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$TPhPFe^{3+}/Al_2O_3//Al$ Biomimetic Sensor of Catalase and Peroxidase Type

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Abstract: Rapid and accurate determination of hydrogen peroxide is very essential, as it is not only a product of reactions catalyzed by a number of infinitely selective oxidases, but also a cardinal combined element of food, pharmaceutical and environmental developments. Among the methods used for analysis of hydrogen peroxide, such as titrimetry, photometry, chemiluminescence, high-performance liquid electrochromatography and electrochemistry, enzyme-based biosensors attract important attention, due to the fact that this class of methods is characterized by sensitivity, convenience and high selectivity. Another, no less important aspect is related to determination of microquantities of C_2H_5OH in aqueous media of various origins. The need to develop express methods for determining the concentration of C_2H_5OH in aqueous solutions follows from the demand for the quality of alcohol products. As is known, the taste and drinking qualities of the product depend on the ratio of methyl and ethyl alcohols. In this aspect, we have carried out a research on the development of a biomimetic sensor of the catalase and peroxidase type for determining trace amounts of hydrogen peroxide in aqueous and aqueous-alcoholic solutions, as well as determining low concentrations of ethyl alcohol in an aqueous solution. The physicochemical features of catalase and peroxidase biomimetic sensors were studied by potentiometric research works, where metals were used as a transducer. Created on the basis of smart biomimetic material (iron tetraphenylporphyrin) and metals, the biomimetic sensor is characterized by long-term stability, highest sensitivity and reproducibility, with the possibility of expanding the range of detectable trace concentrations of H_2O_2 and C_2H_5OH in an aqueous solution. As a result of the study carried out, it was found that the developed $TPhPFe^{3+}/Al_2O_3//Al$ biomimetic sensors of the catalase and peroxidase types have a sensitivity threshold of 10^{-6} wt.% and 10^{-4} wt.%, respectively.

Keywords: Biomimetic Sensor, Catalase, Peroxidase, Iron Tetraphenylporphyrin, Smart Material

1. Introduction

In the last few years, large-scale investigations have been carried out in order to create biomimetic sensors that combine high specificity and selectivity of biochemical analysis methods with the advantages of chemical sensors (compactness, ease of measurement, etc.).

The development of motivated biosensors associated with the study of a large number of various substances is one of the most important directions in the development of analytical chemistry. This goal was necessary in the development of certain biosensors for a clear, fast, high-quality and quantitative determination of the desired component.

The existing range of different types of biosensors is created by varying a number of bioselective structures with different transducers. The type of the sensor is determined by the peculiarity of reactions and transformations in the biological testing element of the biosensor, and it is impossible to find a single universal converter for all cases of analysis [1-4].

It is described in the works [4-6] that chemical reactions in living organisms are carried out with the help of catalysts - enzymes. Enzymes are proteins with prosthetic groups, and proteins are polymers formed from links - amino acids. There are twenty types of amino acids in proteins, the alternation of which in the protein chain determines the specificity of the enzyme, that is, its biological function. As many different enzymes there are in a cell, as many different chemical reactions take place in it.

G.Bala Subbaiah et. al. [7] demonstrate how aluminum oxide-based biosensors have been developed for the detection of various analytes. The creation of such types of biosensors is associated, firstly, with the fact that it is widely used as a good dielectric (due to its high dielectric constant), its hardness and thermal stability, and secondly, considering the structure of aluminum oxide, it should be noted that it has the same size and high density of pores. Over the past few years, Al_2O_3 biosensors, which are used in several areas, such as the preparation of photocatalysts, sensors, capacitors, etc. have been synthesized. This paper presents data on the electrochemical biosensor properties of Al_2O_3 based sensors for the detection of various biomolecules. The prospects of the developed biosensors based on alumina are determined by potentially low cost and relatively simple preparation. In [7], the results of the obtained biosensors based on: zirconium oxide, ZrO_2-carbon, ZrO_2-metals, metal carbides and nitrides are also discussed, the use of which in the detection of various analytes (salicylic and ascorbic acids, nucleic acid, adrenaline, in gas analyzes, superoxide anion, heavy metals such as Cd (II), Pb (II), Cu (II) and Hg (II), uric acid and bromate in water resources, etc.) had high stability, high impact strength, high chemical resistance and desirable resistance to corrosion, chemical and microbial attack.

