

Investigation of oxide electrocatalysts for glucose monitoring systems

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Abstract: This study aimed to find and investigate new oxide catalysts for glucose electrooxidation operating in a neutral medium. The catalysts were prepared in the form of dispersion deposited on a carbon substrate; the obtained electrodes were characterized. The following oxides were studied for the ability to enzyme-free glucose oxidation: tin(IV) oxide, tungsten(VI) oxide, titanium(IV) oxide and manganese(IV) oxide. During the tests, such analysis techniques as cyclic voltammetry and chronoamperometry were applied. A phosphate buffer solution (pH 7.40) was used as a working electrolyte (background solution). The study proves that the electrode based on manganese(IV) oxide mixed with acetylene black shows a stable current for the anodic oxidation of glucose under continuous polarization during at least two hours, and stable under keeping in the working electrolyte. The dependence between the current and the root of the glucose concentration was shown to have a quasilinear character, and therefore this electrocatalyst can act as a promising and inexpensive material for continuous glucose monitoring sensors.

Keywords: continuous glucose monitoring; enzyme-free glucose oxidation; non-noble oxide-based electrocatalyst.

For citation: Nikolaeva EA, Urvanov SA, Filimonenkov IS, Mordkovich VZ. Investigation of oxide electrocatalysts for glucose monitoring systems. *Journal of Advanced Materials and Technologies*. 2022;7(4):299-309. DOI:10.17277/jamt.2022.04.pp.299-309

Исследование оксидных электрокатализаторов для систем мониторинга глюкозы

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Аннотация: Проведены поиск и исследование новых оксидных катализаторов окисления глюкозы, способных работать в условиях нейтральной среды, получены катализаторы в виде дисперсии на углеродной подложке, охарактеризованы полученные электроды. На способность к бесферментному окислению глюкозы были исследованы следующие оксиды: оксид олова(IV), оксид вольфрама(VI), оксид титана(IV) и оксид марганца(IV). При проведении испытаний использовали такие методы анализа, как циклическая вольтамперометрия и хроноамперометрия. В качестве рабочего электролита (фоновое раствора) выступал фосфатный буферный раствор (рН 7,40). Показано, что электрокатализатор на основе оксида марганца(IV), смешанного с ацетиленовой сажей, показывает стабильный ток при непрерывной поляризации электрода в течение двух часов, устойчив при постоянном нахождении в рабочей среде, а зависимость тока от корня из концентрации глюкозы имеет практически линейный характер, в связи с чем данный электрокатализатор может выступать как перспективный и недорогой материал для датчиков непрерывного мониторинга глюкозы.

Ключевые слова: непрерывный мониторинг глюкозы; бесферментное окисление глюкозы; электрокатализаторы на основе оксидов благородных металлов.

Для цитирования: Nikolaeva EA, Urvanov SA, Filimonenkov IS, Mordkovich VZ. Investigation of oxide electrocatalysts for glucose monitoring systems. *Journal of Advanced Materials and Technologies*. 2022;7(4):299-309. DOI:10.17277/jamt.2022.04.pp.299-309

1. Introduction

World statistics of incidence from year to year shows a steady upward trend in the number of people living with diabetes mellitus. Due to the global spread of diabetes, scientists and physicians are increasingly classifying diabetes as a non-communicable epidemic. The uncontrolled course of this disease leads to serious health complications in its various aspects: kidney and heart failure, heart attacks, blindness and much more, which significantly reduces the standard of living of the population [1].

Despite the incurable nature of the disease, modern medicine allows for the qualitative control of this disease by monitoring blood glucose levels, which allows diabetics to maintain a decent standard of living [2]. The most common way to control glycaemia at present is the self-monitoring of blood glucose levels. It involves the individual measurement of instantaneous blood sugar concentration using portable glucometers at home. The operation of such systems is based on an enzyme, for example, glucose oxidase, which is a catalyst for the oxidation of glucose by oxygen [3]. In recent years, due to the development of enzyme-free electrocatalysis and the ever-improving glucose sensors derived from it, continuous glucose monitoring (CGM) systems that show the level of sugar in the form of glycemic fluctuations, measured almost continuously throughout the day have been gaining in popularity. The main advantage of such systems is the ability to see and warn of rising or falling glucose levels [4].

The sensor in the CGM system must provide high-quality operation while constantly being in the interstitial fluid. At the same time, the enzyme, which is a complex protein compound, is affected by temperature, pH, and humidity, is prone to difficult-to-predict transformations in artificial environments, and can work inefficiently under conditions of oxygen deficiency, which imposes restrictions on the use of such structures in CGM systems. Stability and reproducibility in CGM sensors can be provided by non-enzymatic electrocatalysts, the operation of which is based on the direct catalytic oxidation of glucose to gluconic acid on an electrode modified by a metal, or a metal oxide, or a composite based on them [5].

In the vast majority of cases, the glucose sensor is made in the form of a three-electrode circuit, which includes a working electrode, a reference electrode, and a counter electrode. The main electrochemical processes take place on the working electrode; therefore, decades of research have been devoted to the composition and structure of this particular electrode. The working electrode can be made of pure metal, metal oxide, various carbon structures, as well as various composites [6].

In recent years, a huge number of variations of the metal-based working electrode have been tested [7]. For example, platinum, known for its excellent catalytic properties, is the most studied and widely used in enzymeless electrocatalysis. Various manipulations with the electrode structure made it possible to increase the sensitivity and selectivity of the sensor, increase the linear range of the concentration dependence, minimize the detection limit of glucose, etc. Electrodes based on gold, nickel, copper, etc. have also been well studied [5–7].

