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Ion-Beam Formation of Electrocatalysts for Fuel Cells with Polymer Membrane Electrolyte

V. V. Poplavsky, A. V. Dorozhko, and V. G. Matys
Belarusian State Technological University, Minsk, 220006 Belarus
**e-mail: vasily.poplav@tut.by*

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Abstract—Active layers of electrocatalysts are prepared by the ion-beam assisted deposition (IBAD) of platinum onto carbon-based AVCarb® Carbon Fiber Paper P50 and Toray Carbon Fiber Paper TGP-H-060 T supports and Nafion® N 115 polymer membrane electrolyte in the mode where the deposited metal ions are used as ions assisting the deposition process. Metal deposition and mixing of the deposited layer with the substrate under an accelerating voltage of 10 kV by the same metal ions are carried out from a neutral fraction of metal vapor and the ionized plasma of a pulsed vacuum-arc discharge, respectively. The composition and microstructure of the surface layers obtained are studied by Rutherford backscattering spectrometry (RBS), scanning electron microscopy (SEM), electron-probe microanalysis (EPMA), and X-ray fluorescence (XRF) analysis. The platinum concentration in the layers is $(0.5–1.5) \times 10^{16}$ at/cm^2. The prepared electrocatalysts exhibit activity in the process of the electrochemical oxidation of methanol and ethanol, which form the basis for the principle of operation of low temperature fuel cells (direct methanol fuel cells (DMFC) and direct ethanol fuel cells (DEFC)).

Keywords: ion beam-assisted deposition of platinum, carbon catalyst supports, polymer membrane electrolyte, catalytic layers, elemental composition, electrocatalytic activity, oxidation of methanol and ethanol

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INTRODUCTION

The use of ion beams for doping the surface of materials enables the introduction of a thin surface layer of controllable amounts of any impurity on the nanoscale level under nonequilibrium conditions of irradiation with accelerated ions. The ion-beam modification of functional materials, the properties of which are determined primarily by their surface composition, is of greatest interest. Among these materials are heterogeneous catalysts of chemical reactions and, in particular, electrocatalysts, that is, the electrodes of electrochemical devices. Electrocatalysts are an essential component of fuel elements, promising chemical power sources, the operating principle of which is direct conversion of the chemical energy of oxidation of a fuel (hydrogen, methanol, ethanol) into electrical energy.

The main functional component of a fuel cell with a polymer membrane electrolyte is a membrane-electrode assembly consisting of an ion-conducting membrane and diffusion layers in contact with it [1]. The supply of fuel and oxidizer, current collection, and the removal of electrochemical reaction products occur through the diffusion layers of the fuel cell. The diffusion layers of membrane-electrode assemblies of fuel elements are made from carbon materials with a developed specific surface area; layers with deposited catalytic metals are simultaneously electrocatalysts.

Platinum is the main catalytic metal activating electrochemical oxidation of the fuel. Compared to conventional chemical methods of the preparation of support catalysts, based on impregnating the support with a platinum-compound solution, its reduction to metallic platinum, drying, etc., the active surface of electrocatalysts formed by ion-beam treatment acquires catalytic layers in a single stage, which substantially decreases the consumption of the precious metal.

The goal of the present work is to study the composition and properties of the catalyst layers formed by the ion beam-assisted deposition of platinum onto diffusion layers of carbon materials and a polymer-membrane electrolyte of fuel cells based on the direct oxidation of methanol and ethanol.

EXPERIMENTAL

The active layers of electrocatalysts are formed by depositing platinum on carbon supports AVCarb®

