Short communication

Electrosynthesis of poly-*o*-diaminobenzene on the Prussian Blue modified electrodes for improvement of hydrogen peroxide transducer characteristics

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Abstract

Electropolymerisation of nonconducting polymer, poly-(1,2-diaminobenzene) on the top of Prussian Blue (PB) modified electrode led to significant improvement of resulting hydrogen peroxide transducer selectivity and operational stability. The reported transducer retained 100% of response during 20 h under the continuous flow of 0.1 mM H_2O_2, and thus improves the stability level in selective peroxide detection by one order of magnitude. The selectivity value of the PB–poly(1,2-DAB) based H_2O_2 sensor in relation to ascorbate is approximately 600. No signals to acetaminophen and urate were investigated. PB–poly(1,2-diaminobenzene) modified electrode allows the detection of H_2O_2 in the flow-injection mode down to 10^{-7} M with the sensitivity 0.3 A M^{-1} cm^{-2}, which is only two times lower compared to the uncovered PB based transducer. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Hydrogen peroxide, being a natural product of oxidase catalysed reaction, can be detected electrochemically. This fact gives rise to analysis of a variety of oxidases substrates, which are important in food industry, clinical diagnostics and environmental monitoring (glucose, lactate, ethanol, glutamate, glycerol, etc.)

The optimal potential range for biosensor operation is from -0.1 to 0.1 V (Ag│AgCl), where interfering reactions cause only a minor influence on biosensor response [1,2]. Up to now, there are only two low potential transducers for hydrogen peroxide reduction: peroxidase and Prussian Blue (PB) modified electrodes. Selective detection of H_2O_2 in the presence of oxygen on PB modified electrodes was first announced by Karyakin et al. [3]. Sensitivity

of this transducer is around 1 A M^{-1} cm^{-2} in steady-state mode [4] and is not inferior to peroxidase electrodes [5]. The relative interference of other electroactive species (ascorbic and uric acid, acetaminophen) to H_2O_2 sensing by PB-based electrodes does not exceed 0.05, while the ratio of the hydrogen peroxide response to those of oxygen is 400–600 [6]. Such advantages of PB based transducer led to development of biosensors for glucose, ethanol and glutamate detection with high sensitivities and low detection limits (0.1 μM) [3,6,7].

In some cases, in particular, in clinical diagnostics and food quality control, it is necessary to detect low levels of analytes in the presence of 10–100 higher concentration of ascorbate. Thus, the additional permselective membranes have to be deposited on the transducer surface. The most promising results were achieved using poly-diaminobenzenes [8–10]. Such membranes meet the requirements for all-electrochemical sensor fabrication, such as easily controlled thin film electrodeposition on different supports and possibility of enzyme immobilisation during this process.

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Deposition of poly(1,2-diaminobenzene) (poly-1,2-DAB) films was found to cause only minor decrease in response to H_2O_2, whereas interferent rejection was higher than 99% [8].

Electrosynthesis of polymers on PB modified electrodes is possible due to the high oxidising ability of Berlin Green (oxidised state of PB) [10,11], and the growth of non-conductive polymers can be controlled investigating redox activity of the inorganic polycrystal. The aim of this work was use of poly(1,2-DAB) for improvement of hydrogen peroxide sensor characteristics.

2. Experimental

2.1. Materials

All inorganic salts, hydrochloric acid, hydrogen peroxide (30% solution, Reachim, Russia), 1,2-DAB (Calbiochem, CA, USA), uric acid, L-ascorbic acid and acetaminophen from ICN Biomedicals (USA) were of analytical grade.

2.2. Apparatus

Electrochemical studies were performed using Solartron Schlumberger Model 1286 (UK). Experiments were carried out in a three-compartment cell containing a Pt net auxiliary electrode and an Ag|AgCl reference electrode. Glassy carbon disk electrodes (GCE) (GC 2500, Research Institute for Graphite Materials, Moscow, Russia), diameter 1.8 mm, were used as working electrodes. The surface of GCE was polished with alumina powder (0.3 and 0.05 μm) up to a mirror finish. Then, the electrodes were carefully rinsed with water and used immediately. Flow-injection system contained Cole Parmer (USA) peristaltic pump (7519-10), homemade flow-through wall-jet cell with 0.5-mm nozzle positioned at 1-mm distance from the surface of working electrode, homemade injector and Metrohm (Switzerland) potentiostat (641-VA).