A method is proposed for the manufacture of gas sensors, in the structural elements of which materials based on nanostructures are used. The use of such materials in the sensor increases its sensitivity. Two groups of methods are proposed: the first is the use of a substrate or membrane from nanoporous anodic aluminum oxide as a base, the second is the formation of sensitive layers of a gas sensor with a large specific surface based on 1D–3D nanostructures [8].

Work on the search for the creation of highly sensitive biosensors for the qualitative and quantitative determination of various analytes is continuing. The use of biosensors has a number of advantages: they have high selectivity, rapidity and sensitivity; no preliminary separation of the components of the analyzed sample is required. However, sensors developed on the basis of biological objects (enzymes, cells, tissues, antibodies, receptors, etc.) have significant drawbacks, which are, as a rule, vulnerability to environmental influences, instability, short service life, etc.

The importance of the problem of creating analytical systems of a new generation, free from the shortcomings of enzyme sensors, has attracted the attention of scientists from many countries.

The fertile ground for the solution of this problem which is a new area of catalysis - imitation catalysis, was prepared [9, 10]. Based on the successes achieved in the field of imitation catalysis [9, 10], a fundamentally new approach to the creation of chemical analogues of biosensors, the so-called biomimetic sensors, which have significant advantages over enzymes, has been proposed. Thus, by replacing the active part of biosensors with their imitators, a new type of analytical devices has been created.

Considering the practical value of biosensors and their mimetic analogs, it is of fundamental importance to develop the latter by a comparatively conventional method and using lightweight technology. As a result, the search for new and effective developments for the preparation of biomimetic sensors is still an urgent problem.

It should be noted that the urgent task is to develop more active and stable biomimetic sensors of iron porphyrin sensors free from the above mentioned disadvantages.

Determination of low concentrations of hydrogen peroxide using biomimetic sensors is important for environmental pollution control, in medical diagnostics, in chemical industry, for the production of a wide range of products, etc. In medicine, hydrogen peroxide solutions are used as antiseptic and disinfectant agents. In the chemical industry, hydrogen peroxide is used as an oxidizing agent, as a raw material for the production of many peroxide compounds. In connection with the problems of environmental pollution by chemical production wastes, hydrogen peroxide is of particular importance as a "green" oxidizing agent that does not produce toxic substances.

For this purpose, it is necessary to carry out research on the detection of low concentrations of hydrogen peroxide in solutions, i.e. to create a stable, sensitive biomimetic sensor of the catalase type.

On the other hand, it is known that a significant amount of ethanol produced from food raw materials is used for the preparation of alcoholic products. Controlling the ethanol content of these products requires clarity and precision. Therefore, carrying out experimental studies to determine trace amounts of ethyl alcohol in aqueous solutions using a peroxidase-type biomimetic sensor is of practical importance.

A successful research was carried out in this direction [11–14], where experimental data on the study of the catalase activity of the iron porphyrin biomimetic sensors synthesized by us using a model electrochemical cell was presented.

One of the central areas of the research is the use of an Al electrode on the surface of which a TPhPFe^{3+}/Al_2O_3 smart material is deposited. The solution of such issues will allow developing biomimetic sensors, which will have high sensitivity, stability, efficiency and stability in operation with minimal costs and which can be reused.

For this purpose, the created models of biomimetic sensors can be considered as prototypes for the development of industrial highly sensitive and reliable biosensor systems for effective use in medicine and biotechnology.