One of the promising directions in this area is the creation of electrodes based on metal oxides, on the development of which a large number of works have been published to date. It has been established that the process of glucose oxidation on such electrocatalysts as Co_3O_4 , CuO , Cu_2O , MnO_2 goes through the following stages: activation of the metal oxide redox center by hydroxide ions, formation of intermediate products that serve as a catalyst for glucose oxidation, and subsequent reduction of the oxide to original shape [8]. Most researchers and developers of oxide electrodes believe that an important theoretical component of the process of glucose oxidation on oxide catalysts is the assumption of a reversible redox reaction of the metal atom in the oxide, i.e. a metal atom reversibly transforms between its oxidized and reduced state.

To date, the scientific community has a wide range of various variations of the working electrode based on metal oxides. The authors of [9] managed to achieve a detection limit of 2 nM, a wide linear range from 5 nM to 8.6 mM, and a sensitivity of $2058.5 \mu\text{A} \cdot (\text{mM} \cdot \text{cm}^2)^{-1}$ using an electrode based on CuO nanoparticles. An electrode based on a hybrid material obtained from tin(IV) oxide grown *in situ* electrochemically on double- and multi-walled

carbon nanotubes was studied in [10]. Ponnusamy R. et al. [11] studied the glucose sensitivity of electrodes based on tungsten(VI) oxide doped with Pd depending on the crystal structure of the oxide. Monoclinic WO_3 -Pd showed excellent sensitivity characteristics ($11.4 \mu\text{A} \cdot (\mu\text{M} \cdot \text{cm}^2)^{-1}$) compared to the orthorhombic and mixed phases. Structures based on tungsten oxide were also studied in [12] and [13]. The authors of [12] compared the electrochemical properties of WO_3 and WO_3 doped with Ag and found that the sensitivity of pure tungsten (VI) oxide was $11.1 \mu\text{A} \cdot (\text{mM} \cdot \text{cm}^2)^{-1}$, while porous WO_3 -Ag spheres exhibited a sensitivity of $23.3 \mu\text{A} \cdot (\text{mM} \cdot \text{cm}^2)^{-1}$, during the tests in 0.1 M NaOH solution. The experimental observations were qualitatively confirmed by modeling within the framework of the density functional theory by studying the mechanism of binding and charge transfer of glucose on WO_3 and WO_3 -Ag. The authors of [13] managed to obtain nanostructured WO_x/Au electrodes using the laser ablation method. The interesting analytical characteristics of the sensor described in the article make the laser-fabricated WO_x/Au electrode potentially promising for implantable glucose fuel cells and biomedical analysis to measure glucose concentration in biological fluids (phosphate buffer solution with pH 7.2 was used for research). In [14] the characteristics of a sensor based on nanocomposite films of polypyrrole-chitosan-titanium dioxide, which showed an increase in sensitivity, as well as a linear dependence in the range of 1–14 mM, were studied. Titanium (IV) oxide is also a common material for making electrodes. In [15] the researchers obtained a Ni-TiO₂ nanocomposite electrode, which showed excellent electrocatalytic activity for the electrooxidation of glucose in an alkaline environment, the sensitivity was $844.85 \mu\text{A} \cdot (\text{mM} \cdot \text{cm}^2)^{-1}$ with selectivity for glucose in the presence of interferences such as uric acid, ascorbic acid and dopamine. The study of electrodes based on manganese oxide was carried out in [16]. Electrolytic manganese dioxide was used as a non-enzymatic electrode catalyst in a neutral environment (pH 8.0). The researchers proposed a mechanism for the reaction of glucose oxidation on this oxide based on the comparative behavior of the electrocatalytic decomposition of four different saccharides, as well as a method for reducing the interfering effect of various substances contained in the blood by applying a polyionic complex capable of molecular sieving to the electrode surface. It was found that the electrode exhibits an excellent response to glucose with a wide detection range from 0.7 to 7.5 mM·dm⁻³ [16].

In recent years, the design of composites based on metal oxides and nanostructuring of electrocatalyst materials has become promising [17]. A composite based on manganese (IV) oxide obtained by an electrochemical method was developed and tested in 50 mM NaOH solution in [18]. The Ni/MnO₂ composite sensor had a sensitivity of $1.04 \text{ mA} \cdot (\text{mM} \cdot \text{cm}^2)^{-1}$ and a detection limit of $10^{-7} \text{ mol} \cdot \text{L}^{-1}$ [18]. A three-dimensional nanostructured electrode based on β -MnO₂ grown on a flexible carbon fiber fabric was studied in [19], the obtained results showed a high sensitivity of $1650.6 \mu\text{A} \cdot (\text{mM} \cdot \text{cm}^2)^{-1}$. In [19] a phosphate buffer solution with different pH values (from 6.2 to 8.6) was used. A 3D porous composite electrode based on manganese(IV) oxide and carbon nanotubes (CNT/MnO₂) obtained by potentiostatic deposition was used for nonenzymatic detection of glucose in [20]. The finished sensor could accurately determine the glucose content in 0.5 M NaOH solution in the presence of foreign substances such as ascorbic acid, uric acid and fructose, with high sensitivity up to $3406.4 \mu\text{A} \cdot (\text{mM} \cdot \text{cm}^2)^{-1}$ [20].

CGM systems work according to the *in vivo* principle, i.e. inside a living organism, which implies a neutral environment (pH ~ 7). However, despite the large number of papers presented, the vast majority describe experiments in an alkaline environment, so their results cannot be used for *in vivo* measurements. Thus why the search and development of a working electrode material capable of oxidizing glucose in the absence of an enzyme in a neutral medium is extremely relevant.

