doi: 10.56761/EFRE2022.C3-P-018001

Composition of catalytic layers prepared by ion beam assisted deposition of dysprosium and platinum from a pulsed arc discharge plasma onto carbon catalysts carriers

V. Poplavsky[*], *A. Dorozhko, V. Matys*

Belarusian State Technological University, Minsk, Belarus
[*]*vasily.poplav@tut.by*

Abstract. Plasma produced in metal vapors of a low-voltage vacuum arc discharge between two metal electrodes at their periodic contact was used to preparation surface catalytic layers by ion beam assisted deposition (IBAD) of dysprosium and platinum onto special carbon fiber catalysts carriers. Formation of layers in IBAD mode, by means of the deposition of metal and mixing of precipitating layer with the substrate by accelerated (U = 5 kV) ions of the same metal, was carried out. In this process, a neutral fraction of metal vapor and ionized plasma of vacuum pulsed electric arc were used. Investigation of the composition of prepared layers was carried out by EDX, SEM, RBS and WD-XRF methods. Electrocatalysts with the prepared layers are active in the oxidation of methanol and ethanol reactions, which are the basis of the principle of operation of low-temperature fuel cells.
Keywords: arc discharge plasma, ion beam assisted deposition of dysprosium and platinum, preparation of catalytic layers, composition of deposited layers.

1. Introduction

Ion-plasma technologies provide the possibility of modifying the surface of structural and functional materials in order to improve the performance characteristics of products made of them without changing the structure and bulk properties of the material. Of great interest is the ion-plasma modification of functional materials, the properties of which are primarily determined by the surface composition, in particular, the introduction of active impurities into the near-surface layer of heterogeneous catalysts for chemical reactions [1, 2].

The aim of this work is to study the composition of the catalytic layers prepared on special carbon carriers of catalysts in the process of ion beam assisted deposition from plasma generated in metal vapors of a vacuum arc discharge, platinum as the main catalytic metal and dysprosium as an activating additive.

2. Experimental

2.1. Materials

As substrates for the preparation of the studied layers we used special carbon materials: Toray Carbon Fiber Paper TGP-H-060 T and AVCarb® Carbon Fiber Paper (Ballard Material Products Inc.), which are used as material of diffusion layers of the membrane electrode assemblies for low-temperature fuel cells with a polymer membrane electrolyte. Membrane-electrode assembly, consisting of an ion-conducting membrane and the catalytic and diffusion layers in contact with it, is the main functional component of the fuel cell. Diffusion layers are made of porous materials; fuel and oxidizer are fed through them, current is collected and the products of the electrochemical reaction are removed. The catalysts for fuel oxidation and oxygen reduction reactions are arranged in layers between the membrane electrolyte and the diffusion layers [3]. In this paper, we form the catalytic layers during the deposition of active metals directly on the material of the diffusion layers.

Formation of the catalytic layers under study was carried out in order to obtain electrocatalysts for methanol and ethanol oxidation based on special carbon materials Toray Carbon Fiber Paper TGP-H-060 T (Toray) and AVCarb® Carbon Fiber Paper P50 (AVCarb), which are meant for the manufacture of diffusion layers of membrane electrode assemblies of low-temperature fuel cells with a polymer membrane electrolyte. Toray Carbon Fiber Paper TGP-H-060 T and AVCarb® Carbon Fiber Paper P50 carbon catalysts carriers are based on polyacrylonitrile filaments subjected

to thermal-oxidative stabilization and subsequent carbonization [4, 5]. Toray Carbon Fiber Paper TGP-H-060 T carrier was hydrophobized with Teflon, and the AVCarb® Carbon Fiber Paper P50 was not hydrophobized. Pretreatment of the modified surface of the carbon carriers was not performed.

2.2. Layers preparation

Catalytic layers on surface of carbon fiber catalysts carriers were prepared with use of the experimental setup by ion beam assisted deposition (IBAD) of platinum as basic active metal and one of rare earth metals – dysprosium as an activating additive. The choice of deposited metals is determined by the peculiarities of the mechanism of oxidation of organic fuels – methanol and ethanol [6, 7]. We carried out IBAD mode where deposited metal ions are used as ions assisting. The deposition of the metal and the mixing of the deposited layer with substrate by accelerated ions of the same metal were performed from neutral fraction of metal vapor and ionized fraction of plasma, respectively, of a vacuum arc discharge of the pulsed arc ion source. Evaporation of the deposited metal and ionization of its atoms occur in a low-voltage vacuum arc discharge between two working metal electrodes of an ion source at their periodic contact. Samples of the carrier on which the metal deposition is carried out are under high negative potential that accelerates metal ions from the arc discharge plasma. The ions of the metal produced in the discharge were accelerated by a voltage of 5 kV. The repetition frequency of the ion current pulses was 50 Hz; the ion current density was 4–5 μA/cm^2. The pressure in work chamber was ~10^{-2} Pa.