2. Materials and Methods

The main working components of sensors designed to determine H_2O_2 and C_2H_5OH is a smart material, which is further immobilized on the surface of Al-plates. At first, Al plates of AE brand, measuring ~ 0.6x0.6 sm were processed: a clean ready plate was cut out, samples were etched in 5–6% NaOH alkali solution at 40–50°C for 2 minutes in order to get rid of the air oxide film. Then the samples were clarified in concentrated HNO_3 for 30 seconds. After being thoroughly washed in distilled water, the samples were dried (to give a uniform color).

In order to create the most sensitive biosensor, we attempted to study an improved electrode of the catalase and peroxidase type to determine low concentrations of H_2O_2 and C_2H_5OH in an aqueous solution. To detect trace concentrations of hydrogen peroxide in an aqueous solution, we used Al as a transducer [15].

2.1. Experimental Plant

Determining the concentration of hydrogen peroxide is very important in various fields, including medicine, cosmetics industry, environmental control, etc. Peroxide compounds can be formed in the body, both during the development of pathological processes, and during certain medical procedures that change balance of metabolic processes. Along with peroxide compounds, various toxins can easily enter the cell through their oxidative effect on proteins, membranes and DNA and cause destruction of healthy cells. The formation of peroxide as an intermediate product can be used to determine a number of biologically active compounds (glucose, lysine, glutamate, etc.) through conjugated polyenzyme systems. The determination of hydrogen peroxide is also important in environmental monitoring. This is due to the growth of atmospheric pollution and the destruction of the ozone layer. Therefore, hydrogen peroxide must be determined in a fairly wide range of concentrations. In this regard, there is a need to create very sensitive biosensors for determining trace amounts of hydrogen peroxide.

The first scientifically proposed and successfully implemented biosensors were based on electrochemical sensors for several analytes. Electrochemical biosensors have been studied for a very long time. At present, semiconductor-based converters represent a typical platform for creating biosensors [12–14].

The review [16] describes electrochemical biosensors and their principles. The corresponding systems are divided into three types according to the principle of operation that determines their measurement method: potentiometric, amperometric and impedimetric transducers.

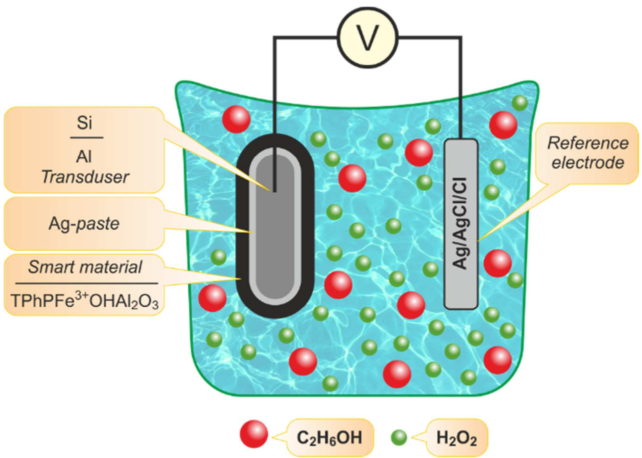

Figure 1. *Infographics.*

The work was done by the potentiometric method to determine the catalase and peroxidase activity. The experimental plant consisted of an electrode part, a cell, and a B7-21A universal voltmeter. The electrode part of the plant consisted of a reference electrode (Ag/AgCl/Cl-) and a biomimetic sensor prepared by us. Bidistilled water served as the background solution. An electrochemical cell is presented in the form of infographics for illustrative purposes (Figure 1). The biomimetic electrode was prepared by gluing a smart material ($TPhPFe^{3+}/Al_2O_3$) onto a substrate (electrode, transducer). Silver paste was used as an adhesive material.

2.2. Active Materials

Active materials (smart materials) – iron tetraphenylporphyrin. Smart material - biomimetic must be in direct contact with the transducer. To create this contact, we used silver paste.

Iron tetraphenylporphyrin was applied to the electrode by gluing (silver paste was used as an adhesive).