Carbon Fiber Paper P50 (AVCarb CFP) (Ballard Material Products) and Toray Carbon Fiber Paper TGP-H-060T (Toray CFP), used as the material of the diffusion layers, and a Nafion® N 115 polymer membrane electrolyte. The AVCarb CFP and Toray CFP carbon supports are based on polyacrylonitrile filaments subjected to thermal-oxidative stabilization and subsequent carbonization; their basic characteristics are given in [2, 3]. The nominal thickness of AVCarb CFP is 175 μm, and for Toray CFP, it is 190 μm. Toray CFP is hydrophobized with Teflon, and AVCarb CFP is not hydrophobized. The modified surface of the carbon supports was not subject to pretreatment. The Nafion® N 115 membrane was taken as the electrolyte; its thickness was 125 μm. The Nafion membrane material is a fluorocarbon polymer containing functional sulfonic groups [4]. The main features of the Nafion membrane is its capability of exchanging its constituent cations to cations of the external medium and extremely high ionic conductivity. In contrast to hydrophobic Teflon, Nafion is a hydrophilic polymer and possesses cation conductivity only in a wet state. Charge transfer in the polymer occurs on account of the transfer of cations between sulfonic groups. Because of the inertness of its fluorocarbon base, Nafion is extremely resistant to chemical exposure, mechanically strong, and thermally stable [4]. The membrane electrolyte was subject to preliminary thermochemical treatment, including boiling in a 3% solution of hydrogen peroxide to remove organic contaminants and in 0.5-M H_2SO_4 to remove impurities containing metals, alternating with boiling in deionized water [5].

The ion beam-assisted deposition (IBAD) of platinum was carried out in the mode where deposited metal ions are used as ions assisting the deposition process [6–8]. The deposition of the metal and the mixing of the deposited layer with substrate atoms by accelerated ions of the same metal were performed in an experimental setup, respectively, from a neutral fraction of metal vapor and the vacuum arc plasma of a pulsed arc ion source at a chamber pressure of $\sim 10^{-2}$ Pa. The discharge pulse-repetition frequency was 50 Hz. Assisting ions were accelerated at a voltage of 10 kV. A SH-0105/–20 kV power supply unit was used as the accelerating-voltage source.

The element composition and microstructure of the layers were studied by Rutherford backscattering spectrometry (RBS), scanning electron microscopy (SEM), electron-probe microanalysis (EPMA), and X-ray fluorescence (XRF) analysis.

The RBS analysis of the layers was carried out by measuring the scattering spectra of ^{4}He ions accelerated to the energy E_0 using an AN-2500 accelerator complex (High-Voltage Engineering Europe). The spectra were recorded at normal incidence of the beam of analyzing particles on the sample surface and at a scattering angle of $\theta = 170°$. The energy resolution of the spectrometer with a surface-barrier silicon detector was 18 keV. The obtained RBS spectra were processed in the conventional way.

Scanning electron microscopy (SEM) of the modified surface together with electron-probe microanalysis (EPMA) with the energy dispersion of quanta of the characteristic X-ray radiation emitted by atoms of the elements included in the test layer was conducted using scanning electron microscope + spectrometer systems: JSM-5610LV + EDX JED-2201 (JEOL) and LEO 1455 VP + AZtec Energy Advanced X-Max80 (Oxford Instruments). The distribution of elements over the surface of the test layers was also analyzed. The energy of electrons scanning the surface of the materials was 20 keV.

X-ray fluorescence (XRF) analysis of the electrocatalysts with wavelength dispersion was carried out using a PANalytical Axios spectrometer. A LiF (200) crystal served as a monochromator-analyzer of detected X-ray radiation. The analytical chamber of the spectrometer was filled with helium.

The activity of electrocatalysts formed on the basis of carbon supports was studied in reactions of the electrochemical oxidation of methanol and ethanol, which determine the principle of action of low-temperature fuel cells. Their activity was studied by cyclic voltammetry [9, 10] using a conventional three-electrode electrochemical cell, a PI-50-1 potentiostat with a PR-8 programmer unit, and an analog-to-digital converter and a PC (AVCarb CFP samples) or an Autolab 302N potentiostat (Toray CFP samples). The test sample was used as the working electrode, a platinum electrode was the auxiliary electrode, and a saturated silver chloride half-cell (Ag–AgCl) was the reference electrode. The values of the potential U of the working electrode were taken with respect to the reference-electrode potential. Measurements were carried out at 20°C in solutions of methanol and ethanol in sulfuric acid (1 M CH_3OH + 0.5 M H_2SO_4 and 1 M C_2H_5OH + 0.5 M H_2SO_4). The solutions were prepared in distilled water using sulfuric acid (analytical grade), methanol (HPLC grade, Merck), and rectified ethanol. The potential scan rate of the test electrodes in the potentiodynamic mode was 50 or 100 mV/s.