2.3. Layers investigation

The composition of the layers were studied by energy dispersive electron-probe microanalysis (EDX) with scanning electron microscopy (SEM), wave dispersive X-ray fluorescence analysis (WD-XRF), and Rutherford backscattering spectrometry (RBS).

Scanning electron microscopy of the modified surface together with electron-probe microanalysis 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 a JSM-5610LV scanning electron microscope with an EDX JED-2201 (JEOL) spectrometer, as well as with a LEO 1455 VP microscope (Karl Zeiss Group) equipped with an AZtec Energy Advanced X-Max80 (Oxford Instruments) spectrometer. 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 analysis of the modified samples with wavelength dispersion was carried out using a PANalytical Axios spectrometer (Netherlands). A LiF (200) crystal served as a monochromator-analyzer of detected X-ray radiation.

The RBS analysis of the layers was carried out by measuring scattering spectra of ^{4}He ions accelerated to the energy 1.5 MeV 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 170 degree. 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.

The activity of electrocatalysts with prepared layers 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 using a conventional three-electrode electrochemical cell and IPC-Pro M potentiostat. 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.

3. Results and discussion

3.1. SEM and EDX analysis

SEM analysis showed differences in the microstructure of Toray Carbon Fiber Paper TGP-H-060 T and AVCarb® Carbon Fiber Paper P50 carriers (Fig.1 and Fig.2). The surface morphology of the carriers during the formation on their surface of investigated layers does not change.

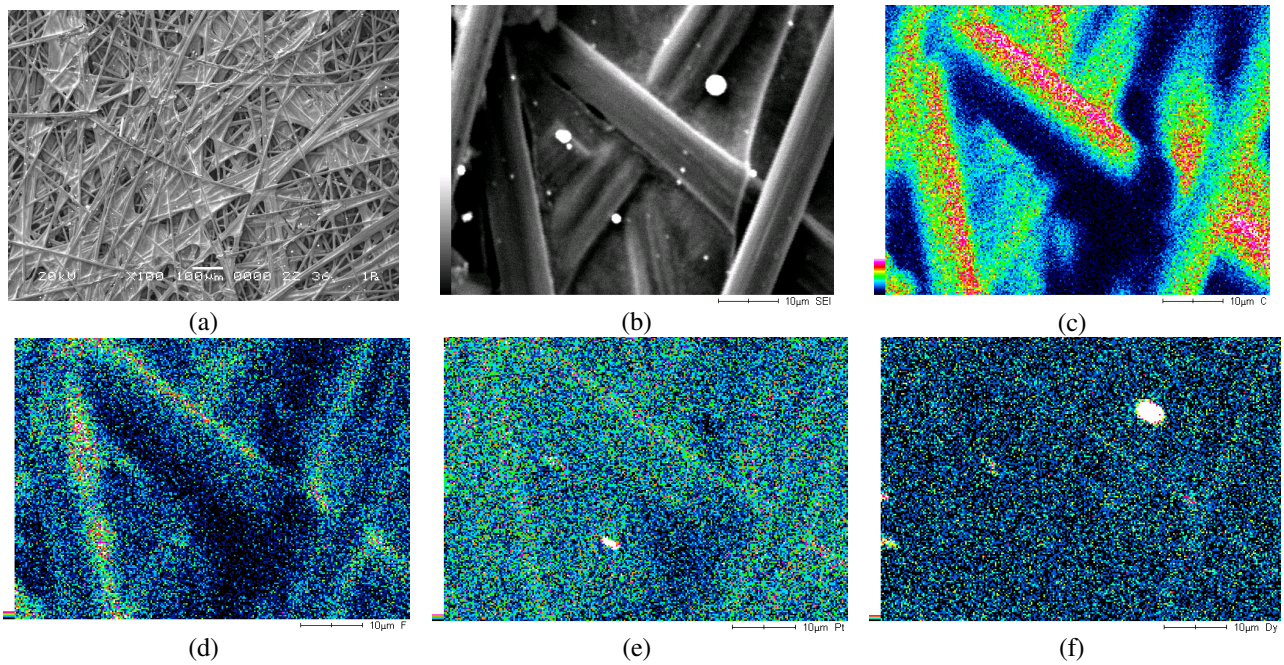

Fig.1. SEM images (a, b) of the Toray Carbon Fiber Paper TGP-H-060 T carrier with layer prepared by IBAD of dysprosium and platinum, and distribution over the surface of the elements: C (c), F (d), Pt (e), Dy (f).

