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STUDY OF CATALASE ACTIVITY OF BIOMIMETIC SENSORS AT DIFFERENT TEMPERATURES AND AMOUNTS OF SMART MATERIAL**N.N.Malikova, N.I.Ali-zade, T.M.Nagiev***M.Nagiev Institute of Catalysis and Inorganic Chemistry NAS of Azerbaijan**tnagiev@azeurotel.com*

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Biomimetic sensors based on semiconductor (Si), metal (Al) and smart material (TPhPFe³⁺OH/Al₂O₃) have been developed. It has been found that a biomimetic sensor, where a semiconductor (Si) is used as an electrode, exhibits high sensitivity, stability and reproducibility. The effect of temperature and the amount of smart material on the catalase activity of biomimetic sensors was studied. At the study of the Si-electrode for catalase activity, it was revealed that the amount of smart material and temperature do not affect the detection limit of hydrogen peroxide in an aqueous solution, the sensitivity threshold, which was 10⁻⁶ mass%. When detecting the catalase activity of the TPhPFe³⁺OH/Al₂O₃/Al biomimetic sensor, it was established that the sensitivity threshold was also 10⁻⁶ mass %.

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

doi**Introduction**

Determination of the concentration of hydrogen peroxide is very important in various fields, including medicine, in the textile industry, the cosmetic industry, for environmental control, etc. In this regard, based on bioimitation modeling of the known catalase, peroxidase and monooxygenase processes, it is possible to synthesize biomimetic analogs of the corresponding enzymes, the use of which in sensors will eliminate many of the above disadvantages. In works [1, 2] the results of research in this direction are given.

Developed on the basis of a smart biomimetic material (iron tetraphenylporphyrin) and a semiconductor – Si, the biomimetic sensor is characterized by long-term stability, high sensitivity and reproducibility, with the possibility of expanding the range of detectable trace concentrations of H₂O₂ in an aqueous solution. The sensitivity threshold was 10⁻⁶ mass % [3, 4].

To detect trace concentrations of H₂O₂ in aqueous solutions, we have created and developed the simplest and cheapest to use potentiometric biomimetic sensors with rapidity and high sensitivity. An experiment carried out with a metal, namely with aluminum, on the surface of which TPhPFe³⁺OH/Al₂O₃ was applied,

made it possible to determine the trace concentrations of H₂O₂ in an aqueous solution, the sensitivity threshold of which was 10⁻⁶ mass % [5].

In the presented work, the effect of temperature and amount of smart material on the catalase activity of biomimetic sensors made of Al, Si electrodes and a smart biomimetic catalyst – TPhPFe³⁺OH/Al₂O₃ was studied.

Experimental part

Catalase activity of biomimetic sensors was determined by potentiometric method. Two biomimetic Si electrodes were prepared with a working surface size of 0.3 × 0.3 sm and 0.6 × 0.6 sm. The prepared biomimetic electrode contained an amount of smart material of 0.012 and 0.025 mg. To study the catalase activity, we used an extremely low concentration of H₂O₂. The results of experimental studies are shown in Figures 1 and 2.

Figure 1 shows the results of experimental studies of the catalase activity of a biomimetic electrode based on a Si-electrode and TPhPFe³⁺/Al₂O₃ smart material in amounts equal to 0.012 and 0.025 mg.

The observed jumps of the electrochemical potential at different amounts of smart material (while the temperature remained at 22⁰C) have the same character (curves 1 and 2 in

Figure 1), differing in the initial value of the potential.

For a biomimetic sensor containing 0.025 mg $\text{TPhPFe}^{3+}\text{OH}$ (curve 1), this value is (-0.305 mV). The content of 0.012 mg of smart material – $\text{TPhPFe}^{3+}\text{OH}$ in the biomimetic sensor changes the initial value of the potential and is (-0.14 mV)

A change in the temperature of the reaction medium up to 40°C does not change the character of the curves (Figure 2, curves 1 and 2), and is reflected in the values of the electrode potential. For a biomimetic sensor with a content of 0.025 mg $\text{TPhPFe}^{3+}\text{OH}$ (curve 1), this value is (-0.131 mV). The content of 0.012 mg of smart material – $\text{TPhPFe}^{3+}\text{OH}$ in the biomimetic sensor changes the initial value of the potential and is (-0.109 mV).

As a result of experimental studies, it was established that independently of the amount of $\text{TPhPFe}^{3+}\text{OH}$ smart material and temperature change, it does not affect the catalase activity of the biomimetic sensor. The sensitivity threshold is 10^{-6} mass % [6].

