

Synthesis of Catalytic Filamentous Carbon on a Nickel/Graphite Catalyst and a Study of the Resulting Carbon–Carbon Composite Materials in Microbial Fuel Cells

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Abstract—The carbon–carbon composite materials obtained via the synthesis of catalytic filamentous carbon (CFC) on a Ni/graphite supported catalyst in the process of the pyrolysis of C₃–C₄ alkanes in the presence of hydrogen were systematically studied. The effects of the following conditions on the catalytic activity expressed as the yield of carbon (g CFC)/(g Ni) and on the character of CFC synthesis on graphite rods were studied: procedures for supporting Ni(II) compounds (impregnation and homogeneous precipitation), the concentrations of impregnating compounds (nickel nitrate, urea, and ethyl alcohol) in solution, graphite treatment (oxidation) conditions before supporting Ni(II) compounds, and the pyrolysis temperature of C₃–C₄ alkanes in the range of 400–600°C. Optimum conditions for preparing CFC/graphite composite materials, which are promising for use as electrodes in microbial fuel cells (MFCs), were chosen. The electrochemical characteristics of an MFC designed with the use of a CFC/graphite electrode (anode) and *Gluconobacter oxydans* glyceral-oxidizing bacteria were studied. The morphology of the surfaces of graphite, synthesized CFC, and also bacterial cells adhered to the anode was studied by scanning electron microscopy.

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INTRODUCTION

Scientific research for preparing synthetic porous carbon materials, including composite carbon–carbon supports with a phase of catalytic filamentous carbon (CFC), makes it possible to substantially extend the range of practically significant carriers and adsorbents [1, 2]. Supported catalysts prepared on the basis of iron subgroup metals (Ni, Co, Fe, and their alloys) for the pyrolysis of different hydrocarbons are used for the synthesis of carbon with a pronounced filamentous nanostructure (nanofibers and nanotubes) [3–5]. The following materials prepared on supported Ni catalysts can serve as the examples of new porous composite carbon materials: CFC/graphite felt (plates and rings of various diameters were made of this material for the use in catalytic reactors [6]) and CFC/Sibunit, whose granules have a shell structure (a microglobular pyrolytic carbon phase and CFC are located inside and outside, respectively) [7, 8].

Earlier, we studied the processes of the synthesis of CFC on Ni and Co catalysts supported on the surface of oxide carriers (Al₂O₃, SiO₂, and aluminosilicates) with different textural characteristics and geometric

shapes (honeycomb monoliths, foam materials, and granules) [9–12]. As a result of these studies, composite carbon–mineral carriers were obtained, for example, CFC/ceramics, which combine the adsorption properties of porous carbon with the mechanical strength of ceramic materials; this is promising for practical applications, for example, in biocatalysis and biotechnology [9–11, 13].

Undoubtedly, studies on the construction of microbial fuel cells (MFCs), in which the energy of the redox metabolism of various microorganisms is converted into emf, are foremost and promising in the field of alternative energetics. Communications under the titles “Bacteria make electricity” and “Bacteria are forced to convert waste into electricity” appear on various websites. Yuan et al. [14] described an MFC on the basis of *Proteus vulgaris* bacteria immobilized by mixing microbial biomass, carbon nanoparticles, and an emulsion of Teflon followed by supporting the resulting paste on the anode. Power in this cell was as high as 705 mW/m², which is a maximum of currently available published values. Aelterman et al. [15] proposed using a consortium of gram-negative microorganisms and connecting in parallel six MFCs in order

to increase the emf. The total energy yield of these cells was 228–258 W m⁻³ h⁻¹; in this case, the voltage and current were as high as 2.02 V and 255 mA, respectively. In the course of operation of this block (more than 200 days), the species composition of a microbial association dramatically changed. Initially, bacteria from *Geobacter* and *Shewanella* genera were present, whereas *Brevibacillus agri* bacteria predominated in the colony at the end of the experiment; these latter were found most productive in the bioconversion of organic waste into electricity. At the end of testing the MFC block, its parameters were improved by a factor of ~3, as compared with the initial values.

Previously [16, 17], it was shown that, in principle, bacteria from the *Gluconobacter* genus can be used as a biocatalyst for the generation of a potential by an anodic half-cell.

The aims of this work were the following: (1) to study the effects of the procedure and conditions of the preparation of supported Ni/graphite catalysts on their activity in the pyrolysis of C₃–C₄ alkanes and on the synthesis of a uniform and tightly bound CFC layer on the surface of graphite rods, (2) to optimize conditions for the preparation of a CFC/graphite composite material and to make electrodes for MFCs based on this material, and (3) to examine the electrochemical characteristics of MFCs depending on procedures used for the immobilization of *Gluconobacter oxydans* glycerol-oxidizing bacteria on a CFC/graphite anode.