According to EDX analysis the composition of the obtained layers includes atoms of the deposited metals and substrate material (carbon and in the case of hydrophobized Toray Carbon Fiber Paper TGP-H-060 T also fluorine), as well as oxygen, present due to its deposition from the residual atmosphere of the working vacuum chamber and sorption processes. In particular, the oxygen distribution in the composition of the layer formed as a result of the deposition of dysprosium and platinum correlates with the distribution of dysprosium (Fig.3), which suggests the formation of a rare-earth metal oxide.

Due to the inhomogeneity of the structure of the substrates, the distribution of atoms of elements over the surface is also non-uniform (Figs. 1–3). There are inclusions of metals with a size of the order of several micrometers on the surface, which were caused by the deposition of metal droplets from the arc discharge of the ion source. The presence of such droplet formations, most often is undesirable, since it leads to heterogeneity of the composition and properties of the metal-containing coating formed by plasma deposition. To prevent droplets on the treated surface, special plasma flow transport systems are used, whose operating principle is based on a deviation in the charged fraction in the magnetic field. However, this leads to the separation of ionized and neutral fractions, which does not allow the implementation of ion beam assisted deposition to obtain catalytic layers.

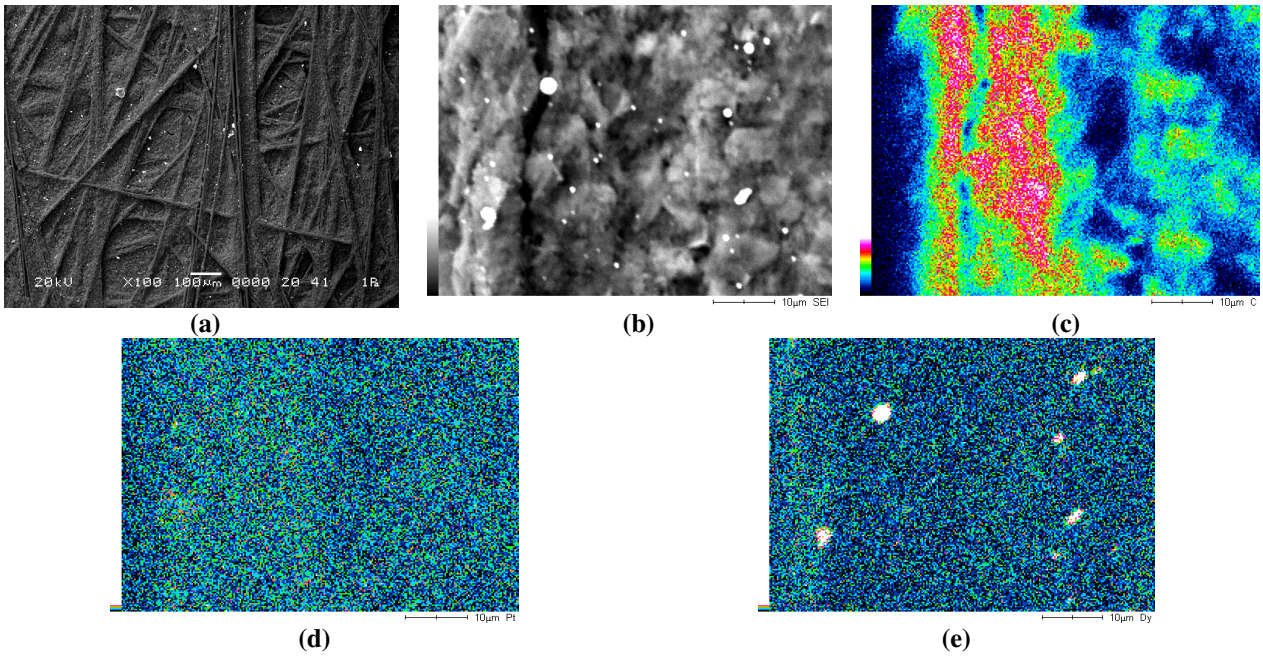

Fig.2. SEM images (a, b) of the AVCarb® Carbon Fiber Paper P50 carrier with layer prepared by the IBAD of dysprosium and platinum, and distribution over the surface of the elements: C (c), Pt (d), Dy (e).