2.3. Procedures

2.3.1. Electrodeposition of PB

Electrodeposition of PB was performed at constant cathodic current of 80 μA cm^{-2} for 50 s from the initial solution containing 4 mM $K_3[Fe(CN)_6]$ and 4 mM $FeCl_3$ with (0.1 M KCl + 0.1 M HCl) as supporting electrolyte. Posttreatment of modified electrodes was the same as reported earlier [13].

2.3.2. Electrodeposition of poly(1,2-DAB)

The PB modified electrodes were placed in deaerated solution of DAB (5–10 mM) in 0.02 M phosphate buffer with 0.1 M KCl, pH 6.0 (PBS). Polymerisation was carried out by cycling the applied potential in the range from −0.05 to 0.7–0.8 V at a sweep rate of 20 mV s^{-1} (10–20 cycles).

2.3.3. Analysis of hydrogen peroxide and interferences

The modified electrodes were poised to 0.0 V for 10 min to reach a constant baseline in PBS at flow rate of 1 ml min^{-1}. H_2O_2, acetaminophen, ascorbic and uric acids were tested in both flow-injection (FI) and continuous flow (CF) modes.

3. Results and discussion

3.1. Electrodeposition of poly(1,2-DAB) on the top of Prussian Blue modified electrodes

Basing on previously reported data concerning cyclic voltammetric procedure for poly-(1,2-DAB) electrosynthesis [8], we decided to perform its electrodeposition on PB modified electrodes. Fig. 1 presents cyclic voltammograms of poly(1,2-DAB) synthesis on PB-modified GCE. Irreversible oxidation of 1,2-DAB is observed at high anodic potentials (~ 0.7 V). Reduction of PB to Prussian White at 0.13 V is accomplished by consumption of alkali metal ions [12]. Since cations cross the film–solution interface during oxidation–reduction, the redox activity of PB is sensitive to appearance of film on its surface. In coarse of 1,2-DAB electropolymerisation, the PB/Prussian White peaks become broader, and the peak separation value
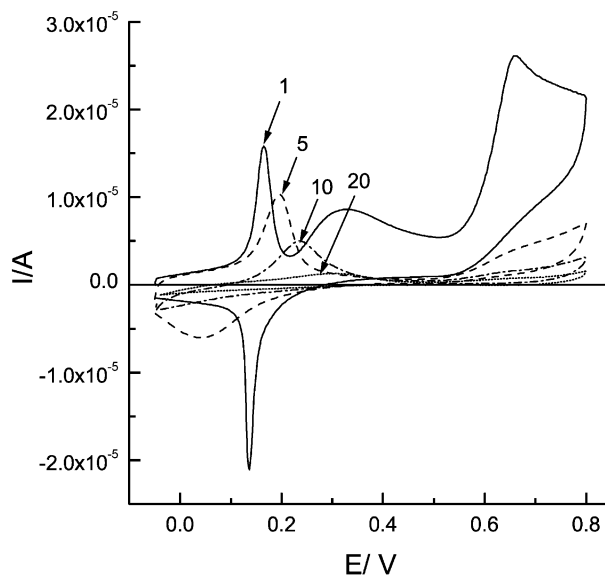

Fig. 1. Cyclic voltammograms of poly-(1,2-DAB) electrodeposition on PB modified electrode (0.02 M phosphate buffer with 0.1 M KCl and 5 mM of 1,2-DAB, pH 6.0; scan rate 20 mV s^{-1}). Numerals indicate the numbers of cycles.

increases (Fig. 1). Thus, the growth of nonconducting films on electroactive surface can be independently controlled.

3.2. Analytical characteristics of the Prussian Blue based hydrogen peroxide transducers

PB based transducers were tested under CF of either H_2O_2 or interferents in concentration of 0.1 mM. The selectivity in relation to ascorbate was characterized as a ratio of the current of H_2O_2 reduction to the current of interferent oxidation. Operational stability was estimated as time, during which the transducer remained 100% response under CF of 0.1 mM H_2O_2.