EXPERIMENTAL

Spectral graphite as cylindrical rods with a diameter of 6 mm (ZAO Karbotek, Russia) was used for the preparation of a supported Ni catalyst. The geometric surface area of graphite rods (S) was 0.6 cm²/g, and the specific surface area (S_{sp}) of the initial graphite was 1 m²/g, as measured on a SORBI-M instrument (ZAO META, Russia) using the thermal desorption of argon. According to mercury porosimetry data, which were obtained on an AUTO-PORE 9200 instrument (Micromeritics, United States), S_{sp} = 0.4 m²/g, the average pore diameter was 3.1 μ m, and the total pore volume was 0.3 cm³/g. For the preparation of the supported Ni catalyst, graphite rods preoxidized either in boiling 20% HNO₃ (1 h) or with atmospheric oxygen at 400°C (4 h) were also used.

The compounds of bivalent nickel were supported onto the surface of graphite by two methods. Impregnation consisted in the repeated (3 to 40 times) spraying of rods with a 0.1 M solution of nickel nitrate in 50% aqueous ethanol. The homogeneous precipitation of the hydroxides of Ni(II) was performed from aqueous and water–ethanol (10–20% EtOH) solutions of nickel nitrate (0.01–0.2 M) in the presence of an excess of urea (0.1 and 1 M) at 85°C for 3 h. Ethanol was added to the solution for the more complete wetting of the surface of hydrophobic graphite with an aqueous solution of nickel nitrate. In homogeneous

precipitation in aqueous organic media, the following optimum order of mixing the reagents was chosen: initially, ethanol was added to distilled water; then, urea, and, finally, nickel nitrate were added. The resulting solution was transparent, and the finely dispersed precipitate of the hydroxides of nickel was formed upon heating to 85°C. If urea was added to the prepared aqueous ethanol solution of nickel nitrate, the solution immediately became turbid; in this case, the conditions of homogeneous precipitation, which were described in detail elsewhere [8], obviously, changed. Graphite rods with the supported hydroxides of Ni(II) were washed with distilled water and dried under an IR lamp for 5 h. The resulting catalyst is referred to as Ni/graphite.

The concentration of supported Ni (wt %) was determined by atomic absorption spectrometry on an ASSIN instrument with a flame-ionization detector. Graphite cylinders with supported Ni(II) compounds were thoroughly ground before the analysis.

Filamentous carbon was synthesized on the Ni/graphite catalysts by performing the catalytic pyrolysis of C₃–C₄ alkanes in the presence of hydrogen at 400–600°C (in the majority of cases, at 500°C) for 1 h in a reactor with a fixed bed of the catalyst, as described previously [8–12].

The amount of synthesized carbon was determined gravimetrically and calculated (wt % C) from an increase in the weight of the Ni/graphite catalysts after the completion of pyrolysis. In the calculation of C, the hygroscopicity of the initial graphite, which was estimated from weight losses after drying at 200°C for 4 h (to constant weight), was taken into account. We found that the hygroscopicity of the initial graphite was no higher than 0.06%. The weight loss of the Ni/graphite catalyst (0.3–0.5%) in the presence of H₂ under the conditions of pyrolysis (without C₃–C₄ alkanes) was also considered in the calculation. The resulting carbon–carbon composite materials (referred to as CFC/graphite) were tested as electrodes in MFCs, as described below.

The surface morphology of graphite and carbon deposits was studied using JSM 6460 LV (JEOL, Japan) and LEO 1430 (LEO, Germany) scanning electron microscopes (SEM). A mark in the SEM images corresponded to distance in micrometers.

For designing an MFC, we used *G. oxydans* subsp. *industrius* VKM B-1280 bacteria from the All-Russian Collection of Microorganisms (Skryabin Institute of the Biochemistry and Physiology of Microorganisms, Russian Academy of Sciences, Pushchino). The bacteria were cultivated at 28°C for 20 h on a nutrient medium of the following composition: D-sorbitol, 100 g/l, and yeast extract, 10 g/l. The microbial biomass was harvested by centrifugation at 12000 rpm for 3 min and then washed three times with a 10 mM sodium phosphate buffer solution (pH 6.6).