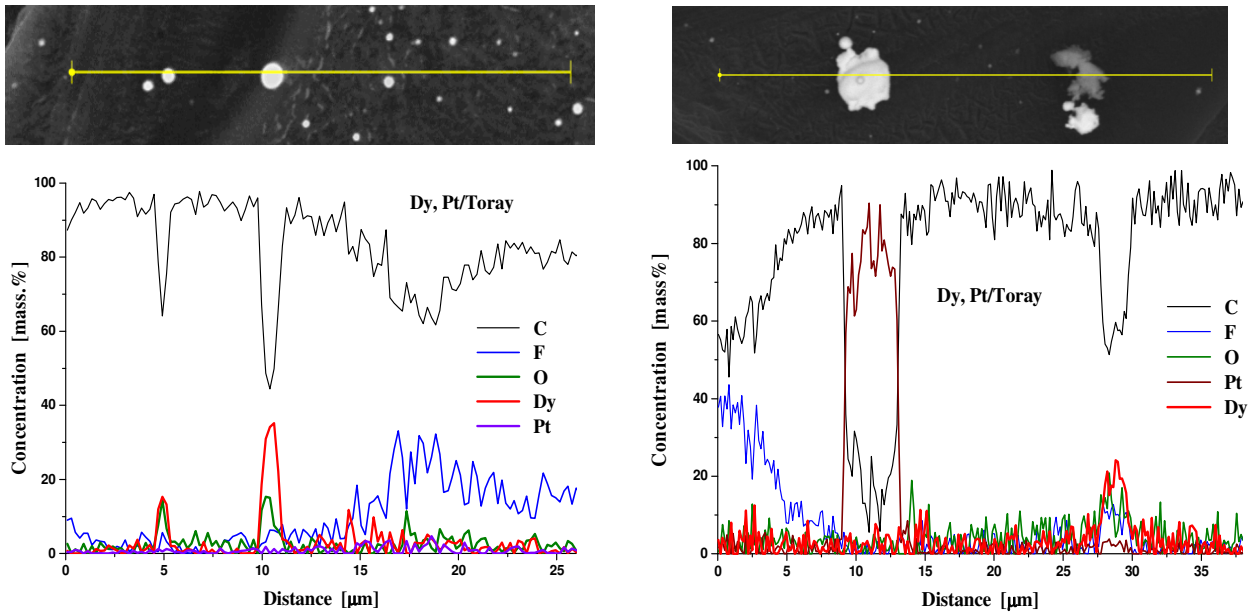

Fig.3. Distributions of atoms of elements across the scanning line over the surface of Toray Carbon Fiber Paper TGP-H-060 T carrier with layer formed by the IBAD of dysprosium and platinum (according EDX analysis).

The approximate quantitative composition of the layers obtained EDX analysis is given in Table 1, which shows the results of determining the content of elements (excluding oxygen) in the composition of the samples under study. We studied the composition of the samples with surface layers obtained by the deposition of only platinum (Pt) and alternate deposition of dysprosium and platinum (Dy, Pt) on Toray and AVCarb carriers, respectively. The results of analysis of the average composition over the surface (A), obtained from the surface of the samples at ×100 magnification, as well as the composition of areas on which the droplet formations of dysprosium (Dy) or platinum (Pt) are located. The concentration of atoms of deposited metals on the main part of the surface of the samples, excluding droplet formations, according to energy-dispersion

microanalysis is on average a fraction of percent. Their concentration in the areas of the droplets is significantly higher.