It was interesting to conduct experiments and find out how low concentrations of H_2O_2 can be detected by an advanced biomimetic sensor based on an Al electrode, i.e., to determine its sensitivity threshold at different temperatures and amounts of smart material.

Fig. 1. Change in emf systems depending on time at low concentrations of H_2O_2 for $\text{TPhPFe}^{3+}\text{OH}/\text{Al}_2\text{O}_3//\text{Si}$ biomimetic sensor; $C_{\text{H}_2\text{O}_2} = 10^{-6}$ mass %; $T=22^\circ\text{C}$: quantity $\text{TPhPFe}^{3+}\text{OH} = 0.025$ mg (1) and 0.012 mg (2).

Continuing research on the study of the 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 determined trace H_2O_2 concentrations in an aqueous solution, we prepared two biomimetic electrodes from Al with a working surface size of 0.3×0.3 cm and 0.6×0.6 cm.

Prepared biomimetic electrodes contained 0.016 and 0.030 mg. of smart material.

Figures 3 and 4 show the experimental data obtained in the study of H_2O_2 at low concentrations in an aqueous solution depending on temperature.

As shown by the results of experiments carried out with 0.016 mg $\text{TPhPFe}^{3+}\text{OH}$ containing electrode (curves 1, 2, 3, 4, Figure 3), the electrode potential of the background solution is (0.562 – 0.565 mV). With this the temperature remained equal to 22°C . And at a temperature of 30°C (Figure 4), the electrode potential of the background solution vade (0.580 – 0.590 mV).

The amount of $\text{TPhPFe}^{3+}\text{OH}$ deposited on the surface of the Al electrode was 0.016 mg in both cases.

Thus, the developed biomimetic sensor makes it possible to determine low concentrations of H_2O_2 in an aqueous solution. The sensi-

Fig. 2. Change in emf systems as a function of time at low concentrations of H_2O_2 for $\text{TPhPFe}^{3+}\text{OH}/\text{Al}_2\text{O}_3//\text{Si}$ biomimetic sensor $C_{\text{H}_2\text{O}_2} = 10^{-6}$ mass %. $T=40^\circ\text{C}$; quantity $\text{TPhPFe}^{3+}\text{OH} = 0.025$ mg (1) and 0.012 mg (2).

tivity threshold at these temperatures (22 and 30°C) was 10^{-6} mass %. Simultaneously the effect of the amount of smart material in the reaction medium on the catalase activity of the developed biomimetic sensors was studied using the potentiometric method. To study the catalase activity of biomimetic sensors, an extremely low concentration of H_2O_2 was used. The experimental data are shown in Figure 5. The amount of $\text{TPhPFe}^{3+}\text{OH}$ smart material (0.016 and 0.030 mg) does not affect the catalase activity of the biomimetic sensor and bears identical character with different background potentials. The initial value of the electrochemical poten-

tial for a biomimetic sensor containing 0.016 mg (Figure 5) of smart material ($\text{TPhPFe}^{3+}\text{OH}$) is 0.562–0.565 mV. However, for a biomimetic sensor containing 0.030 mg of smart material ($\text{TPhPFe}^{3+}\text{OH}$) the initial value of the electrochemical potential is in the range of 0.572–0.581 mV.

Thus, there was synthesized an oxidation-resistant catalase-type biomimetic sensor based on the iron porphyrin complex. It was discovered that the developed biomimetic sensor can detect low concentrations of H_2O_2 (up to 10^{-6} mass %) in an aqueous solution, regardless of the amount of smart material and temperature.

Fig. 3. Change in emf systems depending on time at low concentrations of H_2O_2 for $\text{TPhPFe}^{3+}\text{OH}/\text{Al}_2\text{O}_3/\text{Al}$ biomimetic sensor. $T = 22^\circ\text{C}$. Quantity $\text{TPhPFe}^{3+}\text{OH} = 0.016$ mg. 1 – Al+silver paste+ $\text{TPhPFe}^{3+}\text{OH}/\text{Al}_2\text{O}_3$ (10^{-6} mass %), 2 – Al+silver paste+ $\text{TPhPFe}^{3+}\text{OH}/\text{Al}_2\text{O}_3$ (10^{-4} mass %), 3 – Al+silver paste+ $\text{TPhPFe}^{3+}\text{OH}/\text{Al}_2\text{O}_3$ (10^{-3} mass %), 4 – Al+silver paste+ $\text{TPhPFe}^{3+}\text{OH}/\text{Al}_2\text{O}_3$ (10^{-2} mass %).