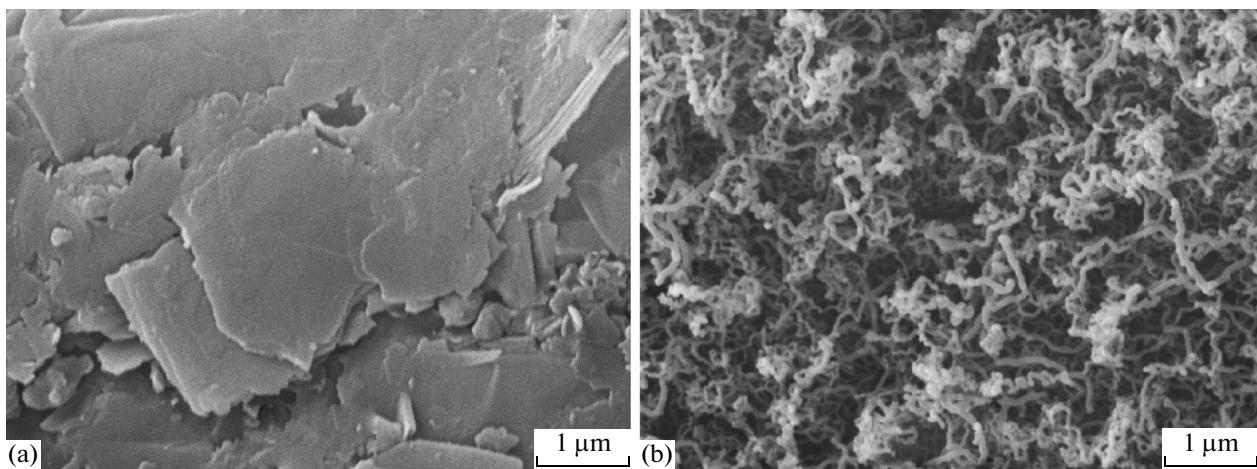


Fig. 1. Electron-microscopic images of the surfaces of (a) initial graphite and (b) CFC synthesized on the Ni/graphite catalyst prepared by the homogeneous precipitation method (0.06% Ni, 3.5% C).

The MFC was an open two-electrode cell, which consisted of ~1-ml cylindrical chambers. The CFC/graphite rods served as electrodes. The electrodes were immersed in anolyte and catholyte solutions at a depth of 6 mm; in this case, the working geometric surface area of an electrode was 1.4 cm². The anodic and cathodic chambers were connected through an opening covered with an MF-4SK protonated cation-exchange membrane (Plastpolimer, Russia). After operations, the chambers were treated with a 10% solution of H₂O₂ for 1 h. The external circuit was closed through a potentiostatic control unit. All of the measurements were performed using an IPCMicro combined potentiostat–galvanostat (Kronas, Russia). The MFC parameters (emf and potential

drop) were determined in an open-circuit line at 25°C. The cell potential E was scanned at an average rate of ~2 mV/min. A peak current was observed after every change in the specified potential; then, this peak current decreased to the steady-state value I at the given voltage U . When the stabilization of current was not observed, the last value of I was measured after 300–500 s, and it was taken as a characteristic of the discharging current of the MFC at the given voltage $U-E$. The fuel-cell power P was calculated from the equation $P = U \times I$.

A CFC/graphite rod was used as a cathode. The catholyte composition (in the cathode chamber) was the following: 30 mM potassium hexacyanidoferate(III) and 30 mM sodium phosphate buffer (pH 6.0). Under these conditions, the cathode potential was +350 mV against a silver–silver chloride reference electrode.

The following two anode types were used to determine the characteristics of MFCs: type 1, a CFC/graphite rod placed in an anolyte containing a cell suspension in a concentration of 10 mg of crude biomass per milliliter and type 2, a CFC/graphite rod with the immobilized cells of *G. oxydans*. Immobilization was performed by the adhesion of bacteria to CFC/graphite. For this purpose, a dense cell suspension, which contained ~10 mg of microbial biomass, was directly applied to the electrode surface and then partially dried in air for 20 min. The prepared anodes were placed in the anodic half-cell with the anolyte of the following composition (mM): 2,6-dichlorophenol indophenol (DCPIP), 0.3; glycerol, 5; and sodium phosphate buffer, 30 (pH 6.0). As noted above, a cell suspension was added to the anolyte for the type 1 anode. DCPIP was used as a mediator of electron transfer from the metabolic pathways of a bacterial cell to the anode; DCPIP was chosen because of the high stability of its reduced form to oxygen. Glycerol was used as a metabolite—electropassive fuel, which participates in

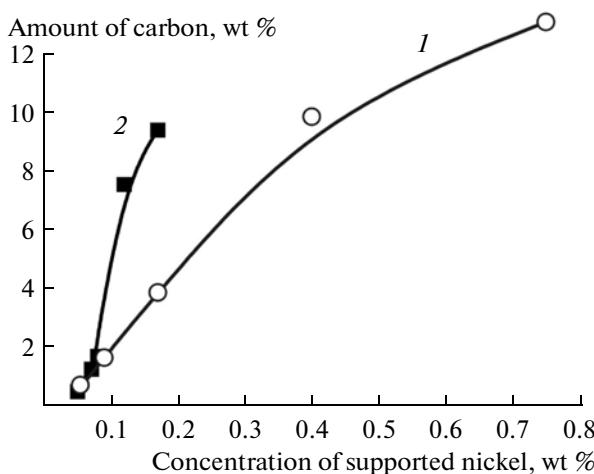


Fig. 2. Dependence of the amount of CFC synthesized on graphite on the concentration of nickel supported by the (1) impregnation and (2) homogeneous precipitation methods.

