UDC 544.344; 577.1.08

PHYSICO-CHEMICAL FEATURES OF CATALASE BIOMIMETIC SENSORS

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Received 17.03.2020

Accepted 20.05.2020

The physicochemical features of biomimetic sensor have been studied, using various materials as a transducer. It is shown that biomimetic sensor prepared on the basis of a smart material and semiconductors had a number of technological advantages. It was found that among the selected various materials, the biomimetic sensor prepared from the smart material $\text{TPhPFe}^{3+}\text{OH}/\text{Al}_2\text{O}_3$ and the semiconductor Si proved to be the most effective. The developed biomimetic sensor is differed by high activity, sensitivity, stability and reproducibility with the possibility of expanding the range of detectable trace concentration of H_2O_2 in aqueous solutions to 10^{-6} mass %.

Keywords: biomimetic sensor, catalase, iron tetraphenylporphyrin, semiconductors, smart material.

doi.org/10.32737/0005-2531-2020-4-65-68

Introduction

The development of highly sensitive, express and accurate biosensors and their mimetic analogues is of great interest in various types of diagnostics. Biosensors are successfully used to control environmental pollution in medical diagnostics, in industry for the production of a wide class of products and etc. Enzyme biosensors take the leading position in this area due to the high specificity of the enzyme to the substrate. Enzyme biosensors take the leading position in this area due to the high specificity of the enzyme to the substrate. At enzymes adsorption of solid surfaces (metals, ceramics, polymers), they, as a rule, retain their structure and catalytic activity. The enzyme in the amperometric biosensor mode exhibits electrocatalytic activity, that is, accelerates the process of electrons exchange between the substrate and electrode. This allows to measure directly in the sample of a multicomponent composition.

In this regard, the topic of work is certainly actual. In the work proposed biomimetic sensors used as the active material iron tetraphenylporphyrin was deposited on various electrodes. The use of these materials has increased the sensitivity of the biomimetic sensor. With the help of the developed biomimetic sensor, the possibility of determining the trace concentrations of hydrogen peroxide in aqueous and in aqueous-alcohol solutions was shown.

A promising direction in the field of modern biotechnology is the creation of highly sensitive biosensors and their mimetics, in which enzymes are used as working materials (bioselectors). In [1, 2] studies in this direction were carried out.

In the present work, potentiometric studies of the catalase activity of biomimetic sensors prepared from different electrodes and smart biomimetic catalyst $\text{TPhPFe}^{3+}\text{OH}/\text{Al}_2\text{O}_3$ were carried out.

Materials and Methods

Studies were performed in an electrochemical cell, which for clarity, is presented in the form of infographics (Figure 1).

The catalase activity of biomimetic sensors was determined by a potentiometric method.

Fig.1. Infographics.

The experimental setup, to carry out these studies, consisted of the electrode part, the cell, and the B7-21A universal voltmeter. The electrode part of the installation consists of a reference electrode (Ag/AgCl/Cl⁻) and a biomimetic sensor prepared by us. As background solution served as bidistilled water.

Potentiometric studies were carried out as follows: in the cell filled with a certain amount of bidistilled water, the e.m.f of (E) element was determined and then, adding different concentrations of H₂O₂ of solution, determined the changes in e.m.f. of system.

All measurements were performed with continuous stirring with a magnetic stirrer.

Results and Discussions

As you know, one of the main indicators of sensors is their sensitivity to the lowest concentrations of substances determined by them – the threshold of sensitivity.

Metals

Pb-electrode

Initially, our studies were devoted to potentiometric measurements of low concentrations of H₂O₂ in an aqueous solution for a Pb-electrode. For this, solutions with low concentrations of H₂O₂ were prepared – 10⁻⁶ and 10⁻⁸ mass % (Figure 2).

In Figure 2 are given experimental data on the catalase activity of a biomimetic sensor when determining trace concentrations of H₂O₂ in an aqueous solution. When H₂O₂ is added to the system, there is a sharp change in the values of

Fig.2. Change e.m.f. systems depending on time at low concentrations of H₂O₂ for TPhPFe (III)/Al₂O₃/Pb electrode: 1 – 10⁻⁶, 2 – 10⁻⁸ mass %.

the electrochemical potential and it makes up (–0.15 mV) for both concentrations (curves 1 and 2). Starting from 1 minute, the value of the electrochemical potential continues to change until the practical decomposition of H₂O₂. This is evidenced by the fact that the value of the pH solution by the end of the experiment is 6.8, meaning that the background solution had the same value.

