New electrodes for biofuel cells

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Abstract. Two new types of electrodes for biofuel elements (BFC) are proposed. One of them is based on a microchannel plate (MCP). Its peculiarity is a special structure with a large number of glass channels being 6-10 μm in diameter with an internal semiconducting surface. The MCP operation is based on the principle of the channel secondary emission multiplication of the electrons. The second type of electrode presented in the work is made of silicon carbide. This type of electrodes has a developed porous structure. The electrode pores account for at least 30% of the total volume. The pore size varies from 10 to 100 μm. Such porosity greatly increases the anode area and volume. This allows us to achieve sorption of a larger number of microorganisms interacting with the anode and transformed by electron donors. The work of the electrodes developed in BFC was tested, their effectiveness was estimated. A comparison is made with electrodes made of carbon cloth, the most widely used material for working with BFC. It is shown that the MCP based electrode is not inferior to the power characteristics of carbon cloth. The generated power when using silicon carbide was slightly lower than the other two electrodes. However, the stability of silicon carbide to aggressive media (alkalis, acids, strong oxidants, etc.), as well as to mechanical damages gives additional advantages to such electrodes compared to the materials that are commonly used in BFC. The noted features are extremely important for the BFC to work in harsh conditions of treatment facilities and to utilize wastewater components.

1. Introduction

Electrodes are an important element of BFC. They cause the possibility of generating electricity BFC. From the ability of the electrode to interact with microorganisms and substrate, accumulate electricity and transmit it to the external circuit depends on the power characteristics of the BFC. When using BFC in treatment plants, an extremely important characteristic of electrodes is their resistance to aggressive sewage conditions. This determines the duration of the operation of the BFC.

Carbon-based materials, in particular carbon cloth [1,2], carbon paper [3,4], etc. [5,6], are most widely used as electrodes for BFC. Unfortunately, they are not suitable for Work in the conditions of treatment plants. The reason for this is, on the one hand, a strong flow of effluent, which causes a significant mechanical effect on the functioning electrode. On the other hand, the multicomponent chemical composition of wastewater is a fairly aggressive environment. In this connection, the
purpose of the message was to describe the materials on the development of new types of electrodes for BFC.

2. Materials and methods of research
Estimation of the efficiency of the electrodes being developed was carried out in BFC. Its design features are described in detail in the "New designs of biofuel cells and testing of their work" (Stom D I, et all.). The commercial complex microbiological preparations "Doctor Robic 109K" ("VIPEKO", Russia) and "Vostok EM-1" ("Primorskiy EM-Center” Co.Ltd Russia) were used as bioagents. The measurement of generated electrical parameters was also carried out in accordance with the procedure described in "New designs of biofuel cells and testing of their work" (Stom D I, et all.). To compare the efficiency of different electrodes, the value of the obtained power per unit area of the anode was recalculated. All the experiments were carried out in at least 5 independent experiments with 3 parallel measurements in each. Statistical processing of the experimental data was carried out using the Excel software package. The tables show the average values for the sample and their standard deviations. The findings are made with the probability of an error-free forecast $P \geq 0.95$.

3. Results and discussion
The work used carbon fabric brand "Ural" (JSC "SvetlogorskKhimvolokno", Republic of Belarus). To produce electrodes from carbon fabric, strips of 12 cm in length and 3 cm in width were cut. For the correctness of the calculation of power characteristics and the comparison of the results, the strips of fabric resulted in a single area and mass. The edges of the fabric were pasted with hot melt to reduce the intensity of the fiber shedding. An electrically conductive copper wire was attached to one end of the carbon cloth. He exited through the cap with a thread. It made it possible to hermetically fix the obtained electrode in the BFC. To reduce the risk of acidification of the anolyte and catholyte with copper, the copper wire was insulated from the bottom of the cover. For this, a layer of graphite was applied to it (graphite conductive graphite varnish GRAPHITE 33, Kontakt Chemie, Belgium). At the outer end of the wire, a terminal was attached to connect the measuring equipment.