2. Materials and Methods

2.1. Materials

The following materials, which are stable in a neutral medium and, as shown in the literature, have catalytic activity in an acidic or alkaline medium, were studied for the ability to enzymatically oxidize glucose: tin(IV) oxide (SnO₂), titanium(IV) oxide (TiO₂), tungsten(VI)oxide (WO₃), obtained at different temperatures, and manganese(IV) oxide (MnO₂).

Oxide materials were obtained in the form of a dispersed layer on a carbon substrate (3.5 mm diameter), made from graphite foil (GF) Graflex (UNICHIMTEK, Russia) and GF-200 (Silur, Russia), purified in a mixture of acetone (99 %) and ethanol (96 %) at a ratio of 1 : 1 for 10 minutes, followed by drying at 200 °C for 30 minutes to remove technological impurities.

2.2. Formation of a dispersed SnO₂ layer on the surface of carbon substrates

A solution containing stannate ions was obtained by dissolving sodium metastannate (Na₂SnO₃, pure, TC 6-09-05-1452-94) in distilled water with the addition of NaOH (analytical grade, Russian Standard 11078–78); it was applied (dropped) on GF-samples by using an insulin syringe (volume 0.3 mL). To obtain tin(IV) oxide particles, the samples with the applied solution were kept in a flow of carbon dioxide, then dried at 110 °C for 30 minutes in an oven SNOL 58/350 (AB UMEGA-GROUP, Lithuania, Russian Standard 31828–2012). Next, they were calcined in an inert atmosphere (Ar) up to 500 °C at a rate of 20 °C·min⁻¹ for 30 min. The final step was rinsing from carbonates in distilled water and drying at 110 °C for 1 hour. The weight of the applied oxide was measured by weighing the samples before and after the application on an analytical balance brand GR-200 (A&D Co., LTD, Japan, Russian Standard 24104–88). The surface structure of a carbon substrate coated with a catalytic tin oxide layer was studied using an optical microscope (Nikon, SMZ25, Japan).

2.3. Formation of a TiO₂ dispersed layer on the surface of carbon substrates

To obtain a solution containing titanate ions, aqueous potassium titanate (K₂TiO₃·4H₂O, special purity grade, TC 6-09-01-514–78) was dissolved in distilled water in the presence of sodium hydroxide. Next, the solution was manually applied using an insulin syringe drop by drop. Samples coated with a solution of potassium titanate were subjected to the same operations that were used to obtain samples with tin(IV) oxide.

2.4. Formation of a dispersed WO₃ layer on the surface of carbon substrates

By adding ammonium paratungstate (NH₄)₁₀W₁₂O₄₁·5H₂O, analytical grade, TC 6-15-02075232–88) to distilled water, a solution containing tungstate ions was obtained. Next, the solution was applied dropwise with a syringe and dried at 110 °C for 30 minutes in an oven. Then, to obtain oxide particles, calcination was carried out in an Ar atmosphere to 500 or 700 °C at a rate of 20 °C·min⁻¹ for 30 minutes.

2.5. Formation of a dispersed layer of MnO₂/AB (manganese dioxide with acetylene black) on the surface of carbon substrates

Manganese dioxide was synthesized by the reduction of potassium permanganate (KMnO₄, analytical grade, Russian Standard 20490–75) with an excess of ethanol (96 %) in a neutral medium (distilled water). The MnO₂/AB composite was obtained by grinding manganese(IV) oxide with acetylene black (Acetylene black (AB), 99.9+ %, Alfa Aesar, 75 m²·g⁻¹) in an agate mortar in a ratio of 1 : 1 by weight. Further, to obtain dispersion, 5.4 mL of a mixture of isopropyl alcohol and deionized water in a ratio of 1 : 4 was added to the resulting mixture with a mass of 10.8 mg, followed by treatment in an ultrasonic bath (Skymen JP-040, China) for 3 min. The application was carried out using a 5–50 µL pipettor (Accumax, India) in portions of 10 or 50 µL.

For the resulting manganese(IV) oxide, the specific surface area was calculated by the method of low-temperature nitrogen sorption on a Quantachrome NovaTouch setup (Quantachrome Instruments, USA), which was 179 m²·g⁻¹. To determine the phase composition and structure of the crystal lattice of the prepared oxide, the XRD analysis was carried out.

A phosphate buffer solution (PBS) consisting of 10 mM Na₂HPO₄, 2 mM KH₂PO₄, 2.7 mM KCl, and 137 mM NaCl, and deionized water (16 MΩ·cm) was prepared as a working electrolyte (backing solution). The pH value of the buffer was measured and adjusted by adding a few drops of alkali to a value of 7.40 on a pH meter (pH–150 MI, Russia).

The analyzed solution (10 mM glucose solution in PBS) was prepared by dissolving a sample of glucose in the background solution.

Electrochemical measurements were carried out in a three-electrode cell using a Vertex.1A potentiostat (Ivium Technologies B.V., the Netherlands) at room temperature. The working electrode was a smooth glassy carbon electrode (GC, *d* = 4 mm), the side surface of which was insulated with polyetheretherketone (PEEK), with a carbon substrate glued with an ionomer and coated with a catalytic layer. A platinum wire served as the counter electrode, and a saturated calomel electrode (SCE; Hg₂Cl₂/Hg/sat. KCl) served as the reference electrode. The studies included cyclic voltammetry and chronoamperometry.

3. Results and Discussion

Figure 1 shows a micrograph of a carbon substrate with a catalytic tin oxide layer applied.