Table 1. Elemental composition of the analyzed layers (according to EDX analysis)

Sample	Content (at.%)			
	C	F	Pt	Dy
Toray (A)	68.52	31.48	–	–
Pt/Toray (A)	80.28	19.35	0.37	–
Pt/Toray (Pt)	69.27	1.79	28.94	–
Dy, Pt/Toray (A)	83.04	15.82	0.53	0.61
Dy, Pt/Toray (Dy)	44.00	0.44	0.25	55.32
Dy, Pt/Toray (Pt)	84.90	5.58	8.85	0.67
Pt, Dy/Toray (A)	90.59	8.20	0.58	0.63
Pt, Dy/Toray (Dy)	39.39	4.10	0.43	56.07
Pt, Dy/Toray (Pt)	87.90	5.45	6.13	0.52
Pt, Dy/AVCarb (A)	98.74	–	0.05	1.21
Pt, Dy/AVCarb (Dy)	89.00	–	0.02	10.98

3.2. RBS analysis

The RBS spectra (Fig.4) contains signals conditioned by the scattering of ^{4}He ions on the nuclei of atoms that make up the carbon fiber carriers (C, F), as well as O and deposited metals atoms that are distributed in a thin near-surface layer.

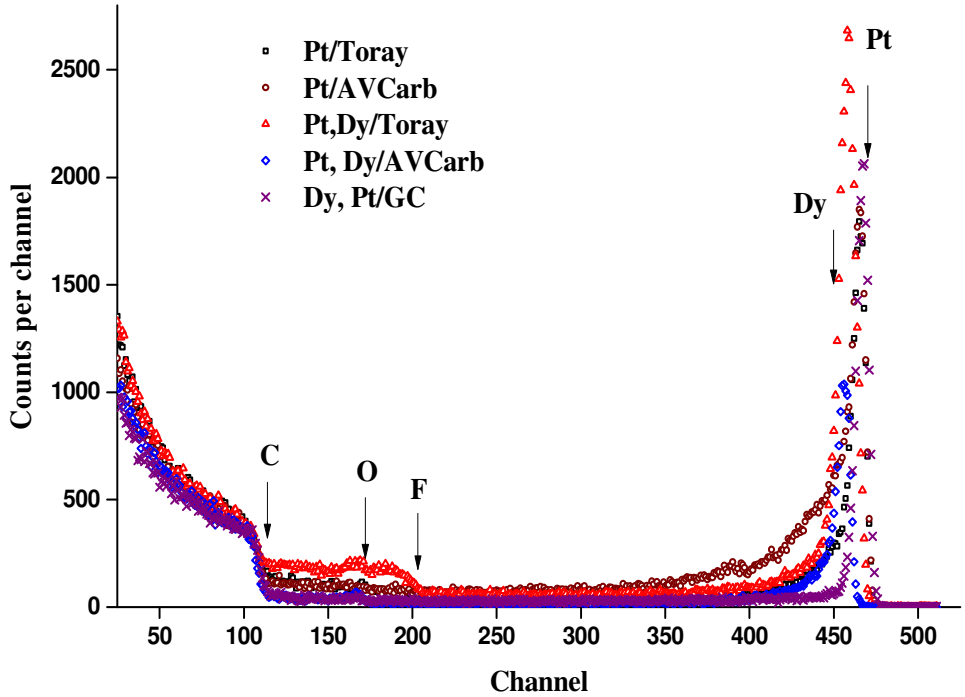

Fig.4. RBS spectra of ^{4}He ions scattered by atomic nuclei of elements that make up layers obtained by IBAD of metals on Toray Carbon Fiber Paper TGP-H-060 T and AVCarb® Carbon Fiber Paper P50 carriers, and dense carbon material – glassy carbon (GC).

It should be taken into account that the correct quantitative processing of the Rutherford backscattering spectra of the studied samples is difficult due to the irregular porous structure of the carriers. The results of estimated calculations of the atomic composition of the analyzed layers after spectrum processing are listed in Table 2. The Σ column shows the total content of atoms in the

analyzed layer, which determine the thickness of the layer in atoms per square centimeter. The values of the concentration of deposited metals at the maximum distribution, C_{max}, located near the surface are also reported. The results of spectrum analysis showed that the concentration of each deposited metal in the formed layers is about $(1–2)\cdot10^{16}$ cm^{-2}. The concentration of deposited metals at the maximum of the distribution near the surface depends on the bulk content of the metal and amounts to several atomic percent. The thickness of the layers obtained on Toray Carbon Fiber Paper TGP-H-060 T and AVCarb® Carbon Fiber Paper P50 carriers, expressed in atoms per square centimeter, is 2.5–3 higher than the thickness of the layer formed on dense carbon material – glassy carbon (GC).