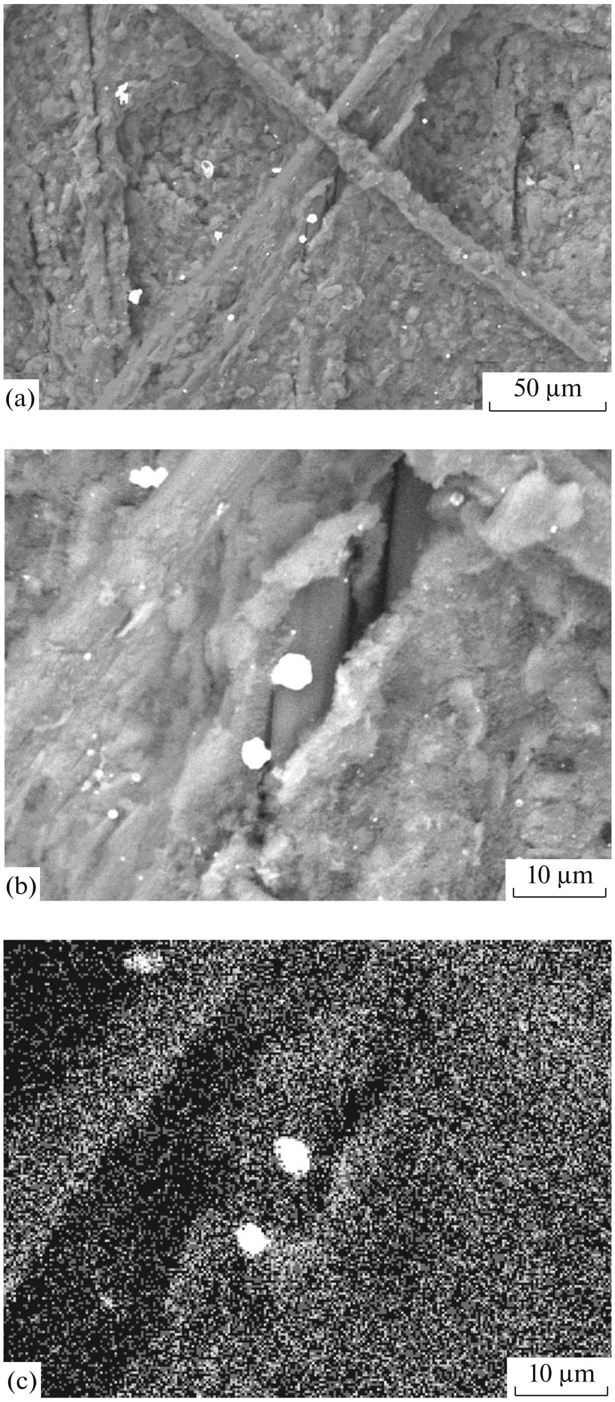

Fig. 1. SEM images of (a and b) the electrocatalyst formed by the ion beam-assisted deposition of platinum onto an AVCarb® Carbon Fiber Paper P50 carbon support and (c) the distribution of platinum atoms over its surface.

