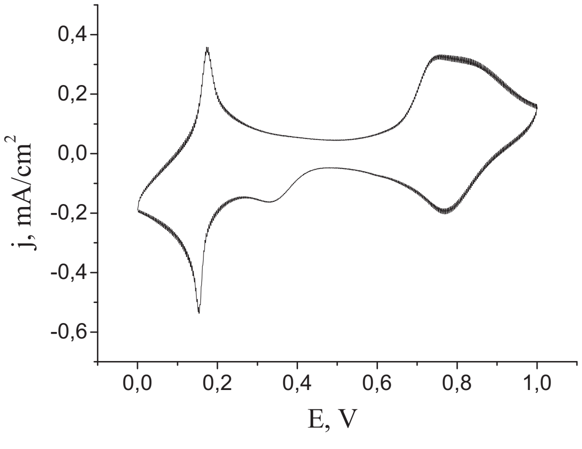

Fig. 1. Cyclic voltammograms of PB/NiHCF bi-layer in a case of deposition of NiHCF on a top of so-called conventional PB film; 0.1 M HCl, 0.1 M KCl, sweep rate is 0.04 V/s.