Synthesis of the biomimetic was carried out according to the known method: iron tetraphenylporphyrin and benzene were placed into the flask. By being stirred during the day, iron tetraphenylporphyrin was dissolved and brought to a homogeneous mass. Then, using a PEC spectrophotometer (spectrophotometer), the initial reading of the prepared solution was made. Al_2O_3 (carrier) dried in a muffle furnace was added to this solution, and thus iron tetraphenylporphyrin was adsorbed on Al_2O_3. Then, the reading of the solution after adsorption was made, and the amount of adsorbed iron tetraphenylporphyrin on Al_2O_3 was determined from the difference in values. Following, the finished compound - $TPhPFe^{3+}/Al_2O_3$ was applied to the electrode, according to the above mentioned method.

Taking into account the stability and long service life of biomimetic sensors [9, 10, 17] with the iron tetraphenylporphyrin as active centers, we prepared catalysts for biomimetic sensors in an amount that could be used for several years.

An electrochemical system consisting of a biomimetic selector of catalase and peroxidase type “merged” with the electrode made it possible to determine low concentrations of H_2O_2 and C_2H_5OH in aqueous solutions at 22°C. It formed the basis of cheap and easy-to-use potentiometric biomimetic sensors.

3. Experimental Part

3.1. Study of the Catalase $TPhPFe^{3+}/Al_2O_3//Al$ Biomimetic Sensor at 22°C

Experimental data on the catalase activity of the $TPhPFe^{3+}/Al_2O_3//Al$ biomimetic sensor in determining trace concentrations of H_2O_2 in an aqueous solution at the temperature of 22°C and with the amount of smart material of 0.030 mg is presented in Figure 2.

There are two successive reactions occurring on the electrode in the electrochemical mode - catalase and electrochemical, which are responsible for the total change in the electrochemical potential of the system:

$$2H_2O_2 \rightarrow 2H_2O + O_2 \quad (1)$$

$$O_2 + 4e + 2H^+ \rightarrow 2OH^- \quad (2)$$

The catalase reaction of hydrogen peroxide decomposition (1) is complex and consists of several elementary steps, in which electron transfer occurs between the electrode, H_2O_2, and its active fragments.

The electrochemical reduction reaction of molecular oxygen formed in reaction (2) is also a staged redox reaction.

The $TPhPFe^{3+}$, preliminarily adsorbed on Al_2O_3, was applied to the Al electrode by gluing (silver paste was used as an adhesive). Artificial mixtures of hydrogen peroxide (10^{-2} wt% - 10^{-6} wt%) and various amounts of $TPhPFe^{3+}/Al_2O_3$ smart material (0.030 mg. 0.016 mg) were prepared.

As can be seen from the data in Figure 2, the background solution of H_2O for 10^{-6} wt.% (curve 1), 10^{-4} wt.% (curve 2) and 10^{-3} wt.% (curve 3) was (0.572V), (0.575V) and (0.581V) respectively. When H_2O_2 was added to the system, the values of the electrochemical potential changed (Figure 2 curves 1 - 3).

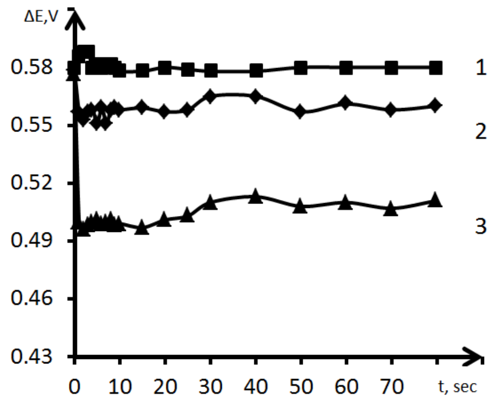

Figure 2. *Change e.m.f systems depending on time at low concentrations of H_2O_2 for $TPhPFe^{3+}OH/Al_2O_3//Al$ biomimetic sensor t = 22°C. Quantity $TPhPFe^{3+}/Al_2O_3$ - 0,030 mg.*

1) Al+ silver paste +$TPhPFe^{3+}/Al_2O_3$ (10^{-6}wt%)
2) Al+ silver paste +$TPhPFe^{3+}/Al_2O_3$ (10^{-4} wt%)
3) Al+ silver paste +$TPhPFe^{3+}/Al_2O_3$ (10^{-3} wt%)

Figure 3 demonstrates changes in e.m.f. systems depending on time at low concentrations of hydrogen peroxide for $TPhPFe^{3+}/Al_2O_3//Al$ biomimetic sensor. It can be seen from the curves 1-4 in Figure 3 that starting from 3–4 seconds, the catalase reaction for all curves accelerates, and the value of the electrochemical potential continues to change. This means that the catalase reaction proceeds at a high rate.