Table 2. Elemental composition of the analyzed layers (according to Rutherford backscattering spectrometry)

Sample	Atomic composition (cm^{-2})						C_{max} (at.%)	
	C	O	F	Pt	Dy	Σ	Pt	Dy
Pt/Toray	$1.93\cdot10^{18}$	$2.11\cdot10^{17}$	$1.26\cdot10^{17}$	$1.19\cdot10^{16}$	–	$2.28\cdot10^{18}$	6.0	–
Dy, Pt/Toray	$2.55\cdot10^{18}$	$3.86\cdot10^{17}$	$2.57\cdot10^{17}$	$1.35\cdot10^{16}$	$1.08\cdot10^{16}$	$3.22\cdot10^{18}$	2.8	3.8
Pt, Dy/Toray	$2.18\cdot10^{18}$	$3.49\cdot10^{17}$	$2.35\cdot10^{17}$	$1.36\cdot10^{16}$	$1.05\cdot10^{16}$	$2.78\cdot10^{18}$	2.6	3.8
Pt, Dy/Toray	$2.95\cdot10^{18}$	$3.54\cdot10^{17}$	$2.14\cdot10^{17}$	$1.91\cdot10^{16}$	$1.48\cdot10^{16}$	$3.55\cdot10^{18}$	3.8	3.8
Pt/AVCarb	$2.59\cdot10^{18}$	$2.65\cdot10^{17}$	–	$2.10\cdot10^{16}$	–	$2.88\cdot10^{18}$	6.6	–
Pt, Dy/AVCarb	$2.36\cdot10^{18}$	$1.24\cdot10^{17}$	–	$1.00\cdot10^{16}$	$0.92\cdot10^{16}$	$2.51\cdot10^{18}$	2.7	6.6
Pt, Dy/GC	$0.25\cdot10^{18}$	$0.19\cdot10^{17}$	–	$4.68\cdot10^{16}$		$0.92\cdot10^{18}$	5.0	

3.3. WD-XRF analysis

Fig.5 and Fig.6 show two fragments of the X-ray fluorescence spectra of atoms of elements of the layer prepared by the IBAD of metals onto Toray Carbon Fiber Paper TGP-H-060 T carrier.

In the spectra obtained in studying samples the spectral lines *L*- and *M*-series of the characteristic X-ray emission of deposited platinum, *M*-series of ytterbium atoms are observed. There are also lines of K_α-radiation of oxygen and fluorine atoms, also the lines of the reflected radiation of rhodium atoms, which is used as the exciting X-ray fluorescence.

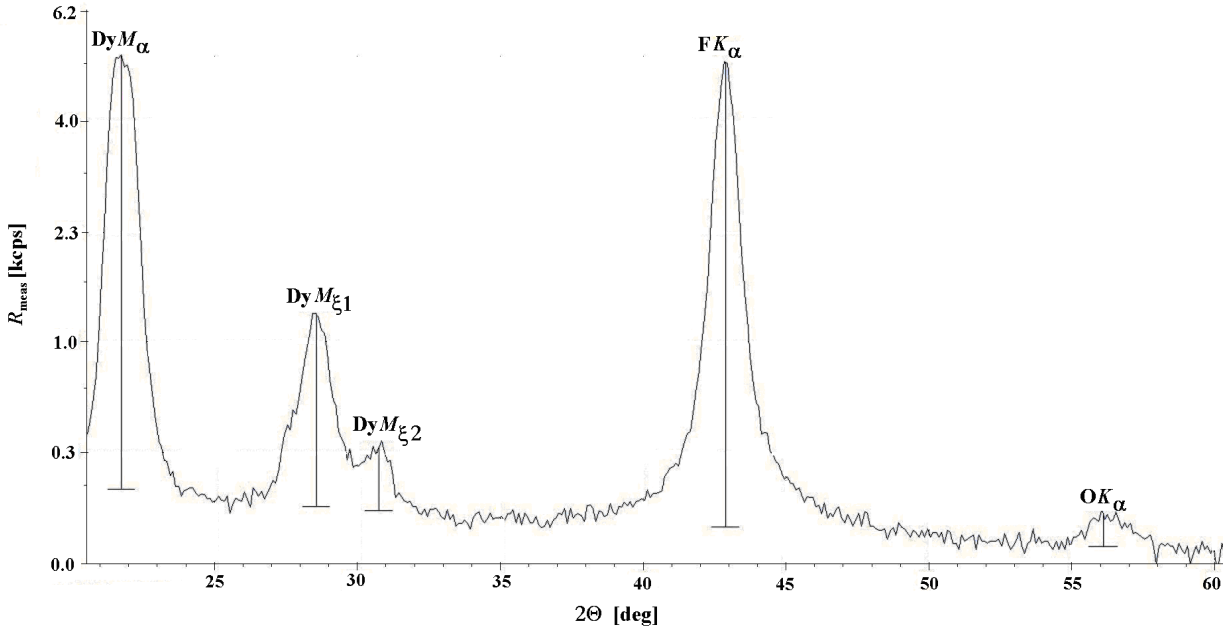

Fig.5. Fragment of the WD-XRF spectra of elements in the composition of the layer formed by IBAD of dysprosium and platinum on Toray Carbon Fiber Paper TGP-H-060 T carrier.