The X-ray diffraction analysis showed that the diffraction pattern of the synthesized sample according to the inorganic crystal structure databases (ICSD) mainly corresponds to manganese(IV) oxide and manganese(IV) hydroxide. The resulting diffraction pattern is shown in Fig. 2. Based on the obtained diffraction pattern the approximate sizes of crystallites of the obtained substance were estimated using the Selyakov–Scherrer formula (1):

$$\beta = \frac{K\lambda}{d \cos \theta}, \quad (1)$$

where β is the intrinsic broadening ($\beta = \frac{B + \sqrt{B}}{2}$,

B is the observed broadening), K is the particle shape factor (~ 0.9), λ is the X-ray wavelength ($\lambda = 1.5418 \text{ \AA}$), d is the average crystallite size. When performing calculations, it was assumed that the main contribution to the peak broadening is made by the sizes of crystallites, while the contributions of other factors (crystal lattice defects, instrumental broadening, etc.) can be neglected. According to the above formula, the average crystallite size was $\sim 15 \text{ \AA}$. In this case, the calculation according to the porosimetry data using formula (2) showed the average particle size $d \sim 66 \text{ \AA}$:

$$d = \frac{6}{\rho S_{sp}}, \quad (2)$$

where S_{sp} is the specific surface area ($179 \text{ m}^2\text{g}^{-1}$), ρ is the density ($5.02 \text{ g}\cdot\text{cm}^{-3}$).

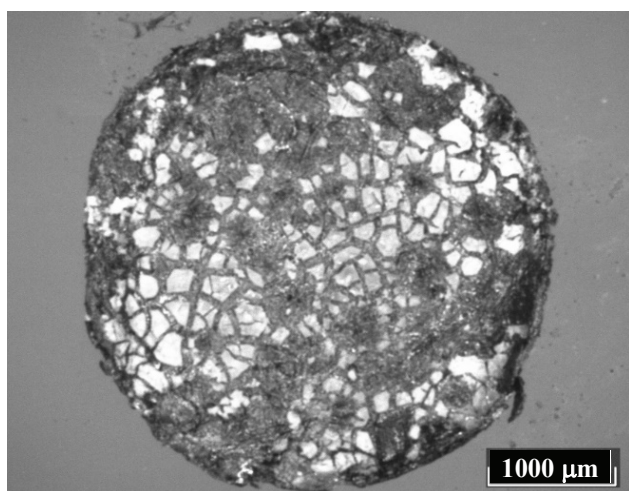


Fig. 1. Microphotograph of a carbon substrate with a deposited catalytic layer of tin(IV) oxide

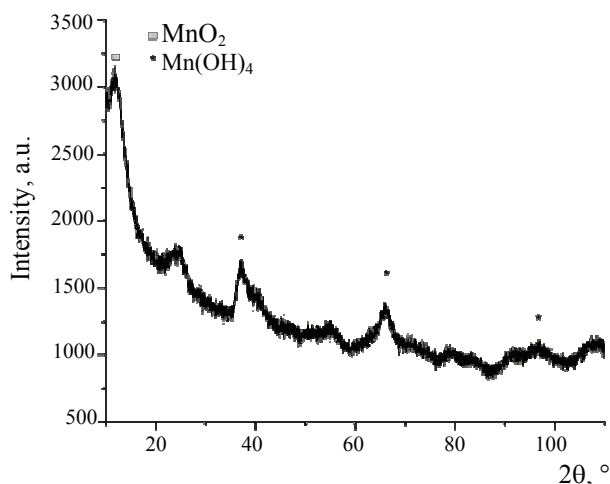


Fig. 2. Diffractogram of the synthesized MnO_2

Thus, the X-ray diffraction analysis showed that the resulting precipitate is a mixture of manganese oxide and hydroxide. A comparison of the XRD and porosimetry data showed that the coherent scattering region is much smaller (by a factor of ~ 5) than the particle size calculated from the specific surface area. Consequently, the particles of the obtained substance consist of a crystalline core surrounded by an X-ray amorphous shell.

First, a study was made of the possible contribution to the electrooxidation of glucose by the substrate materials, GC and acetylene black, which is part of a mixture with manganese oxide. Figure 3 shows the corresponding cyclic voltammograms (CVs) recorded in the background solution and 10 mM glucose solution. The range of potentials applied to these electrodes (preceding the evolution of chlorine/oxygen from the electrolyte) was also used in the future when testing oxide materials.

According to the CVs shown in Fig. 3, it can be seen that during the anodic sweep in glucose solution, the tested materials do not show an increase in current relative to the background solution, which indicates that these materials are not active in glucose oxidation. However, at elevated potentials of $+0.7 \text{ V} \dots +0.8 \text{ V}$, a small anodic current is observed, which is associated with carbon oxidation.

Figure 4 shows the CVs of tin, titanium, and tungsten oxides obtained at different temperatures. The tests were carried out by recording CVs first in a background solution (PBS) and then in a 10 mM glucose solution in PBS.

As can be seen from the given CVs, none of the electrodes based on tin, titanium, or tungsten oxides exhibits noticeable electrocatalytic activity in the anodic oxidation of glucose.