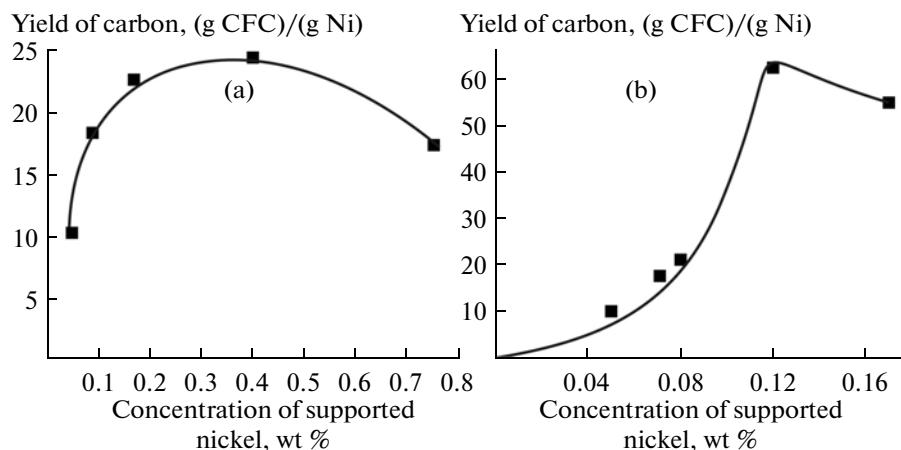


Fig. 3. Dependence of the yield of carbon on the concentration of nickel supported by the (a) impregnation and (b) homogeneous precipitation methods.

the generation of current in the MFC. In the course of measurements, glycerol was added at 20-min regular intervals so that its concentration in the anolyte was no higher than 5 mmol/l; otherwise, high concentrations of glycerol and dihydroxyacetone (the product of glycerol oxidation by alcohol dehydrogenase) exerted an inhibiting effect. The periodicity of the introduction of glycerol into the anolyte was determined additionally based on the consumption of oxygen, whose concentration in the solution was determined with the use of a Clark electrode, by the suspension of *G. oxydans*.

RESULTS AND DISCUSSION

The electron-microscopic study showed that the prepared Ni/graphite catalysts exhibited activity in the processes of C_3 – C_4 alkane pyrolysis, as a result of which carbon nanofibers ~100 nm in thickness and more than 1 μ m in length (Fig. 1b) were synthesized on the smooth surface of graphite (Fig. 1a) analogously to that described previously [8–12].

A comparative analysis of the texture characteristics demonstrated that the specific surface area of the initial graphite ($S_{sp} = 1 \text{ m}^2/\text{g}$) increased to 7–13 m^2/g upon the synthesis of CFC. According to mercury porosimetry data, the average diameter of pores decreased from 3.1 to 1.0 μm . The total pore volume substantially decreased from 0.3 cm^3/g (for the initial graphite) to 0.01 cm^3/g (for CFC/graphite); this fact suggests that the synthesis of carbon nanofibers occurred in the macropores of graphite.

In the preparation of catalysts by the impregnation method, we found that the supporting of an active component and the subsequent synthesis of CFC occurred predominantly inside the cylindrical graphite rods, whereas their surface remained smooth and gray, analogously to that of the initial graphite. If the amount of CFC was greater than 10 wt % C, the rods

lost mechanical strength and easily delaminated along the cylinder axis; in this case, each layer had a velvet-black surface on one side (CFC) and a gray and shining surface as that in graphite on the other. We found that the total amount of synthesized carbon increased as the concentration of supported nickel was increased (Fig. 2, curve 1). The curve that characterizes the dependence of the yield of carbon on the concentration of Ni exhibited a pronounced maximum of 24 (g CFC)/(g Ni) (Fig. 3a). We found that the concentration of Ni in CFC/graphite decreased by a factor of ~2: thus, the concentrations of Ni before and after pyrolysis were 0.17 and 0.09%, respectively; that is, it is likely that a loss of the Ni catalyst occurred as a result of the synthesis of CFC under the test conditions of the pyrolysis of C_3 – C_4 alkanes.

Upon homogeneous precipitation, the active component of catalysts was mainly supported on the external surface of a graphite rod, whereas CFC was almost not formed inside the rods. If the total amount of CFC was greater than 5–7% C; the synthesis of carbon as large bulky agglomerates weakly fixed on the surface was observed. In this case, these carbon agglomerates fell off under a weak mechanical shaking. We found that the concentration of Ni supported on graphite was a linear function of the initial concentration of nickel nitrate in solution. The total amount of carbon dramatically increased with the concentration of supported nickel (Fig. 2, curve 2). As in catalyst preparation by the impregnation method, the curve that reflects the dependence of the yield of carbon on the concentration of Ni exhibited a pronounced maximum of 62 (g CFC)/(g Ni) (Fig. 3b); furthermore, at the initial segment of the curve in the range of 0–0.10 wt % Ni, the yield of carbon increased exponentially.