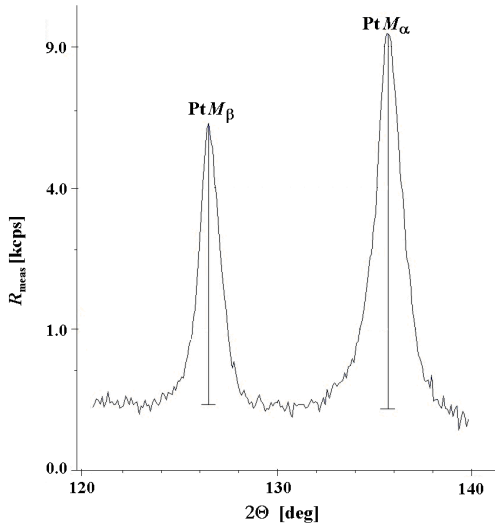

Fig.6. Fragment of the WD-XRF spectra of elements in the composition of the layer formed by IBAD of dysprosium and platinum on Toray Carbon Fiber Paper TGP-H-060 T carrier.

3.4. Layers electrocatalytic activity

The results of studying the activity of electrocatalysts, prepared by IBAD of metals from arc discharge plasma on the carbon-based carriers, in the reactions of the electrochemical oxidation of methanol and ethanol are shown in the form of cyclic voltammograms in Fig.7.