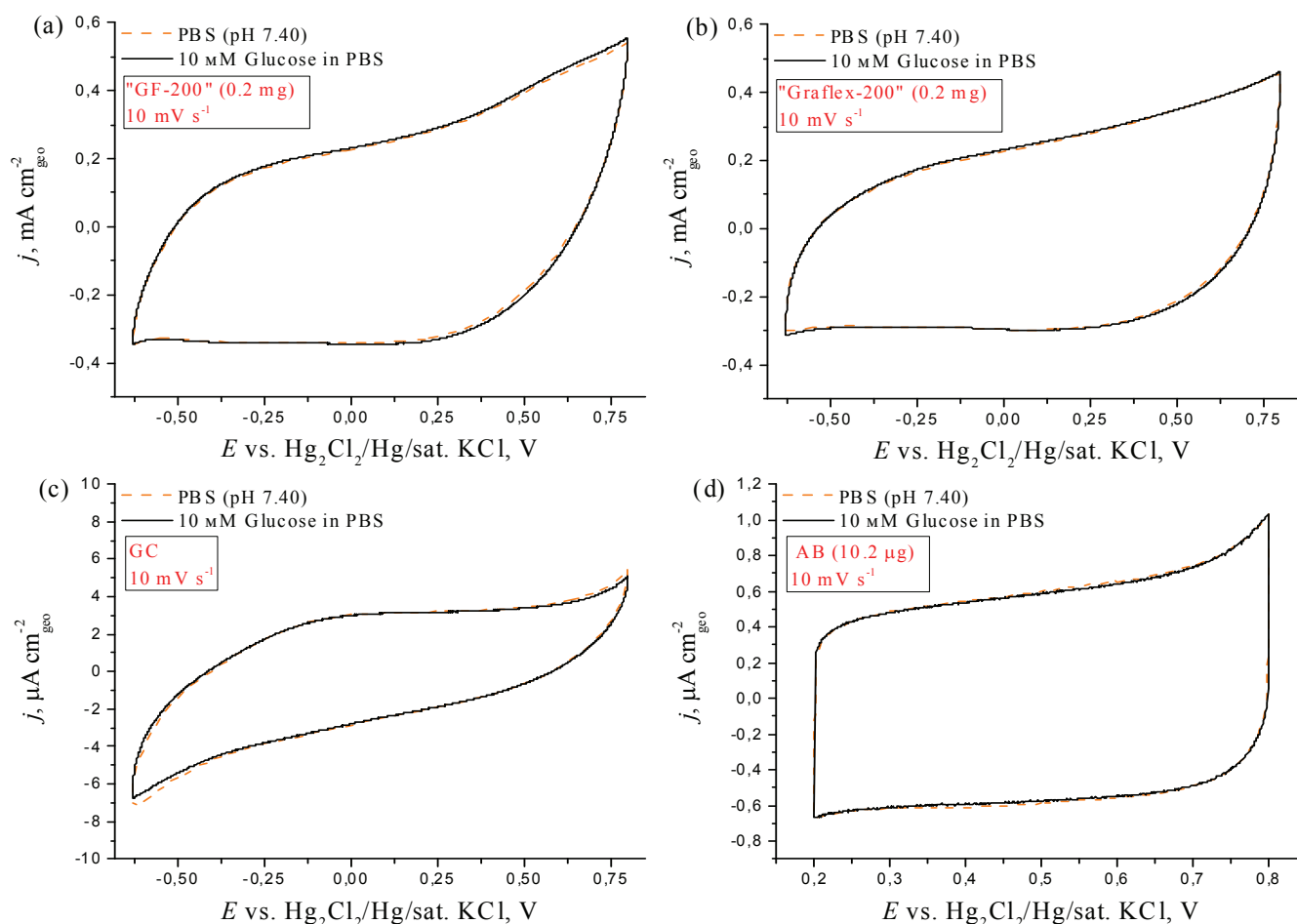


Fig. 3. CVs of (a) graphite foil “GF-200”, (b) graphite foil “Graflex”, (c) glassy carbon (GC) electrode and (d) acetylene black (AB) deposited on GC in the background solution (phosphate buffer solution (PBS)) and 10 mM glucose solution in PBS

Among the tested materials, an electrode based on manganese oxide mixed with acetylene black showed a noticeable rate of glucose oxidation. The obtained cyclic voltammograms and chronoamperograms are shown in Fig. 5.

On the CVs of an electrode based on manganese oxide (Fig. 5a) mixed with acetylene black, a region (+0.5 V...+0.8 V) of glucose oxidation is clearly visible. The obtained chronoamperograms (Fig. 5b) at various potentials (+0.2 V...+0.8 V, with a step of 0.05 V) also confirm the presence of a glucose oxidation current.

The current of glucose oxidation at a potential of +0.8 V vs. SCE was $0.5 \text{ A} \cdot \text{g}^{-1}$ oxide. For comparison, in article [16] at a potential of +0.85 V vs. AgCl/Ag (corresponding to +0.8 V vs. SCE, if the silver chloride electrode was filled with a saturated solution of KCl) on electrochemically obtained manganese(IV) oxide, the glucose oxidation current was $6.9 \text{ A} \cdot \text{g}^{-1}$

oxide. It should be emphasized that such a comparison is very approximate, since in [16] the filling solution for the reference electrode is not indicated. If it was filled with a dilute rather than saturated KCl solution, its standard potential was higher, and the current obtained in [16] actually corresponded to a higher potential in the SCE scale than +0.8 V, which would explain its higher value. Moreover, the mass of MnO_2 on the electrode in [16] was not determined directly, but was estimated according to the Faraday's law, and actually could be different. In addition, the electrochemical deposition of MnO_2 in [16] was carried out on a platinum substrate, which itself is electroactive in the glucose oxidation reaction and could make an additional contribution to the measured current, which is even more enhanced if a synergistic effect occurs in the presence of MnO_2 . Finally, the phosphate buffer

solution in [16] did not contain potassium or sodium chlorides, the presence of which can also have a negative effect on the rate of electrocatalysis. Taking

into account all these circumstances, we can conclude that the activity of MnO_2 investigated in this paper is comparable with the literature data.