As a result of the research, it was found that a Pb-electrode with TPhPFe³⁺OH/Al₂O₃ allows detecting trace concentrations of hydrogen peroxide in an aqueous solution in an amount of 10⁻⁸ mass % [3].

Al-electrode

It was interesting for us to conduct experiments with another metal, namely with aluminum, on the surface of which TPhPFe³⁺OH/Al₂O₃ was applied. Under identical conditions carried out with TPhPFe³⁺OH/Al₂O₃//Pb biomimetic electrode, the Al electrode was investigated.

In Figure 3 experimental data on catalase activity TPhPFe³⁺OH/Al₂O₃//Al biomimetic sensor when determining trace concentrations of H₂O₂ in aqueous solution are shown.

As is seen the background solution for 10⁻⁶ mass % (curve 1), Al-electrode without imitator (curve 2) and 10⁻⁴ mass.% (curve 3) H₂O is (0.58), (0.55) and (0.383 mV) respectively.

Fig.3. Change e.m.f systems depending on time at low concentrations of H₂O₂ for TPhPFe³⁺OH/Al₂O₃//Al biomimetic sensor CH₂O₂ = 10⁻⁶ mass %. *t* = 22°C. 1 – Al+Ag paste+TPhPFe³⁺OH/Al₂O₃ (10⁻⁶), 2 – Al – without imitator (10⁻⁴), 3 – Al+Ag paste+TPhPFe³⁺OH/Al₂O₃ (10⁻⁴ mass %).

When H_2O_2 is added to the system, there is a change in the values of the electrochemical potential, which is (0.588) for 10^{-6} mass %, (0.407 mV) for 10^{-4} mass % (curves 1 and 3, Figure 3). The sensitivity threshold of $\text{TPhPFe}^{3+}\text{OH}/\text{Al}_2\text{O}_3//\text{Al}$ of the biomimetic sensor was 10^{-6} mass %.

Semiconductors

Our further studies were continued with the use of semiconductors, which have received wide practical application in bioelectronics, primarily silicon, germanium and tellurium (Si, Ge, Te).

Te-electrode

First, we conducted our studies with the semiconductor Te (Figure 4). As can be seen from Figure 4, curve 1, on 10^{-4} mass % H_2O_2 adding to the system, a jump in the electrochemical potential is observed, then a new surface layer is formed at the sensor-solution interface and the potential value stabilizes. In the presence of 10^{-6} mass % H_2O_2 in the reaction system, a low sensitivity of $\text{TPhPFe}^{3+}\text{OH}/\text{Al}_2\text{O}_3//\text{Te}$ biomimetic sensor curve 2 is observed. In the study of the catalase biomimetic sensor, it was found that a Te-electrode with $\text{TPhPFe}^{3+}\text{OH}$ can detect trace concentrations of H_2O_2 in an aqueous solution in amounts of 10^{-4} , 10^{-6} mass % [6].

Ge-electrode

Our research was related to the search for an effective semiconductor for the preparation of a biomimetic sensor. These were the main objectives of our research. In the framework of solving this problem, we used the most com-

Fig.4. Change emf systems depending on time at low concentrations of H_2O_2 for $\text{TPhPFe}^{3+}\text{OH}/\text{Al}_2\text{O}_3//\text{Te}$ biomimetic sensor: 1 – $\text{CH}_2\text{O}_2=10^{-4}$, 2 – $\text{CH}_2\text{O}_2=10^{-6}$ mass %.

mon semiconductor element in electronics – Ge. However, when using Ge as a substrate, it was found that when H_2O_2 is added to the system, Ge dissolves. Therefore, studies using Ge have been discontinued.

Si-electrode

In the next series of experiments for the preparation of a biomimetic sensor we have chosen the simplest one among of semiconductors which are widely used in bioelectronics – silicon.

The results of the experiments carried out at various concentrations of H_2O_2 are shown in Figure 5. From Figure 5 it is clearly seen that the presence of hydrogen peroxide in the system leads to a change in the value of ΔE , and an increase in the concentration of H_2O_2 from 10^{-6} to 1 mass % increases the jump in the electrochemical potential (curves 1–4).

Considering curves 1–4, it is not difficult to notice that in a few seconds, after adding H_2O_2 , all curves reach their maximum.

Then the electrochemical potential in the biomimetic sensor/ $\text{H}_2\text{O}_2//\text{Ag}/\text{AgCl}/\text{Cl}^-$ system continues to change until the practical decomposition of H_2O_2 .