In this paper, we developed electrodes for BFC based on porous silicon carbide tubes [7]. They are made for high-temperature power semiconductor devices, field effect transistors, thermistors, etc. The outer diameter of the silicon carbide tubes used was 18, the inner diameter was 6 mm, and the length was 90 mm. The coupling (3) is put on the upper end of the tubes (1). The coupling is made of stainless steel, resistant to corrosion. To ensure a stable contact between the clutch and silicon carbide, the upper end of the tube was covered with an indium layer 1 mm thick (2). To ensure subsequent tightness, the sleeve was surrounded by a silicone gasket (6). If the electrode was used as an anode in the anaerobic part of the microbial fuel cells, a sealed plug (4) is screwed on top of the coupling. When the electrode was used as a cathode, a fitting (5) was attached to the coupling to connect to an air compressor. A wire was attached to the finished electrode (7). It was clamped between the coupling (3) and the plug (4) or the union (5). On the wire, clamps of the type "crocodile" of a multimeter or an automatic measuring system were attached (figure 1).

Carbide-silicon electrodes have a developed porous structure. At the pores of the electrode account for at least 30% of the total volume. The pore size varies from 10 to 100 μm. Porosity greatly increases the area and volume of the anode. This allows us to achieve sorption of a larger number of microorganisms interacting with the anode and transformed by electron donors. The electrode, which plays the role of a cathode, has a branch pipe in the upper part. Through it, air is introduced into the inner part of the electrode. Its feed at a rate of 1.5 l / h was provided by laboratory compressors. The lower part of the cathode is soldered. Therefore, air under pressure is forced to leak through numerous pores that connect with each other. The cathode is literally covered with tiny air bubbles. The cathode space is saturated with air, and, above all, the cathode itself. This makes it possible to intensify the reactions of oxygen reduction and oxidation of reducing equivalents accumulating on the electrode. This prevents the loss of power BFC. The stability of silicon carbide to aggressive media (alkalis, acids, strong oxidants, etc.), as well as to mechanical damages, gives similar electrodes additional
advantages compared to materials that are commonly used in BFC. The noted features are extremely important for the BFC to work in harsh conditions of treatment facilities and to utilize wastewater components.

![Figure 1](image1.png)

**Figure 1.** Electrodes made of silicon carbide. 1 - silicon carbide tube (OJSC Podolskogneupor, RF); 2 - an indium ring, 3 - stainless steel coupling, 4 - stainless steel stopper for anode; 5 - stainless steel fitting for cathode, 6 - silicone rubber coupling for better sealing of coupler coupling in BFC; 7 - an electrically conductive wire for connection of measuring equipment.

Another type of material, proposed by us as an electrode for BFC, was a microchannel plate (MCP) [8]. MCPs are formed by a large number of glass channels 6-10 μm in diameter with an internal semiconducting surface. MCP from the constructive point of view - a glass disk, which consists of a microchannel insert and a monolithic frame. The microchannel insert is a honeycomb structure of a plurality (500-1000) of regularly arranged and sintered hexagonal microchannel honeycombs. Each honeycomb consists of a set of (5000-10000) regularly arranged and sintered together miniature tubular channels, whose diameter can be 2-12 microns, and the density is of the order of (0.5-5) · 10^6 / cm². Material MCP - lead silicate glass. Due to the special annealing in hydrogen, the hydrogen-containing reduction of lead oxide PbO in the lead-silicate glass to the metallic state Pb occurs. The reduction occurs mainly in the surface layer of lead-silicate glass, due to which the walls of the channels acquire the necessary electrical conductivity. The operation of the MCP is based on the principle of channel secondary emission multiplication of electrons. Thanks to a set of unique properties, MCPs are used in a wide variety of fields and fields of science and technology. In our work we used circular PCCs with a diameter of 1 cm and channels of 6-10 μm (OOO VTC "Baspik", Russia). The current collector was connected to the MCP with a conductive adhesive (figure 2).

![Figure 2](image2.png)

**Figure 2.** Electrode from the microchannel plate. 1 - Microchannel plate, d = 10 mm, channel sizes 6-10 μm (WTC Baspik Ltd, Russia), 2 - copper wire, 3 - layer of conductive adhesive at the junction of microchannel plate and wire

Approbation of the developed electrodes was carried out using bioconcentrated commercial complex biopreparations – Dr. Robic 109K and Vostok EM-1. The consortia of microorganisms of these preparations proved to be capable not only of destroying organic matter, but also of generating electricity in BFC [9].