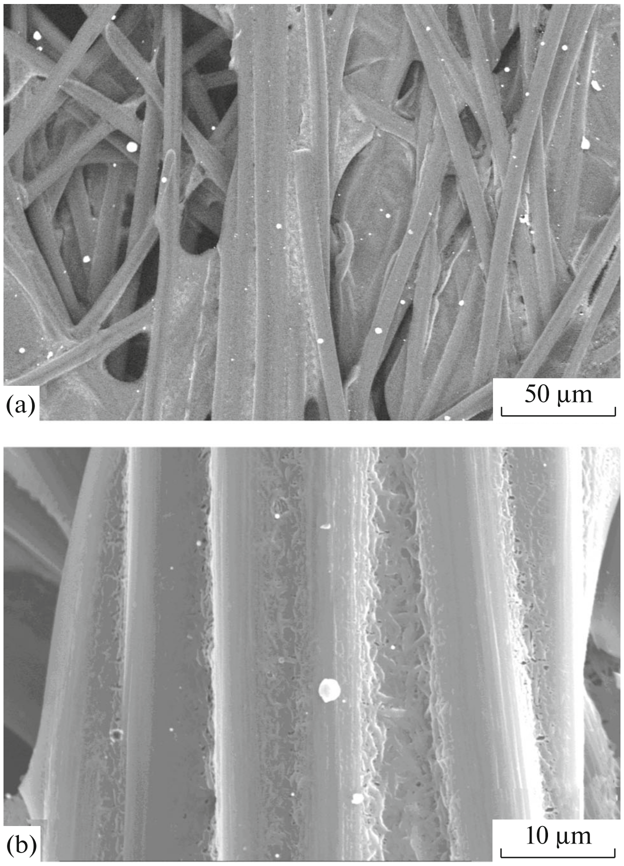

Fig. 2. SEM images of the electrocatalyst formed by the ion beam-assisted deposition of platinum onto a Toray Carbon Fiber Paper TGP-H-060 T carbon support.

RESULTS AND DISCUSSION

According to electron microscopy analysis, the morphology of the formed catalyst layers is virtually the same as the structure of the corresponding carbon substrate (Figs. 1 and 2). EPMA shows that the composition of the layers includes deposited platinum atoms, the substrate material, and oxygen impurities. In contrast to AVCarb CFP, the surface of Toray CFP hydrophobized with Teflon contains a significant amount of fluorine (Fig. 3, Table 1). The concentration of platinum in the resulting catalytic layers is, according to EPMA, a few percent. Analysis of the distribution of elements over the surface (Figs. 1c and 3) shows that along with the deposition of platinum atoms, there are clusters several micrometers in size, the presence of which is due to deposition of metal droplets from the arc ion source. The presence of droplet formations is most often undesirable, because it results in heterogeneity of the composition and properties of the metal coating formed by plasma deposition. To eliminate dripping onto the surface, special systems are used for plasma-flow transportation, the operation of which is based on deflection of the charged fraction in a magnetic field [11]. However, there occurs the separation of ionized and neutral factions, which prevents the implementation of the ion beam-assisted deposition mode.