When using a 1% aqueous solution of H_2O_2 to study the biomimetic sensor for catalase activity (curve 1), at the 3rd second observed the maximum e.m.f. value systems was (–0.461).

Fig.5. Change emf systems depending on time at low H_2O_2 concentrations for $\text{TPhPFe(III)}/\text{Al}_2\text{O}_3//\text{Si}$ biomimetic sensor. $t = 22^\circ\text{C}$. The number of $\text{TPhPFe}^{3+}\text{OH} = 0.025$ mg. 1 – $\text{CH}_2\text{O}_2=1$, 2 – $\text{CH}_2\text{O}_2=0.5$, 3 – $\text{CH}_2\text{O}_2=10^{-6}$, 4 – $\text{CH}_2\text{O}_2=10^{-4}$ mass %.

Experimental data related to the determination of the high sensitivity of the developed biomimetic sensor for determining trace amounts of H_2O_2 in aqueous solution are shown in Figure 5, curves 3, 4. Curve 3 (10^{-6} % concentration of H_2O_2) and curve 4 (10^{-4} % concentration of H_2O_2) after a few seconds (2–5 seconds) reaches a maximum value of ΔE and continues to change

As a result, potentiometric studies of the catalase activity of a biomimetic sensor prepared from a Si electrode and a smart biomimetic catalyst $TPhPFe^{3+}OH/Al_2O_3$ were carried out. The developed biomimetic sensor allows detecting trace concentrations of H_2O_2 in an aqueous solution at a sensitivity threshold of 10^{-6} mass % [4, 5, 7].

Conclusions

The synthesized $TPhPFe^{3+}OH/Al_2O_3/Pb$ and $TPhPFe^{3+}OH/Al_2O_3/Si$ biomimetic sensors had high sensitivity, the threshold of sensitivity to trace H_2O_2 concentrations was 10^{-8} and 10^{-6} mass % respectively.

Developed on the basis of smart biomimetic material (tetraphenylporphyrin iron) and semiconductor – Si, the biomimetic sensor is characterized by long stability, high sensitivity and reproducibility, with the possibility of expanding the range of trace concentrations of H_2O_2 in aqueous solutions.

For a long time, the synthesized biomimetic sensors did not lose their activity both under the influence of an oxidizing agent and its intermediates.

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KATALAZ BIOMİMETİK SENSORLARIN FİZİKİ-KİMYƏVİ XÜSUSİYYƏTLƏRİ

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Transdüser kimi, müxtəlif materiallardan istifadə edilən biomimetik sensorların fiziki-kimyəvi xüsusiyyətləri öyrənilmişdir. Smart material və yarımkəçiricilərdən hazırlanmış biomimetik sensorlar bir sıra texnoloji üstünlüklərə malik olduğu göstərilmişdir. Müxtəlif istifadə olunan materiallardan ən effektiv smart material – $TPhPFe^{3+}OH/Al_2O_3$ və Si-yarımkəçirici biomimetik sensor müəyyən edilmişdir. İşlənib-hazırlanmış biomimetik sensor yüksək aktivliyi, həssaslığı, stabilliyi və təkrar istifadəsi ilə H_2O_2 -in sulu məhlulda təyini diapazonun geniş imkanı ilə xarakterizə olunur (10^{-6} kütl.% qədər).

Açar sözlər: biomimetik sensor, katalaz, dəmir tetrafenilporfirin, yarımkəçiricilər, smart material.

ФИЗИКО-ХИМИЧЕСКИЕ ОСОБЕННОСТИ КАТАЛАЗНЫХ БИОМИМЕТИЧЕСКИХ СЕНСОРОВ

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Изучены физико-химические особенности биомиметических сенсоров, в качестве трансдюсера которых использованы различные материалы. Показано, что биомиметические сенсоры, приготовленные на основе smart материала и полупроводников, имели ряд технологических преимуществ. Установлено, что из использованных различных материалов наиболее эффективным оказался биомиметический сенсор, приготовленный из smart материала – $TPhPFe^{3+}OH/Al_2O_3$ и полупроводника Si. Разработанный биомиметический сенсор характеризуется высокими, активностью, чувствительностью, устойчивостью и воспроизводимостью с возможностью расширения диапазона определяемых следовых концентраций H_2O_2 в водном растворе до 10^{-6} масс %.

Ключевые слова: биомиметический сенсор, каталазный, тетрафенилпорфирин железа, полупроводники, smart материал.