Operational characteristics of the transducers were dependent on conditions of poly(1,2-DAB) synthesis, such as the concentration of monomer, the value of anodic switching potential and the number of cycles. In particular, the value of the anodic switching potential affected the morphology of the resulting polymer film. In this study, the best results in terms of H_2O_2 response and selectivity were obtained for poly(1,2-DAB) films that were deposited from 5 to 10 mM solution of DAB in PBS using anodic switching potential value of 0.75 V. Selectivity of the PB−poly(1,2-DAB) sensor is on average 30 times higher compared to the uncovered PB modified electrode and reached the value of 600, which is significantly higher compared to the known transducers. No signals were detected to 0.1 mM of uric acid and acetaminophen. Response to ascorbate of the recently reported PB−poly(1,2-DAB)−(glucose oxidase) electrode [10] was of 10 ± 1 mA M^{-1} cm^{-2} at applied potentials between -0.2 and 0.0 V, which was 10 times higher compared to the currently reported transducer. Thus, in the coarse of this study the optimal procedure for electrodeposition of poly(1,2-DAB) films has been found.

The most significant improvement of the H_2O_2 sensor is its highly prolonged operational stability. Under taken experimental conditions (nozzle-to-electrode distance 1 mm, 1 ml min^{-1} flow rate), the uncovered PB modified electrodes were completely stable during 0.5 h. For PB−poly(1,2-DAB) modified electrodes, only after 20 h was a decrease of the response observed. Since the operational stability of uncovered PB films was already found to be comparative and even higher than that of the other known low-potential H_2O_2 transducers, for example, peroxidase electrodes [4], the PB−poly(1,2-DAB) sensor improves the stability level in selective peroxide detection by one order of magnitude.

Calibration graphs for hydrogen peroxide detection in the flow-injection mode are presented in Fig. 2. Both sensors based on uncovered conventional PB and PB−poly(1,2-DAB) give straight lines in logarithmic plots over four orders of magnitude of H_2O_2 concentration. Both transducers allow the detection of hydrogen peroxide down to 10^{-7} M in FI. Sensitivity values calculated from the
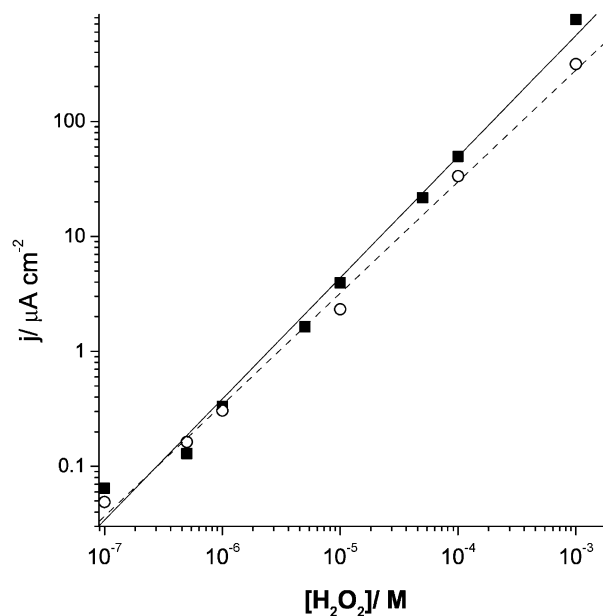

Fig. 2. Calibration plots of hydrogen peroxide detection using (■) PB and (○) PB−poly(1,2-DAB) modified electrodes.

slopes of the straight lines presented in Fig. 2, for uncovered and poly(1,2-DAB) modified PB, are 0.6 and 0.3 A M^{-1} cm^{-2}, respectively. The ratio of sensitivities is similar to the ratio of steady-state responses for the same transducers.

4. Conclusions

The attractive performance characteristics of PB−poly(1,2-DAB) modified electrode are (i) prolonged operational stability improved by one order of magnitude and (ii) selectivity of the PB−poly(1,2-DAB) based H_2O_2 transducer in relation to ascorbate is on average 600, which is much higher compared to the reported systems. Such selectivity provides the possibility to develop the biosensors for use in certain areas of clinical diagnostics (brain research) and food control (juice and wine analysis).

Acknowledgements

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