Fig. 4. Change in e.m.f. systems depending on time at low concentrations of H_2O_2 for $\text{TPhPFe}^{3+}\text{OH}/\text{Al}_2\text{O}_3/\text{Al}$ biomimetic sensor. $T = 30^\circ\text{C}$. Quantity $\text{TPhPFe}^{3+}\text{OH} = 0.016$ mg. 1 – Al+silver paste+ $\text{TPhPFe}^{3+}\text{OH}/\text{Al}_2\text{O}_3$ (10^{-6} mass %); 2 – Al+ silver paste + $\text{TPhPFe}^{3+}\text{OH}/\text{Al}_2\text{O}_3$ (10^{-4} mass %); 3 – Al+silver paste + $\text{TPhPFe}^{3+}\text{OH}/\text{Al}_2\text{O}_3$ (10^{-3} mass %); 4 – Al+silver paste + $\text{TPhPFe}^{3+}\text{OH}/\text{Al}_2\text{O}_3$ (10^{-2} mass %).

Fig. 5. Change in emf systems depending on time at low concentrations of H_2O_2 for $\text{TPhPFe}^{3+}\text{OH}/\text{Al}_2\text{O}_3/\text{Al}$ biomimetic sensor. $T = 22^\circ\text{C}$. Quantity $\text{TPhPFe}^{3+}\text{OH} = 0.030$ mg. 1 – Al+silver paste + $\text{TPhPFe}^{3+}\text{OH}/\text{Al}_2\text{O}_3$ (10^{-6} mass %), 2 – Al+silver paste+ $\text{TPhPFe}^{3+}\text{OH}/\text{Al}_2\text{O}_3$ (10^{-4} mass %), 3 – Al+silver paste + $\text{TPhPFe}^{3+}\text{OH}/\text{Al}_2\text{O}_3$ (10^{-2} mass %).

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MÜXTƏLİF TEMPERATUR VƏ SMART MATERIALIN FƏRQLİ MİQDARINDAN ASILI OLARAQ BİOMİMETİK SENSORLARIN KATALAZ AKTİVLİYİNİN ÖYRƏNİLMƏSİ

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Yarımkeçirici (Si), metal (Al) və smart material (TPhPFe³⁺OH/Al₂O₃) əsasında biomimetik sensorlar işlənib hazırlanmışdır. Yarımkeçiricinin (Si) elektrod kimi istifadə olunduğu bir biomimetik sensorun yüksək həssaslıq, sabillik və təkrar istifadəsi göstərdiyi müəyyən edilmişdir. Temperaturun asılılığı və smart material miqdarının biomimetik sensorların katalaz aktivliyinə təsiri öyrənilmişdir. Si-elektrodun katalaz aktivliyini öyrənərkən müəyyən olunmuşdur, ki smart materialın miqdarı və temperaturun sulu məhlulda hidrogen peroksidin aşkarlanma həddini, 10⁻⁶ küt.% təşkil edir. TPhPFe³⁺OH/Al₂O₃Al biomimetik sensorun katalaz aktivliyini öyrənərək müəyyən olunmuşdur, ki həssaslıq həddi 10⁻⁶ küt.% təşkil edir.

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

ИССЛЕДОВАНИЕ КАТАЛАЗНОЙ АКТИВНОСТИ БИОМИМЕТИЧЕСКИХ СЕНСОРОВ ПРИ РАЗЛИЧНЫХ ТЕМПЕРАТУРАХ И КОЛИЧЕСТВАХ СМАРТ МАТЕРИАЛА

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Разработаны биомиметические сенсоры на основе полупроводника (Si), металла (Al) и смарт материала (TPhPFe³⁺OH/Al₂O₃). Установлено, что биомиметический сенсор, где в качестве электрода использован полупроводник (Si) проявляет высокие чувствительность, стабильность и воспроизводимость. Изучено влияние температуры и количество смарт материала на каталазную активность биомиметических сенсоров. При исследовании влияния Si-электрода на каталазную активность сенсоров выявлено, что количество смарт материала и температура не влияют на предел обнаружения пероксида водорода в водном растворе, порог чувствительности которого составил 10⁻⁶ масс. %. При выявлении каталазной активности биомиметического сенсора TPhPFe³⁺OH/Al₂O₃/Al, было установлено, что его порог чувствительности в таком же растворе также составил 10⁻⁶ масс. %.

Ключевые слова: биомиметик, сенсор, тетрафенилпорфирин железа, каталазный, полупроводник, смарт материал.