The main problem in the development of a CFC/graphite composite material was to obtain a uni-

form and tightly bound CFC layer on the surface of graphite rods because it was found that the synthesis of carbon nanofibers on a Ni catalyst supported by the impregnation and homogeneous precipitation methods occurred extremely irregularly, predominantly along the axis of the rod, as narrow regions that occupied no more than 10% of the total geometric surface area. Earlier, we already encountered the problem of the nonuniform synthesis of a CFC layer on the surface of sintered inorganic carriers with a specific surface area of no higher than $1 \text{ m}^2/\text{g}$: corundum, clay-dite, and glass foam. Kovalenko et al. [18] proposed the use of glycerol for impregnation and the rapid drying of the Ni/corundum supported catalyst in a microwave oven. However, this method of drying is unacceptable for graphite because of its conducting properties. The Ni/graphite catalysts were dried with the aid of an IR lamp. When we assume that drying conditions considerably influence the uniformity of the distribution of an active component, various positions of the regions of the intense synthesis of CFC with a velvety black color could be obtained by fixing the position of a rod with respect to IR radiation (vertically, horizontally, or at an angle) in the course of drying; however, no correlation was found. Therefore, the drying conditions of catalysts did not exert a noticeable effect on the uniformity of CFC synthesis on graphite.

It was also shown previously that, under the conditions of the two-stage synthesis of CFC by the pyrolysis of $\text{C}_3\text{--C}_4$ alkanes with the preliminary hydrogen reduction of Ni(II) hydroxides to Ni^0 , in contrast to the single-stage pyrolysis in the presence of H_2 , CFC was synthesized nonuniformly on the surface of the sintered carriers, and it was localized predominantly in the defects (indentations and cracks) of the smooth surface of these carriers [9]. If the pyrolysis of $\text{C}_3\text{--C}_4$ alkanes was performed in two stages, as described above, the yield of carbon decreased by a factor of 3–6, as compared with that in the single-stage pyrolysis [9].

Under the conditions of two-stage pyrolysis, the amount of CFC on the surface of graphite did not exceed 0.1%, whereas CFC was intensely synthesized (9.3% C) on the same catalysts under the conditions of the single-stage pyrolysis of $\text{C}_3\text{--C}_4$ alkanes in the presence of H_2 . It was also shown that an increase in the roughness of smooth rods by putting macroscopic defects (by emery paper or sharp objects) leads to an increase of many times in the amount of CFC. In this case, it is visible to the naked eye that the carbon fibers were synthesized exclusively on the macroscopic defects to reproduce the supported pattern.

Based on the experimental results and published data [9], we can assume that the particles of Ni^0 , which weakly interact with the sintered carrier, become mobile under the conditions of pyrolysis at 500°C . They are capable of migrating over the smooth surface to form larger particles, which are located predominantly in the macroscopic defects and possess smaller catalytic activity. In turn, the migration of small parti-

cles and the formation of larger particles of Ni^0 are the main reasons for the nonuniform formation of CFC on the surfaces of Ni/graphite catalysts prepared by the impregnation and homogeneous of precipitation methods.

The following approaches were proposed to decrease the migration of small Ni^0 particles and to obtain a uniformly distributed CFC layer over the smooth surface of graphite: the oxidation of a graphite surface for the formation of COO^- groups, which can facilitate the stronger interaction of these groups with the particles of Ni(II) hydroxides and Ni^0 ; the decrease of the temperature of pyrolysis, as a result of which the rate of reduction of Ni(II) compounds by hydrogen to Ni^0 decreased and the migration of Ni^0 particles became limited; and the increase in the temperature of pyrolysis, which increased the catalytic activity of Ni^0 and the rate of formation of CFC became higher than the rates of reduction and Ni^0 migration. Initially, we found that the weight of rods decreased on the average by 6 or 0.06% upon the oxidation of graphite with atmospheric oxygen (400°C , 4 h) or after treatment with 20% nitric acid (100°C , 1 h), respectively; that is, the initial support was oxidized under the test conditions. However, this pretreatment of graphite resulted in only an insignificant increase (on the average, by a factor of 1.2) in the amount of synthesized CFC, while the nonuniformity of the carbon layer over the surface of graphite remained. Thus, on the catalysts prepared with the use of graphite rods (initial and oxidized with HNO_3) under the test conditions of homogeneous of precipitation (0.015 M nickel nitrate, 1 M urea, and 10% ethanol), 1.7 and 1.8% CFC, respectively, were synthesized. Thus, the oxidative pretreatment of the surface of graphite does not lead to a substantial change in the activity of the supported Ni/graphite catalysts or in the distribution of the active component and, as result, in the uniformity of the CFC layer on the surface of rods.