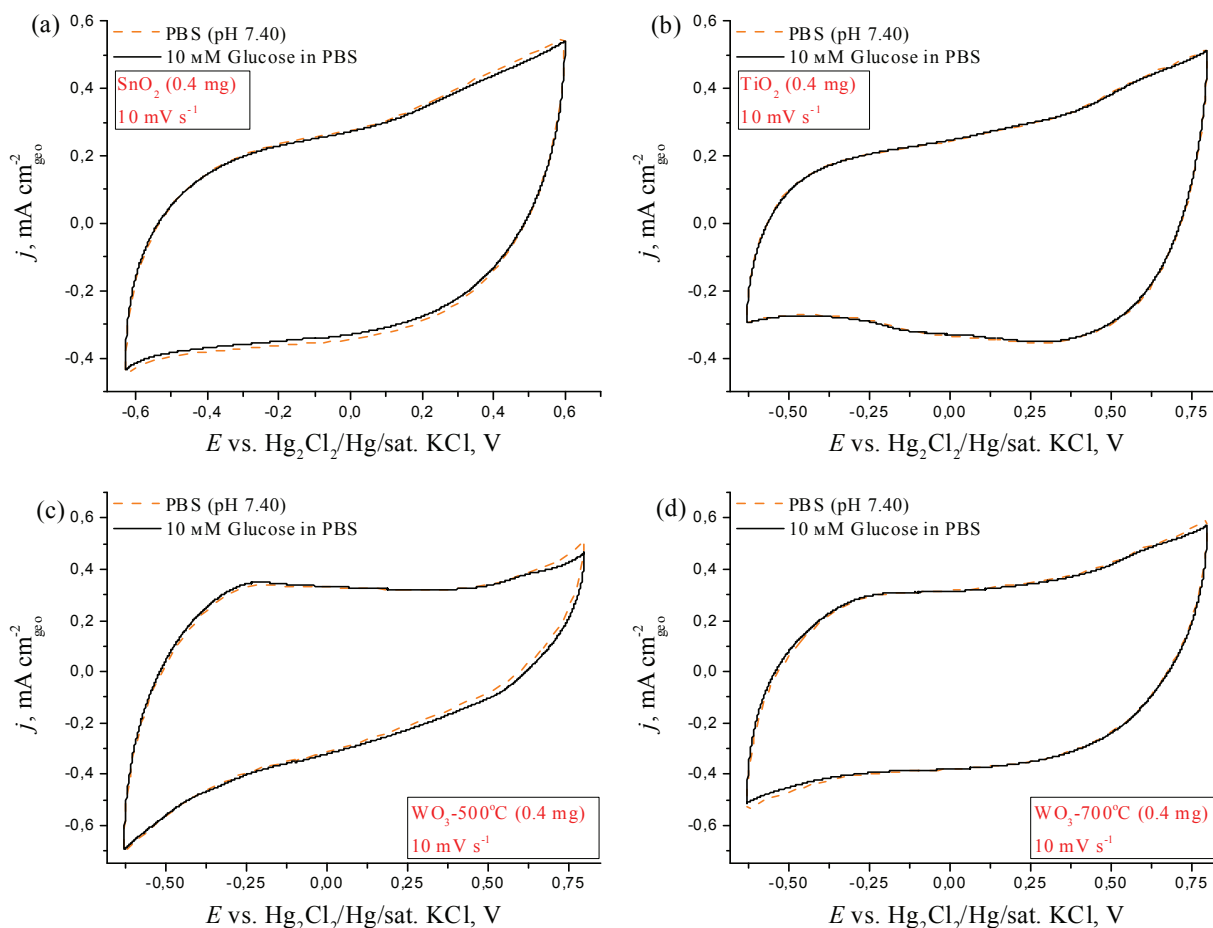


Fig. 4. CVs of (a) SnO_2 ; (b) TiO_2 ; (c) WO_3 synthesized at 500 °C; (d) WO_3 synthesized at 700 °C in the PBS and 10 mM glucose solution in PBS. The materials are deposited on graphite foil discs