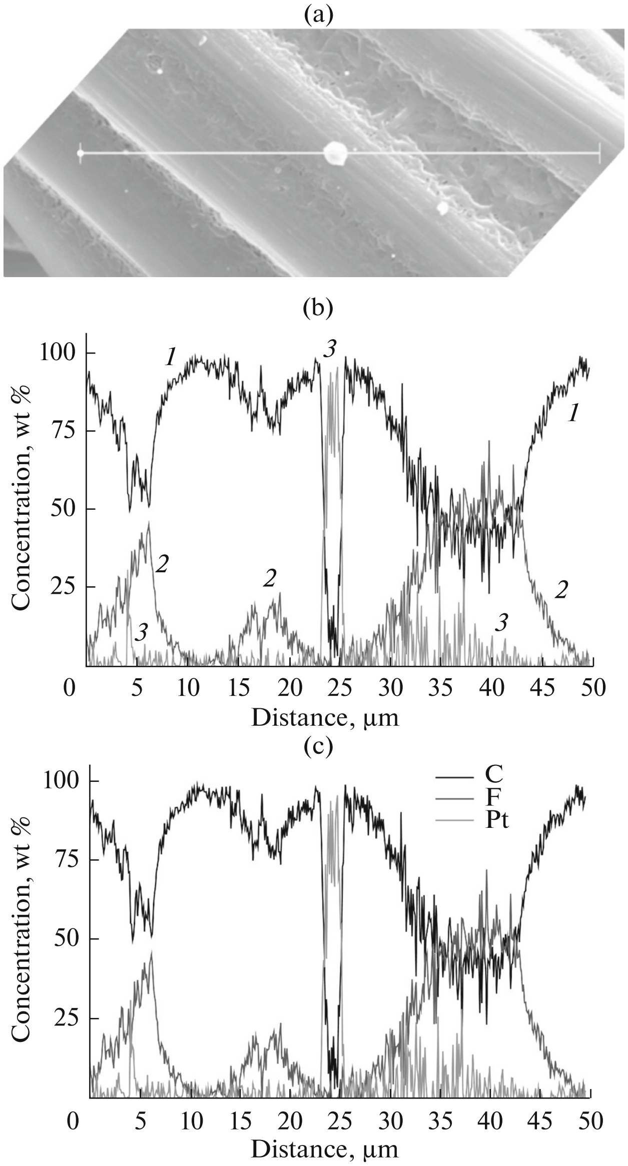

Fig. 3. Distribution of atoms of elements across the scanning line over the surface of the electrocatalyst formed by the ion beam-assisted deposition of platinum onto a Toray Carbon Fiber Paper TGP-H-060 T carbon support: (*1*) C, (*2*) F, and (*3*) Pt.

Table 1. Elemental composition of the surface of carbon supports with a catalytic layer formed by the ion beam-assisted deposition of platinum (EPMA data)

Element	Concentration, wt %	
	Pt/AVCarb CFP	Pt/Toray CFP
C	91.24	81.67
O	3.16	–
F	–	16.42
Pt	5.60	1.91

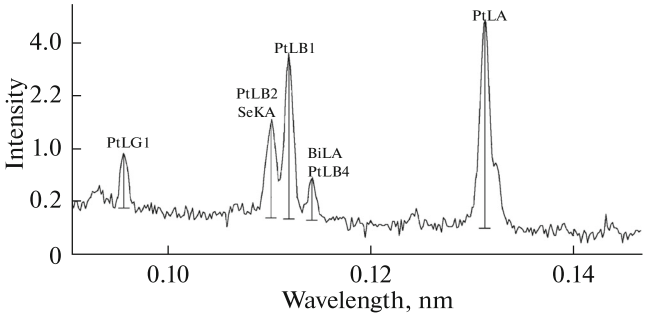

Fig. 4. Fragment of the X-ray fluorescence spectrum of platinum atoms in the composition of the catalytic layer formed on the AVCarb® Carbon Fiber Paper P50 support.

The XRF and RBS data confirm the composition of the layers formed as determined by EPMA. For example, in the X-ray fluorescence spectrum obtained in studying the electrocatalyst based on AVCarb® Carbon Fiber Paper P50, the *L* spectral lines of the characteristic X-ray emission of platinum atoms are observed (Fig. 4). The presence of deposited platinum is also detected in the XRF study of the Nafion® N 115 polymer membrane electrolyte (Fig. 5). The RBS spectra of ^{4}He ions from the surface of the electrocatalysts formed by ion-beam-assisted platinum deposition onto Toray Carbon Fiber Paper TGP-H-060T and AVCarb® Carbon Fiber Paper P50 supports are presented in Fig. 6 and on the surface of Nafion® N 115 polymer membrane electrolyte are shown in Fig. 7 before and after the deposition of platinum. The elements that make up the carbon supports and the polymer membrane themselves and the presence of deposited platinum and oxygen impurities can be identified in the spectra.

Correct quantitative processing of the RBS spectra is difficult because of the irregular porous structure of Toray Carbon Fiber Paper TGP-H-060T and AVCarb® Carbon Fiber Paper P50 carbon supports and the complexity of the composition of Nafion polymer electrolyte. The results of estimations in the processing of the spectra (Table 2) indicate that the content of platinum atoms in the formed layers is ~(0.5–1.5) × 10^{16} at/cm^2. Their maximum concentration $C_{\max}$ in the distribution near the surface depends on the layer concentration of the metal and is a few atomic percent, and then gradually decreases to a value corresponding to ~(1.0–1.5) × 10^{17} at/cm^2. The background signal in the spectra of Pt–Toray CFP and Pt–AVCarb CFP in the range of channels from 200 to 370 (Fig. 6) is due to the scattering of ^{4}He ions at the atomic nuclei of the deposited metal droplet phase.