A comparison of the efficiency of the proposed electrodes showed the following. The BFC with silicon carbide electrodes was the most powerful. Thus, when mannose is used as a substrate for microorganisms, the power generated by the microorganisms of Dr. Robic 109K during the 2-day...
experiment was $8.1 \pm 3.2 \, \text{mW/m}^2$. This was 4 times higher than that of BFC with electrodes made of carbon cloth and microchannel plate, which was about $2.4 \, \text{mW/m}^2$ (figure 3A).

In a similar experiment using peptone (0.5 g/l) as substrate, the thickness of BFC with silicon carbide electrodes was $18.1 \pm 1.5 \, \text{mW/m}^2$, with carbon cloth $15.3 \pm 3.2$, with a microchannel plate - $12.4 \pm 1.6 \, \text{mW/m}^2$ (figure 3B).

In the next series of experiments, the voltage dynamics in BFC with silicon carbide and carbon electrode electrodes were investigated. Two types of bioobjects were used: microbiological preparations "Vostok EM-1" and "Doctor Robic 109K". In an experiment using peptone (0.15 g/l) as a substratum, BFC with silicon carbide electrodes showed higher values than carbonaceous tissue. So, when using the drug "Doctor Robic 109K" as the bioagent, the maximum voltage value in BFC with silicon carbide electrodes was $710 \pm 72 \, \text{mV}$, while with carbon cloth – $492 \pm 36 \, \text{mV}$. The potential generated by the Vostok EM-1 preparation was also higher in BFC with silicon carbide electrodes ($326 \pm 34 \, \text{mV}$) than from carbon cloth ($219 \pm 27 \, \text{mV}$) (figure 4A).

A similar dependence was also observed in experiments using ammonium chloride as a substrate. Electrodes made of silicon carbide showed higher values than the carbon cloth as for the maximum voltage value ($678 \pm 72 \, \text{mV}$ vs. $470 \pm 36 \, \text{mV}$ - in BFC with the drug "Doctor Robic 109K" and $269 \pm 34 \, \text{mV}$ vs. $210 \pm 27 \, \text{mV}$ - by the preparation "Vostok EM-1"), and by the general dynamics during 24 hours of the experiment (figure 4B).

**Figure 3.** The maximum power generated by BFC with different types of electrodes (medium - model wastewater, bioagent - drug "Doctor Robic 109K", time of experiment - 48 hours). A – substrate – mannose 0.5 g/l, B – substrate – peptone 0.5 g/l.

**Figure 4.** Dynamics of voltage in BFC using anodes from silicon carbide (cathode - silicon carbide) and carbon fabric (cathode - carbon paper), bioagents – drugs "Doctor Robic 109K" and "Vostok EM-1". A - substrate peptone 0.15 g/l, B - substrate NH₄Cl 0.15 g/l.
4. Conclusion

Two new types of electrodes for BFC are proposed. One of them is based on microchannel plates (MCP). They are a formation with a large number of glass channels 6-10 μm in diameter with an internal semiconducting surface. The uniqueness of the MCP is that a huge number (several million) of regularly placed and practically identical microchannel amplifiers are combined into a single compact design in the form of a plate. The second type of electrode, presented in the work, is made of silicon carbide. This type of electrodes has a developed porous structure. At the pores of the electrode account for at least 30% of the total volume. The pore size varies from 10 to 100 μm. Porosity greatly increases the area and volume of the anode. This allows us to achieve sorption of a larger number of microorganisms interacting with the anode and transformed by electron donors.

A comparison of the efficiency of BFC with the developed electrodes and BFC with carbon cloth showed that the electrodes based on MCP are not inferior in terms of the power characteristics of the carbon cloth. And the power generated by BFC using silicon carbide was slightly higher than when using two other types of electrodes. The stability of silicon carbide to aggressive media (alkalis, acids, strong oxidants, etc.), as well as to mechanical damages, gives similar electrodes additional advantages compared to materials that are commonly used in BFC. The noted features are extremely important for the BFC to work in harsh conditions of treatment facilities and to utilize wastewater components.

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