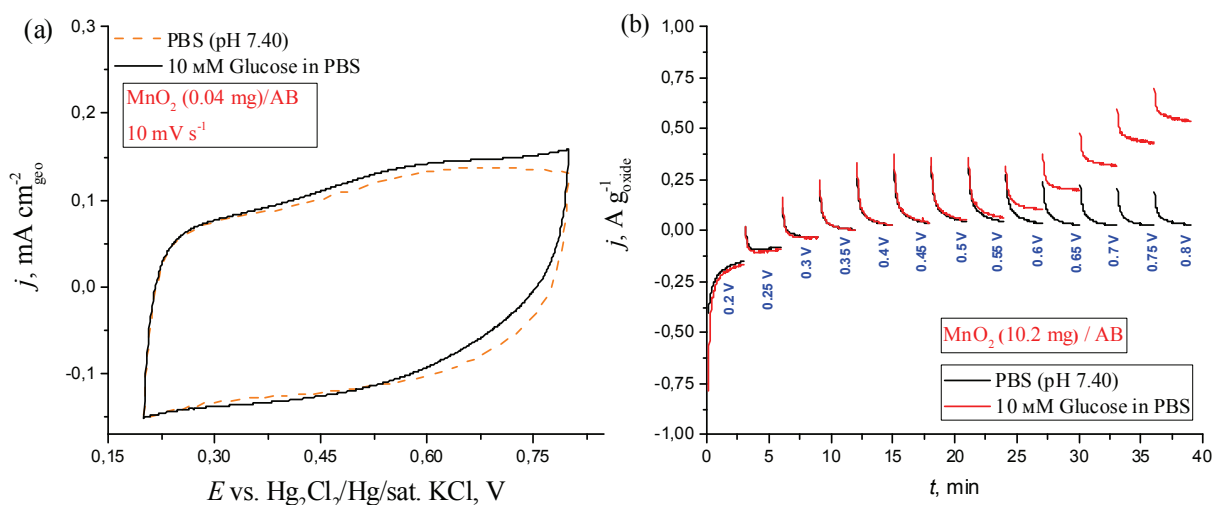


Fig. 5. (a) CVs of MnO_2 mixed with acetylene black in the background solution (PBS) and 10 mM glucose solution in PBS; (b) chronoamperograms of MnO_2 mixed with acetylene black at specified potentials. The materials are deposited on graphite foil discs

A feature of manganese(IV) oxide is its irreversible reduction to lower oxides under the action of high cathodic potentials. That is why, prior to experiments with glucose, in order to establish the cathodic boundary at which this catalyst would not undergo irreversible transformations, CVs were recorded (Fig. 6a) with different cathodic limits. On the other hand, at high anodic potentials, chlorine and/or oxygen can be evolved from the background solution, as well as carbon black oxidation, which can contribute to the observed currents of glucose oxidation. In this regard, an experiment was carried out on a rotating ring-disk electrode. To do this,

the CV (Fig. 6b) of the electrode based on manganese dioxide was recorded up to a potential of +1.3 V, and to reliably determine the boundary of the start of Cl_2 and/or O_2 evolution, a constant cathodic potential (−0.5 V) was applied to the ring electrode.

Based on the test results, the operating potential range (+0.2...+0.8 V) for this catalyst was established, within which the electrode material is not subjected to cathodic degradation, and at which interfering currents of Cl_2 and/or O_2 evolution are excluded.

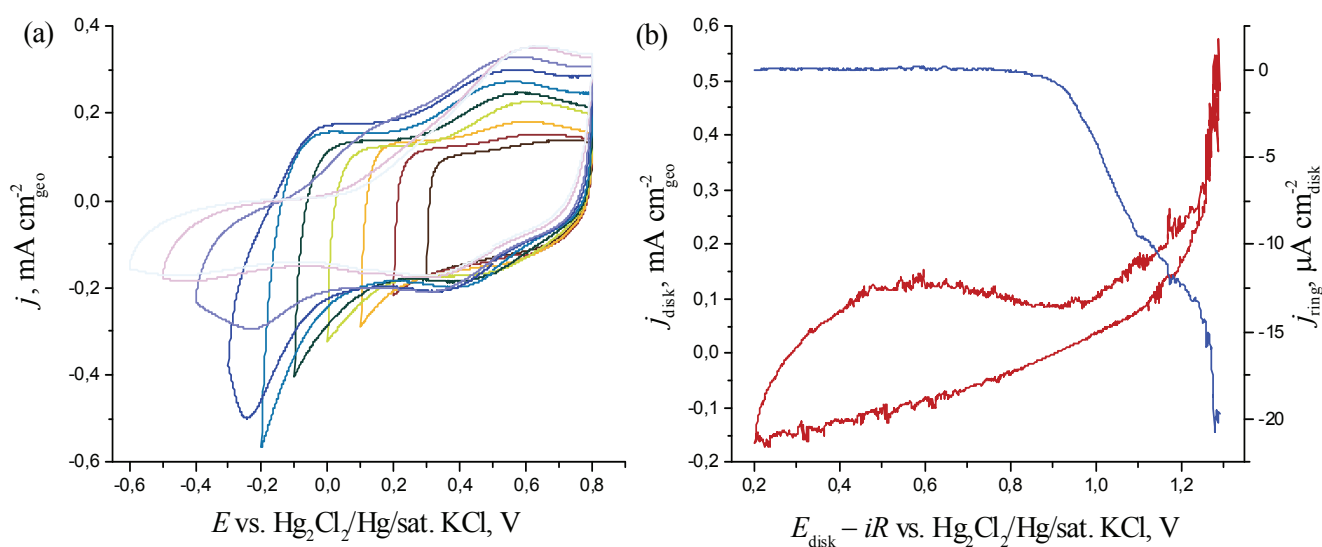


Fig. 6. (a) CVs with various cathodic limits of MnO_2 mixed with acetylene black in the background solution; (b) CV of MnO_2 mixed with acetylene black in the background solution at Cl_2 and/or O_2 evolution potentials, and corresponding ring currents at −0.5 V. The materials are deposited on the CG electrode