As the pyrolysis temperature of $\text{C}_3\text{--C}_4$ alkanes was increased from 400 to 600°C , the amount of CFC synthesized on the catalysts prepared by the homogeneous of precipitation method (0.01 M nickel nitrate, 1 M urea, and 10% ethanol) increased by a factor of 2–4. At 400°C , carbon (0.4% C) was distributed most uniformly to occupy about 10% of the geometric surface area of a rod; this was likely due to a decrease in the mobility of nickel particles. At 500 and 600°C , carbon (0.8 and 1.5% C, respectively) was synthesized extremely nonuniformly to occupy no more than 1–2% of the geometric surface area in the form of narrow zones along the axis of the rod. The electron-microscopic study demonstrated that, at 400°C , carbon deposits did not have a clearly pronounced filamentous structure (Fig. 4a); as the temperature of pyrolysis was increased to 500 and 600°C , the length of a carbon nanofiber substantially increased (Figs. 1b and 4b, respectively). Analyzing electron-microscopic images obtained at different magnifications, we concluded

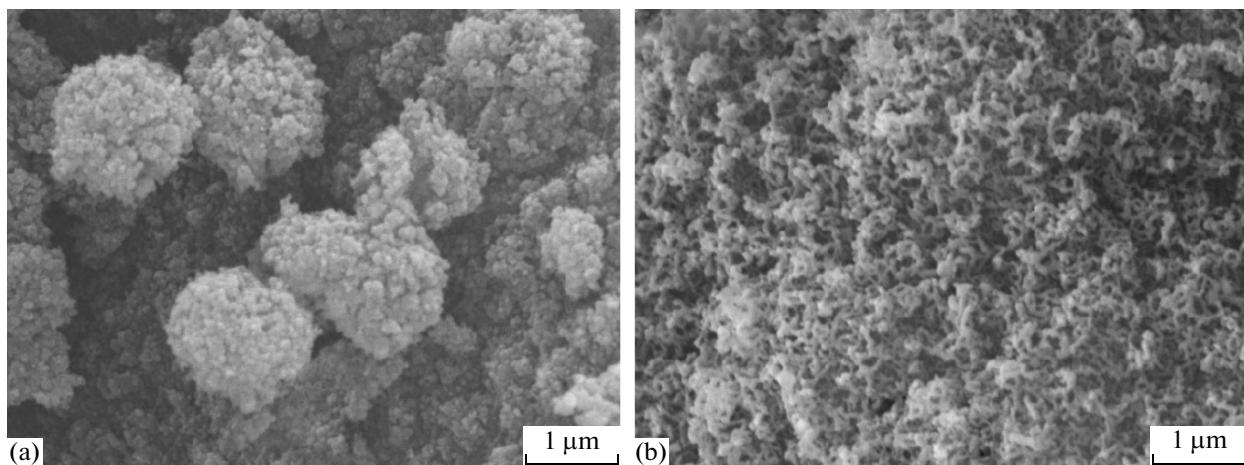


Fig. 4. Electron-microscopic images of the surfaces of C/Ni-graphite catalysts with CFC synthesized at (a) 400 and (b) 600°C.

that nickel particles became larger as the temperature of pyrolysis was increased; this fact also suggests the mobility of nickel at the given temperatures. However, it was obvious that, as before, CFC on the prepared catalysts was nonuniformly distributed regardless of the temperature of pyrolysis. Thus, a variation in the temperature of pyrolysis does not lead to a substantial change in the distribution of the catalytic active component and it has no effect on the uniformity of the CFC layer on the surface of rods.

We thoroughly optimized the composition of solutions for the preparation of Ni/graphite catalysts by the homogeneous precipitation method because the synthesis of CFC on the surface (rather than inside) of a graphite rod is of interest for developing MFC electrodes. In this case, the concentrations of nickel nitrate, urea, and ethanol and also the order of mixing all of the solution components were thoroughly selected. The following optimum composition of solution was chosen: nickel nitrate, 0.0125–0.0175 M; urea, 1 M; and ethanol, 10 vol %. Under the given conditions, the concentration of supported Ni was 0.07–0.08%. Under the conditions of the single-stage pyrolysis of C_3 – C_4 alkanes in the presence of H_2 (500°C, 1 h) on the prepared Ni/graphite catalysts, no more than 2–3% CFC was synthesized (Fig. 2), and the yield of carbon reached a maximum value (Fig. 3b). Under the optimum conditions for the preparation of catalysts and the pyrolysis of C_3 – C_4 alkanes, the synthesis of CFC occurred on the rods of graphite with the formation of a sufficiently tight and uniform surface layer of interlaced carbon nanofibers (Fig. 4b). The CFC/graphite composite materials prepared under the given conditions were used as electrodes for an MFC.

PRACTICAL APPLICATION

Initially, we tested the construction of an MFC proposed in this work with the type 1 anode of CFC/graphite. For this purpose, we estimated a change in the voltage of the broken circuit upon the sequential addition of reaction mixture components of and the connection of a load. We found that the addition of glycerol and DCPIP to the anolyte did not lead to substantial changes in the anode potential, which was measured relative to a cathode immersed in a solution of potassium hexacyanidoferate(III). The addition of a suspension of *G. oxydans* bacterial cells caused a sharp jump of ~100 mV in the potential difference. The connection of a 10-kΩ load into the external electric circuit in parallel with a potentiostat allowed us to detect the useful work of the MFC in the stable operation with a power of more than 2 μW for 1 h. The subsequent studies were conducted with MFCs of the given design.