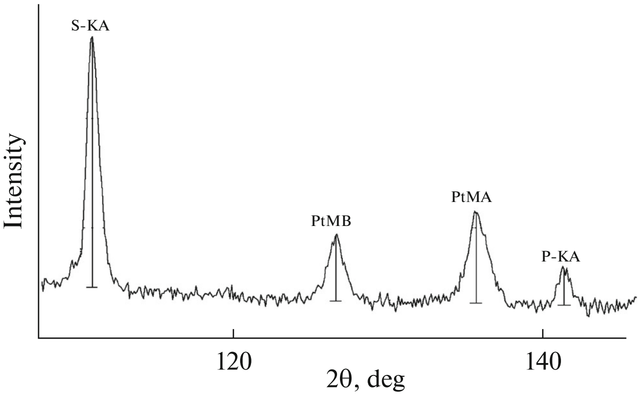

Fig. 5. Fragment of the X-ray fluorescence spectrum of atoms of sulfur and platinum in the composition of the catalytic layer formed on the Nafion® N 115 polymer membrane electrolyte.

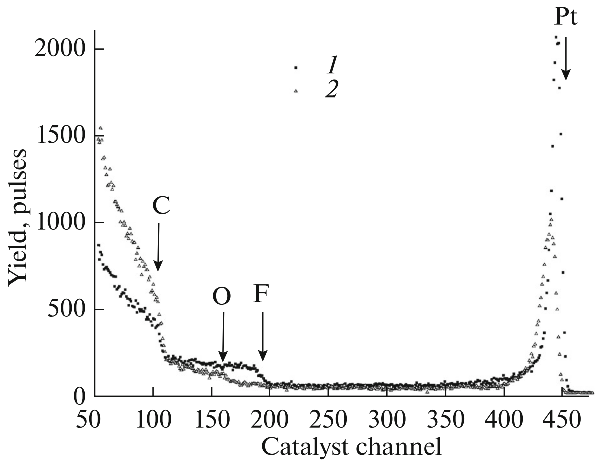

Fig. 6. RBS spectra of ^{4}He ions from the surface of electrocatalysts formed by the deposition of platinum onto (*1*) Toray Carbon Fiber Paper TGP-H-060 T and (*2*) AVCarb® Carbon Fiber Paper P50; E_0 = 1.4 MeV.

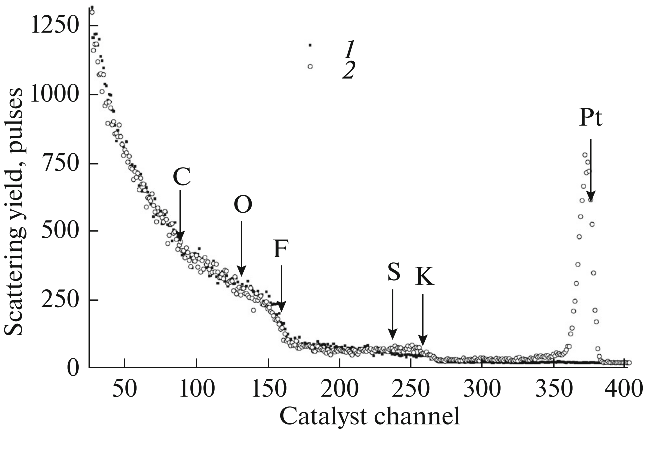

Fig. 7. RBS spectra of ^{4}He ions from the surface of the Nafion® N 115 polymer membrane electrolyte, obtained (*1*) before and (*2*) after the deposition of platinum; E_0 = 1.2 MeV.

The results of studying the activity of electrocatalysts, prepared on the carbon-based supports, in the reactions of the electrochemical oxidation of methanol and ethanol are shown in the form of cyclic voltammograms in Figs. 8 and 9.