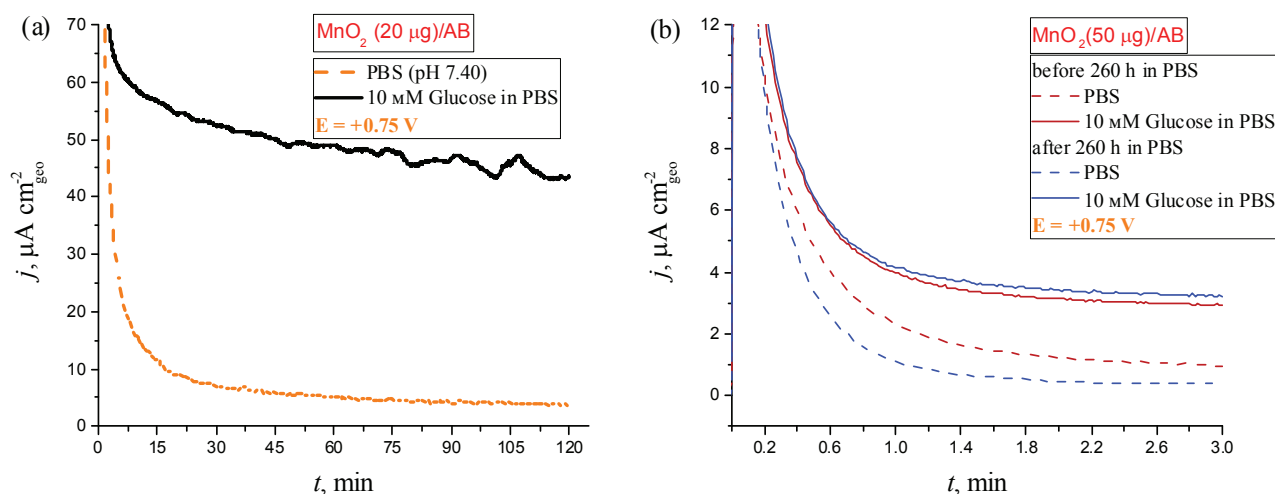


Fig. 7. Chronoamperograms of MnO_2 mixed with acetylene black (a) recorded for 2 hours in a background solution and 10 mM glucose solution, at a potential of +0.75 V and (b) before and after 260 hours of keeping in the background solution. Catalysts are deposited on graphite foil discs

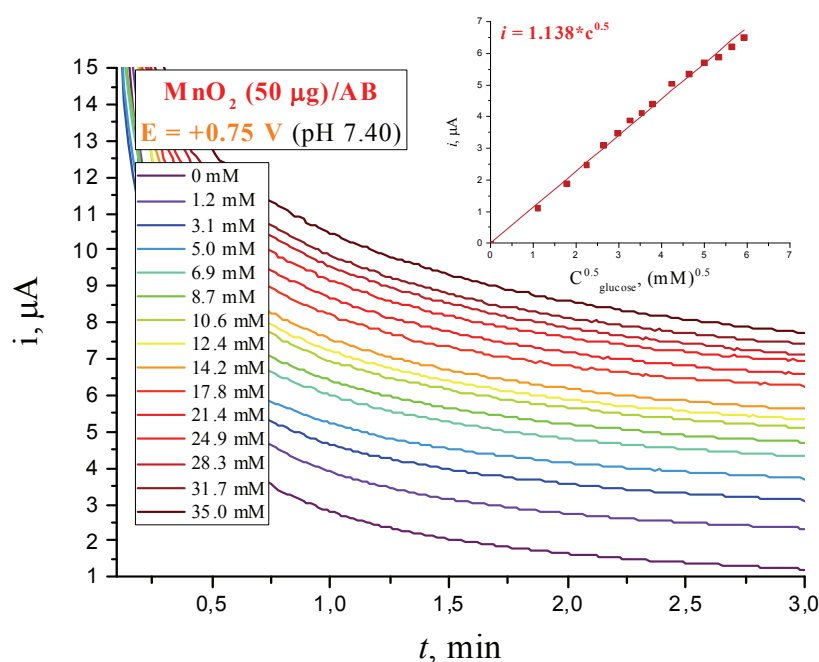


Fig. 8. Chronoamperograms on MnO_2 mixed with acetylene black at a potential of +0.75 V at various glucose concentrations. The inset shows the dependence of glucose oxidation currents (taken at 3 min) on the root of the glucose concentration

Further research is related to the need to test the electrocatalyst for long-term stability. Firstly, with continuous polarization of the electrode at a given potential, and secondly, with a long stay of the electrode in the working fluid (in this case, in PBC), which is due to the intended use of the sensor in continuous glucose monitoring with a minimally invasive implementation technology. Figure 7a shows the chronoamperograms at a constant two-hour polarization of the electrode and Figure 7b shows the chronoamperograms recorded after the electrode was permanently kept in the PBS for 260 hours.

Based on the results of the test, it can be concluded that the manganese dioxide electrocatalyst mixed with acetylene black not only exhibits long-term stability during anodic oxidation of glucose as a result of the continuous application of a potential of +0.75 V, but also does not lose its catalytic properties and does not degrade when it is kept in working solution for at least 260 hours.

To study the concentration dependence of the electrode based on MnO_2 , chronoamperograms were recorded (Fig. 8) for three minutes at various glucose concentrations from 0 to 35 mM.

Based on the obtained chronoamperograms, the dependence of the oxidation current on the root of the glucose concentration was constructed, which showed an almost linear character.

4. Conclusion

Using on the results of testing various oxide materials, it was found that manganese(IV) oxide mixed with acetylene black demonstrates electrocatalytic activity in the glucose oxidation reaction. The operation potentials areas of this catalyst have been established, and it has also been shown that it has long-term stability under continuous polarization at a potential of +0.75 V and does not degrade when it is kept in the working solution. A linear (to a first approximation) dependence of the current of glucose oxidation on the root of the concentration was revealed. Thus, this material can be effectively used in enzyme-free glucose monitoring systems.

5. Funding

This study did not receive external funding.

6. Acknowledgements

The authors are grateful to ELTA Ltd. for all possible assistance and support of this study.

7. Conflict of interests

The authors declare no conflict of interest.

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Received 05 September 2022; Accepted 17 October 2022; Published 27 December 2022



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