The tendency of curves 1-4 in Figure 3 to a constant and identical value of ΔE shows that there is practically no catalase reaction.

The experiment carried out with the $TPhPFe^{3+}/Al_2O_3//Al$ biomimetic sensor, on the surface of which $TPhPFe^{3+}/Al_2O_3$ was deposited, made it possible to determine trace concentrations of hydrogen peroxide in an aqueous solution, the sensitivity threshold of which was 10^{-6} wt.%.

The reproducibility of the results and the activity of the electrode were maintained during all experiments.

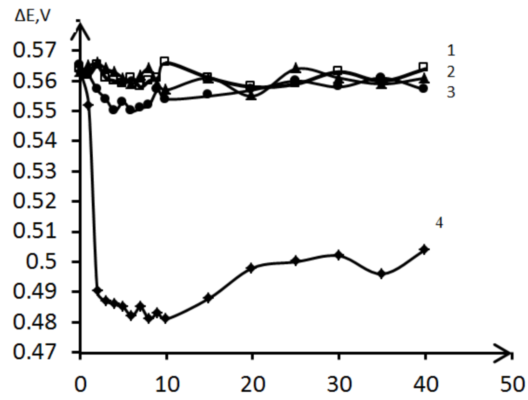

Figure 3. *Change e.m.f systems depending on time at low concentrations of H_2O_2 for $TPhPFe^{3+}OH/Al_2O_3//Al$ biomimetic sensor t = 22°C. Quantity $TPhPFe^{3+}/Al_2O_3$ - 0,016 mg.*

1) Al+ silver paste +$TPhPFe^{3+}/Al_2O_3$ (10^{-6}wt%)
2) Al+ silver paste +$TPhPFe^{3+}/Al_2O_3$ (10^{-4} wt%)
3) Al+ silver paste +$TPhPFe^{3+}/Al_2O_3$ (10^{-3} wt%)
4) Al+ silver paste +$TPhPFe^{3+}/Al_2O_3$ (10^{-2} wt%)

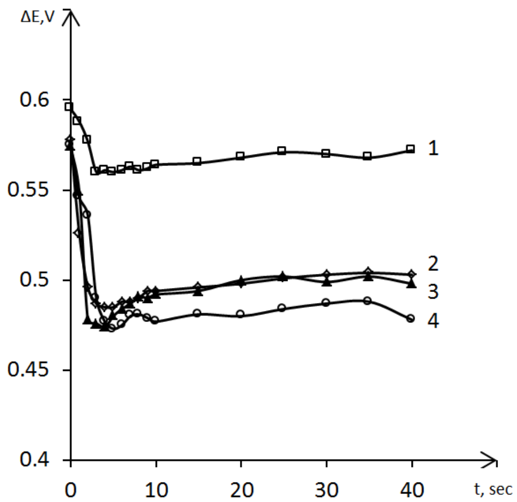

Figure 4. *Change e.m.f systems depending on time at low concentrations of H_2O_2 for $TPhPFe^{3+}/Al_2O_3//Al$ biomimetic sensor. t=30°C.*

1. Al+ Ag paste +$TPhPFe^{3+}/Al_2O_3$ (10^{-6}wt%)
2. Al+ Ag paste +$TPhPFe^{3+}/Al_2O_3$ (10^{-4}wt %)
3. Al+ Ag paste +$TPhPFe^{3+}/Al_2O_3$ (10^{-3} wt%)
4. Al+ Ag paste +$TPhPFe^{3+}/Al_2O_3$ (10^{-2} wt%)