For the fuel cell of an analogous design, which was described by Willner et al. [19], with the use of an Au anode activated by pyrroloquinoline quinone (PQQ) as a mediator and immersed in the anolyte, which contains NADH as the donor of electrons for PQQ, it was found current in the cell linearly increased as the potential difference between the anode and the cathode was decreased (with a decrease in the load of the external circuit). In this case, the load curve in the U – P or I – P coordinates was a comparatively symmetrical bell-shaped curve.

In the tests of an MFC with the type 1 anode, we found that, at the initial moment, the MFC discharging in the potential scanning regime at voltages smaller than the locking value (~250 mV) was accompanied by a linear increase in the current (Fig. 5a). The addition of glycerol at regular intervals makes it possible to maintain the linear increase in the current up to ~200 mV

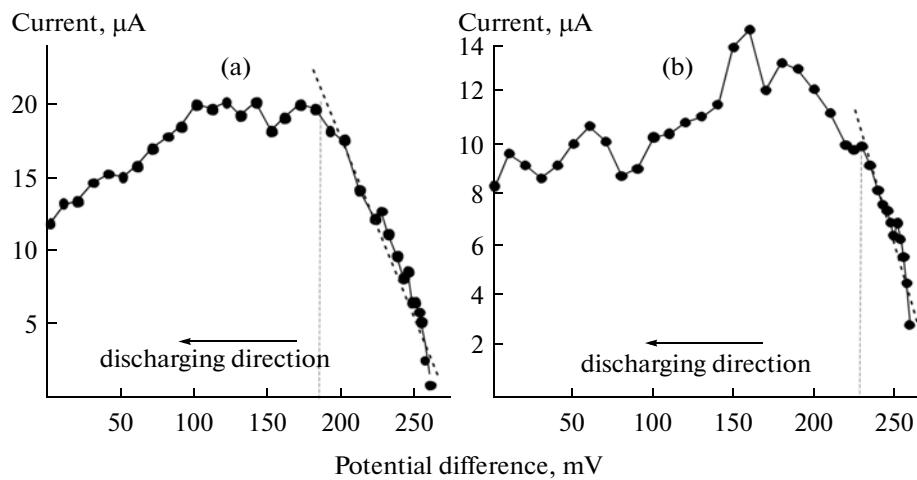


Fig. 5. Current–voltage curves of MFCs with anodes prepared based on the CFC/graphite composite material with the use of *G. oxydans* bacteria: (a) type 1 anode immersed in a cell suspension; (b) type 2 anode with the immobilized cells of *G. oxydans*.

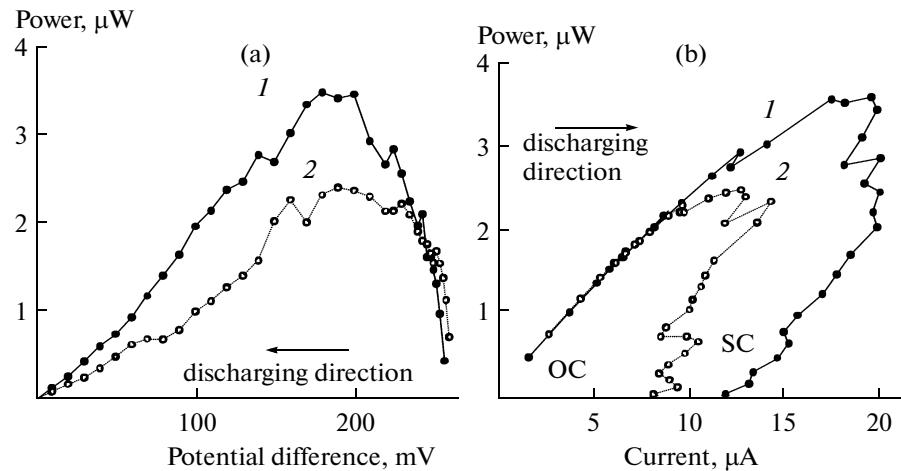


Fig. 6. Load curves for the MFCs with the type (1) and type (2) anodes as functions of (a) voltage and (b) current; OC and SC refer to open-circuit and short-circuit lines, respectively.

analogously to that described by Willner et al. [19] (Fig. 5a, broken line). The current in the test cell did not increase as the potential difference was further decreased (Fig. 5a).

A comparison between MFCs with the type 2 and type 1 anodes showed that the current–voltage curve of the former exhibited a sharper linear increase of current over a narrower range of potentials to ~230 mV (Fig. 5b, broken line). In this case, the maximum current strength was lower by a factor of ~1.5 than that observed with the use of the type 1 anode (Fig. 5). The reasons for the asymmetry of load curves and current losses can be caused by the specific character of *G. oxydans* bacteria and the occurrence of regulator

effects (activation and inhibition by reagents), which are worth of special consideration.