The electrochemical oxidation of each alcohol in a sulfuric-acid solution is manifested in the cyclic voltammograms as specific current peaks appearing with a change in the electrode potential in both the anodic and cathodic direction. In the anode side of the voltammogram, there is a current peak caused by the multistage process of the oxidation of methanol or ethanol, which includes electrochemical adsorption, the decomposition of alcohol molecules, the formation of adsorbed molecules of carbon monoxide CO_{ads}, and their subsequent removal by reaction with chemisorbed water molecules or OH_{ads} groups to form electrons, hydrogen ions, and CO_2. A decrease in current with a further increase in the electrode potential can be explained by a decrease in the rate of the process of electrochemical adsorption of alcohol molecules due to blocking of the platinum surface by the products of the electrochemical adsorption of water. On the subsequent sweep potential in the cathodic direction, a current peak appears in the voltammogram, which is due to resuming of the process of methanol or ethanol oxidation at the recovered catalyst surface [12–14].

These peaks clearly appear on the cyclic voltammograms of all studied samples of electrocatalysts (Figs. 8 and 9), indicating their activity in the reactions of the oxidation of both methanol and ethanol. The magnitudes of the alcohol oxidation current depend on the surface area of the electrocatalyst in contact with the working solution.

Thus, it was found that the ion beam-assisted deposition of platinum in the proposed mode onto Toray Carbon Fiber Paper TGP-H-060 T and AVCarb® Carbon Fiber Paper P50carbon supports, which is the basis of the diffusion layers of the membrane-electrode assemblies of fuel cells with a polymer membrane electrolyte, and a Nafion® N 115 membrane electrolyte, surface layers are formed including the atoms of elements making up the substrate and atoms of deposited platinum. According to the RBS data, the content of platinum atoms in the layers is ~(0.5–1.5) × 10^{16} at/cm^2, which in terms of mass is less than 0.005 mg/cm^2. Electrocatalysts with the layers obtained are active in the processes of electrochemical oxidation of organic fuels (methanol and ethanol) which are the base of the operating principle

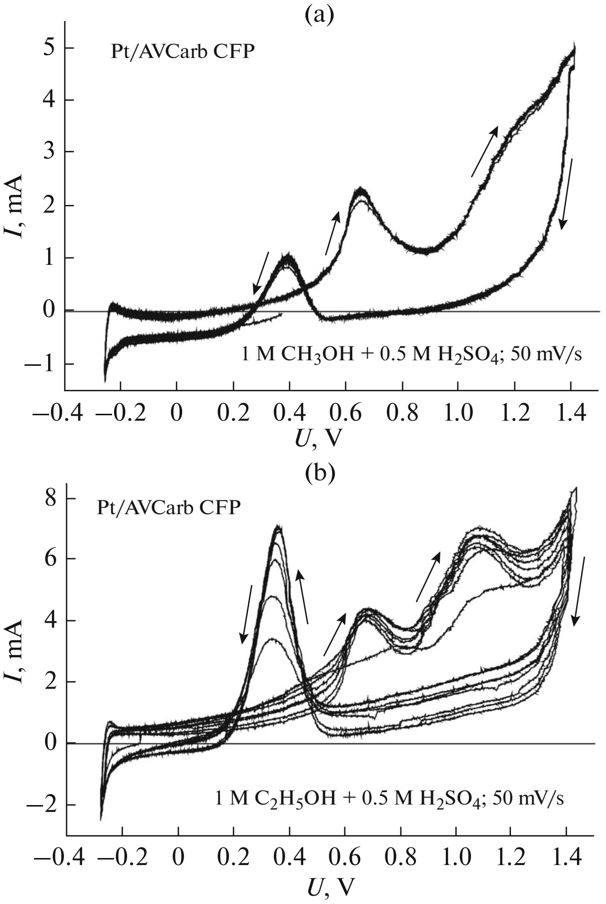

Fig. 8. Cyclic voltammograms of electrocatalysts formed on AVCarb® Carbon Fiber Paper P50 by the ion beam-assisted deposition of platinum, obtained in solutions of (a) 1 M CH_3OH + 0.5 M H_2SO_4 and (b) 1 M C_2H_5OH + 0.5 M H_2SO_4.