3.2. Study of the Catalase $TPhPFe^{3+}/Al_2O_3//Al$ Biomimetic Sensor at 30°C

While continuing research on the study of physicochemical characteristics of a biomimetic sensor developed on the basis of a smart biomimetic material (iron tetraphenylporphyrin), characterized by long-term stability, high sensitivity and reproducibility, with the possibility of expanding the range of detectable trace concentrations of

H_2O_2 in an aqueous solution, we have also studied the effect of the reaction medium temperature and the amount of $TPhPFe^{3+}$ smart material on the catalase activity of the biomimetic sensor using potentiometric method. The prepared biomimetic electrode contained the amount of smart material of 0.016 mg, and the temperature was 30°C. In order to study the catalase activity, we used extremely low concentrations of H_2O_2. As shown by the results of experimental data carried out with 0.016 mg $TPhPFe^{3+}$ containing electrode (curve 1-4, Figure 4), the electrode potential of the background solution was (0.575V - curve 4, 0.574V - curve 3, 0.578V - curve 2, 0.595V - curve 1). When H_2O_2 was added, after a few seconds, we observed a sharp jump in the system potential to (curve 1 - 0.588V, curve 2 - 0.526V, curve 3 - 0.549V, curve 4 - 0.546V). A few seconds later ΔE reached its maximum value and after a few more seconds this value decreased. The further value of the electrochemical potential continued to change. This is apparently due to the fact that the catalase reaction was proceeding.

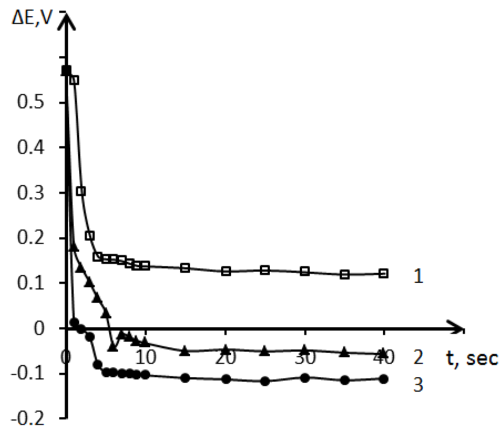

Figure 5. *Change e.m.f systems depending on time at low concentrations of H_2O_2 for $TPhPFe^{3+}/Al_2O_3//Al$ biomimetic sensor. t=30°C.*

Al+ Ag paste +$TPhPFe^{3+}/Al_2O_3$ (0,1 wt%)
Al+ Ag paste +$TPhPFe^{3+}/Al_2O_3$ (0,5 wt %)
Al+ Ag paste +$TPhPFe^{3+}/Al_2O_3$ (1 wt%)

The biomimetic electrode with $TPhPFe^{3+}$ also had a long service life regardless of temperature and amount of smart material applied to the electrode (Figure 4), and its activity practically did not depend on the number of experiments carried out. From the values of ΔE on curves 1-4 in Figure 4, it can be seen that irrespective of the amount of smart material and temperature, the nature of the curves does not change.

Thus, the synthesized $TPhPFe^{3+}/Al_2O_3/Al$ biomimetic sensor containing the amount of $TPhPFe^{3+}$ smart material of 0.016 mg is in an oscillatory mode. The sensitivity limit for H_2O_2 is 10^{-6} wt.%.

The results of experimental studies are shown in Figures 4 and 5.

Change in the temperature of the reaction medium to 30°C does not change the nature of the curves as well.