It should be noted that the load curves for the designed MFCs are asymmetric (Fig. 6). The cell power rapidly increased to reach a maximum at a voltage of ~200 mV as the voltage in the cell decreased and the electrical conductivity of the external circuit increased (Fig. 6a, curve 1). The maximum specific power of an MFC with the type 1 anode was ~3.5 W/m³ anolyte (as compared with 43 W/m³ [15]), ~25 mW/m² electrode surface (as compared with 705 mW/m² [14]), or ~0.35 W/kg crude biomass. It is likely that a decrease in the rate of current increase in the course of further potential scanning toward a short circuit (Fig. 6b) reflects the instability of the internal

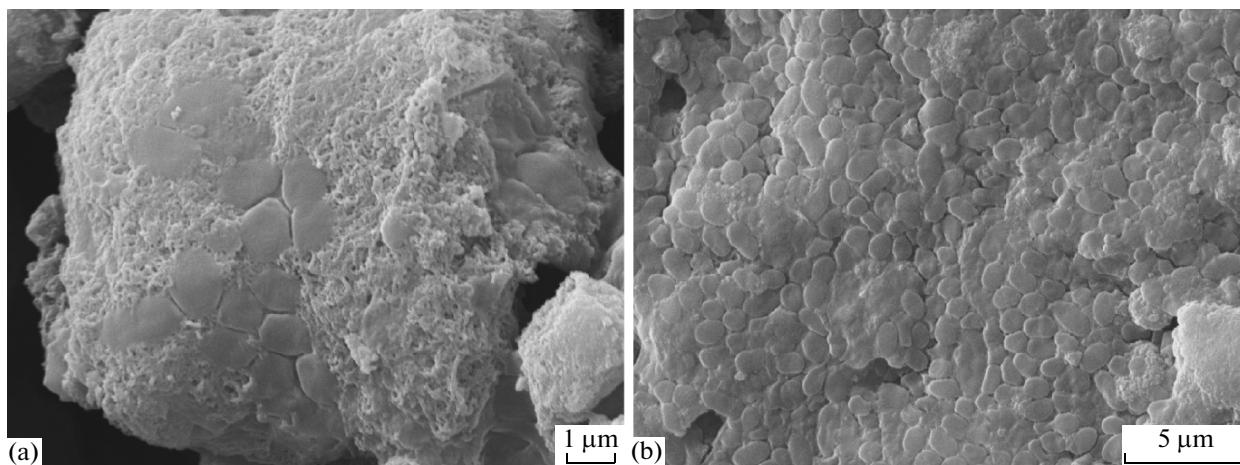


Fig. 7. Electron-microscopic images of the working surfaces of (a) the type 1 anode after MFC discharging for 3 h and (b) the type 2 anode with immobilized *G. oxydans* bacteria after operation for 5 h.

resistance of the cell, which is undoubtedly influenced by physicochemical processes proceeding in the cell. Thus, the observed dependences can be caused by the presence of air bubbles among carbon nanofibers, which can create an insulating gas layer on the electrode surface upon heating by current. An approach to solve this problem is the degassing of electrode materials and the anolyte, for example, with the aid of a water-jet pump. On the other hand, an increase in the internal resistance of the test MFC can be of electrochemical nature. Thus, oxygen absorbed on porous CFC/graphite can react with reduced DCPIP to cause the outflow of electrons from the oxidative biotransformation of glycerol and a decrease in the discharging current and power in the cell. It is well known that the redox indicator DCPIP also reacts to the acid–base properties of the medium. Its solutions are violet and dark blue in acid and alkaline regions, respectively. In the course of MFC discharging, a bluish violet color of the anolyte (pH 6.0) changed to dark blue; this fact indicated the alkalinization of the reaction medium. It is likely that the reduction of oxygen with the formation of OH^- ions occurred in the anode compartment of the cell to decrease the proton conductivity of the separating membrane and, correspondingly, to decrease the MFC power.

Electron-microscopic examinations showed that the adhesion of *G. oxydans* cells to CFC from the anolyte was observed in the course of the operation of an MFC with the type 1 anode (Fig. 7a). The immobilized bacterial cells formed a dense coating on the type 2 anode (Fig. 7b). The observed adhesion can be caused by both the unspecific interaction of a bacterial cell with CFC and the presence of an electropositive taxis of *Gluconobacter*, which are mobile due to the presence of flagella. The presence of the bands of extracellular material as signs of the possible formation of biofilms on the surface of both types of anodes, which was

observed in the electron-microscopic images, is also of interest. There is no doubt that the test microorganisms are promising for further studies in the design of MFCs because of the observed properties (adhesion and taxis).

The subsequent studies will be oriented toward both the development of a new composite material for preparing the anode and the optimization of the design and operation conditions of MFCs in order to improve electrochemical parameters.

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