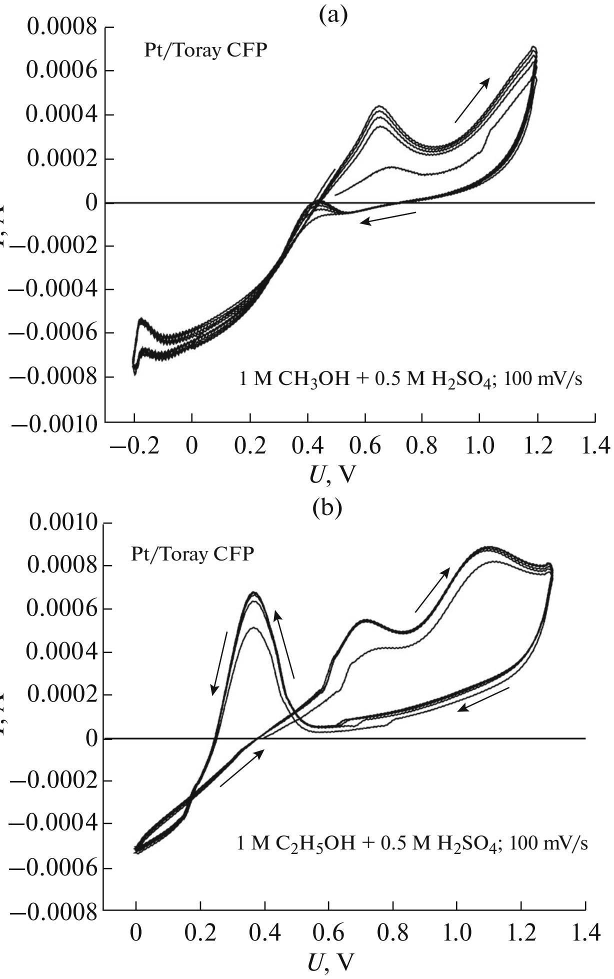

Fig. 9. Cyclic voltammograms of the electrocatalysts formed on Toray Carbon Fiber Paper TGP-H-060 T by the ion beam-assisted deposition of platinum, obtained in solutions of (a) 1 M CH_3OH + 0.5 M H_2SO_4 and (b) 1 M C_2H_5OH + 0.5 M H_2SO_4.

of low-temperature fuel cells with a polymer membrane electrolyte.

CONCLUSIONS

The catalytically active layers on the surface of carbon supports Toray Carbon Fiber Paper TGP-H-060 T and AVCarb® Carbon Fiber Paper P50 used as the material of the diffusion layers of the membrane-electrode assemblies of fuel elements, and a Nafion® N 115 polymer membrane electrolyte are formed by the ion beam-assisted deposition of platinum from the vacuum arc discharge plasma of a pulsed ion source in a mode where the metal is introduced into the catalyst

Table 2. Content of atoms of elements in catalyst layers formed by the ion beam-assisted deposition of platinum onto carbon supports and a membrane electrolyte (RBS data)

Sample	Content of atoms of elements in the layer, 10^{16} at/cm^2					C_{max}, at %
	Pt	C	F	O	S	
Pt/Toray CFP	1.5	122.0	15.0	–	–	8.5
Pt/AVCarb CFP	0.8	262.0	–	1.3	–	2.5
Pt/Nafion	0.5	165.0	38.3	–	2.6	1.0

layer at the nanoscale level under nonequilibrium conditions of treatment with accelerated ions of the deposited metal. This mode ensures the introduction of trace amounts of dopant to the surface layer of the substrate under vacuum conditions and the formation of an active layer with a low (less than 0.01 mg/cm^2) concentration of the activating metal, strongly bound to the matrix. The process of the formation of catalytic layers is usually of the single-stage type, which distinguishes it favorably from conventional chemical methods of the preparation of supported catalysts.

The experimental data indicate the efficiency of using the ion beam-assisted deposition of a catalytic metal in the proposed mode for the formation of the active electrocatalyst surface of fuel cells with a polymer membrane electrolyte, which are promising chemical power sources.

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