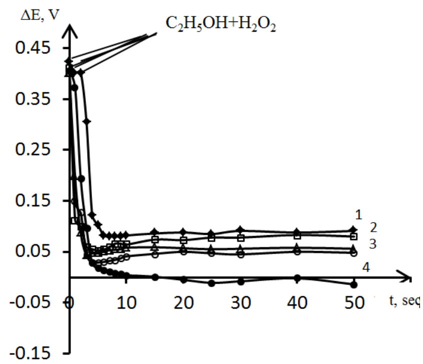

Figure 6. *Change e.m.f. systems depending on time at low concentrations of C_2H_5OH for $TPhPFe^{3+}/Al_2O_3//Al$ biomimetic sensor. Const: H_2O_2=0,1 wt%.*

1.$C_{C_2H_5OH}$=10^{-4}wt.%; 2. $C_{C_2H_5OH}$ =10^{-3} wt.%;
3. $C_{C_2H_5OH}$ =10^{-2} wt.%;
4. $C_{C_2H_5OH}$ =0,1 wt.%; 5. $C_{C_2H_5OH}$ =0,5 wt%

As a result of experimental studies, it was found that the change in the amount of $TPhPFe^{3+}$ smart material and temperature does not affect the catalase activity of the biomimetic sensor. The sensitivity threshold is 10^{-6} wt.% H_2O_2.

3.3. Study of the Peroxidase $TPhPFe^{3+}/Al_2O_3//Al$ Biomimetic Sensor at 22°C

Research is devoted to the development of a peroxidase biomimetic sensor for determining trace amounts of ethanol in solution. A biomimetic sensor operating in the electrochemical mode was developed on the basis of peroxidase mimetics and its peroxidase activity was determined.

Experiments on determining traces of ethanol were carried out in an electrochemical cell of a peroxidase-mimetic sensor of a potentiometric type.

In a series of experiments, the concentration of ethyl alcohol varied from 10^{-4} to 0.5 wt%, and the concentration of hydrogen peroxide was kept constant at 0.1 wt%.

It was necessary to measure the electrochemical potential of 0.1% aqueous solution of ethanol to analyze the peroxidase reaction curves. Its value completely coincided with the potentials of bidistilled water. Thus, the water-alcohol solution practically remained inert with respect to the electrode.

Figure 6 demonstrates the experimental data obtained in the study of peroxidase activity of a tetraphenylporphyrin-containing electrode at a concentration of 0.1 wt% H_2O_2 and various concentrations of C_2H_5OH at the temperature of 22°C.

The prepared sensor was stable in operation and did not lose activity for a long time, which created favorable conditions for repeated use.

4. Conclusion

Based on the modelling of certain functions of the catalase biosensor, a $TPhPFe^{3+}/Al_2O_3/Al$ catalase-biomimetic sensor was developed, and its physicochemical features were studied. A change in the electrochemical potential occurs in these systems as a result of the interaction of the developed biomimetic sensor with trace amounts of H_2O_2 in an aqueous solution. The synthesized $TPhPFe^{3+}/Al_2O_3/Al$ biomimetic sensor had a high sensitivity. The threshold of sensitivity to trace concentrations of H_2O_2 was 10^{-6} wt.%, respectively.

When studying the catalase $TPhPFe^{3+}/Al_2O_3/Al$ biomimetic sensor for peroxidase activity, it was found that the developed biomimetic sensor had a high sensitivity. As a result of the research, it was found that the developed biomimetic sensor made it possible to detect ethyl alcohol in an aqueous solution in an amount of 10^{-4} wt.%, while maintaining high stability and reproducibility with the possibility of expanding the range of trace concentrations of C_2H_5OH in aqueous solutions.

Based on iron porphyrin complexes, oxidation-resistant, affordable and cheap biomimetic electrodes of the catalase and peroxidase types have been synthesized.

Thus, a biomimetic sensor of catalase and peroxidase types based on a smart biomimetic material (iron tetraphenyl porphyrin) and a metal - Al was developed, which is characterized by long-term stability, high sensitivity and reproducibility, with the possibility of expanding the range of detectable trace concentrations of H_2O_2 in aqueous and aqueous-alcoholic solutions, as well as its application in the detection of micro amounts of C_2H_5OH in water.

As a result of these studies, it was found that the developed catalase-imitating sensor has a number of technological advantages over its biosensor counterparts: low cost of preparation, electrodes did not lose their activity for a long time, are sensitive and stable in operation and can be reused.

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