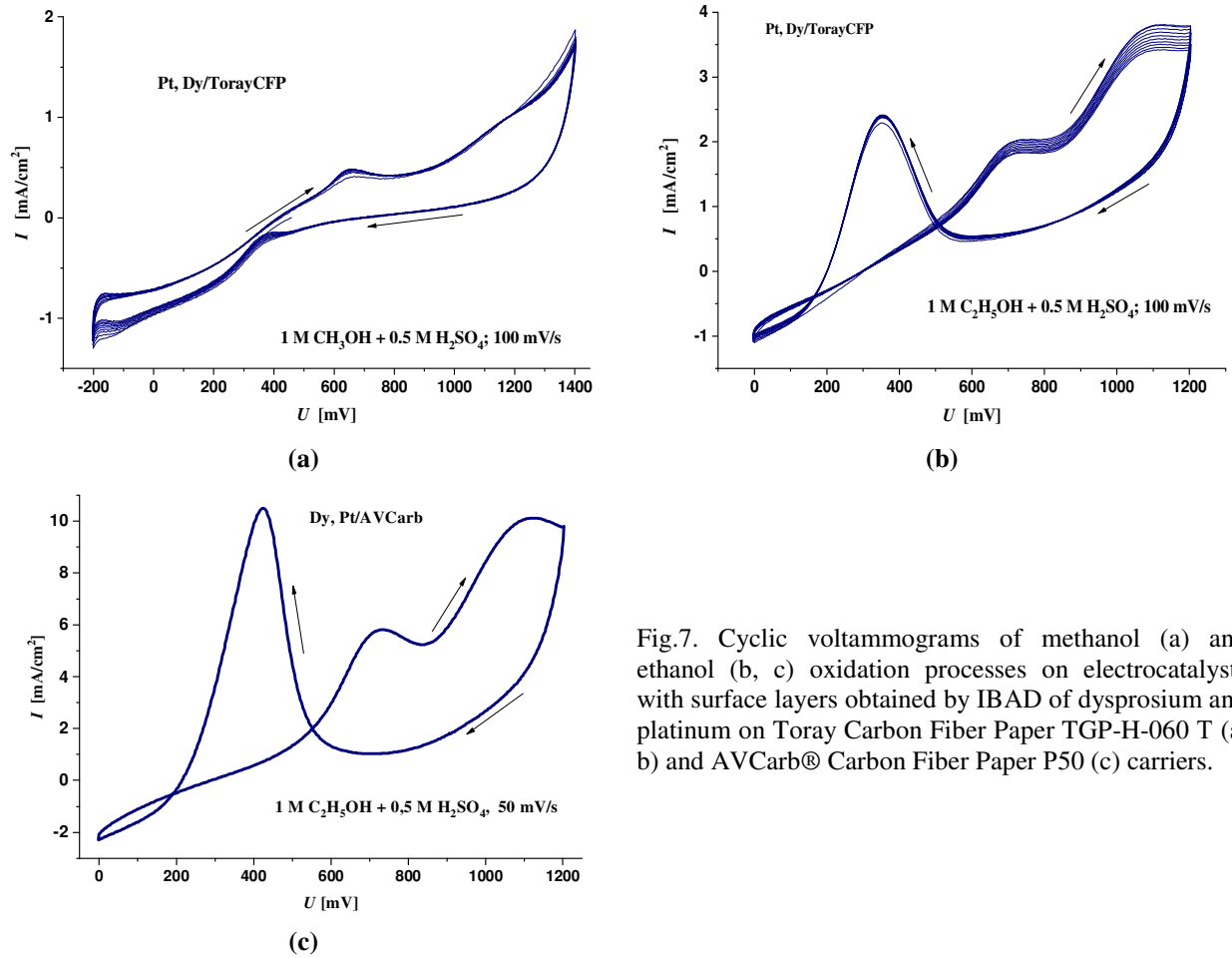

Fig.7. Cyclic voltammograms of methanol (a) and ethanol (b, c) oxidation processes on electrocatalysts with surface layers obtained by IBAD of dysprosium and platinum on Toray Carbon Fiber Paper TGP-H-060 T (a, b) and AVCarb® Carbon Fiber Paper P50 (c) carriers.

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 [6, 7]. These peaks are clearly visible on the received voltammograms (Fig.7), which indicates the activity of the obtained electrocatalysts. A distinctive feature of the electrocatalysts is their higher activity in the process of oxidation of more complex ethanol molecules as compared with methanol, for which it is necessary to ensure breakage of the C–C chemical bond [8].

4. Conclusion

Plasma produced in metal vapors of a low-voltage vacuum arc discharge between two metal electrodes at their periodic contact was used to prepare surface layers by ion beam assisted deposition (IBAD) of metals. We carried out IBAD in mode where ions of deposited metal are used as assisting ions. The deposition of the metal and the mixing of the deposited layer with substrate by accelerated ions of the same metal were performed in the experimental setup from neutral fraction of metal vapor and ionized fraction of plasma, respectively.

Catalytic layers on the surface of special carbon carriers Toray Carbon Fiber Paper TGP-H-060 T and AVCarb® Carbon Fiber Paper P50, intended for the manufacture of diffusion layers of membrane-electrode assemblies of low-temperature fuel cells with a polymer membrane electrolyte by IBAD of ytterbium and platinum. It was established, that under such a deposition mode, the ionic mixing of all components takes place and multicomponent layers are formed containing atoms of deposited metals and carriers, as well as oxygen impurity. Active surface formation during the deposition of two metals was performed in vacuum in two steps, which favorably compares with traditional multi-stage methods of preparing supported catalysts based on carrier impregnation with solutions of compounds of each deposited metal, their reduction to the metallic state, repeated washing to remove impurities, and drying, etc.

Acknowledgement

This work was supported by the Republic of Belarus state research program “Materials science, new materials and technologies”.

5. References

[1] Poplavsky V.V., *Nucl. Instrum. Meth. in Phys. Res.*, **B28**(4), 534, 1987; doi: 10.1016/0168-583X(87)90499-X

[2] Komarov F.F., and Poplavsky V.V., *Radiat. Effect*s, **106**(1–2), 1, 1988; doi: 10.1080/00337578808013724

[3] Basu S., *Fuel Cell Systems* [online], https://web.iitd.ac.in/~sbasu/FC-Descrip.pdf

[4] Toray Carbon Paper TGP-H-060 [online]; https://www.fuelcellearth.com/fuel-cell-products/toray-paper-060/

[5] Avcarb [online]; https://www.avcarb.com/product-page-paper/

[6] Iwasita T., *Electrochimica Acta*, **47**(22–23), 3663, 2002; doi: 10.1016/S0013-4686(02)00336-5
[7] Ye Wang, Shouzhong Zou, and Wen-Bin Cai, *Catalysts*, **5**(3), 1507, 2015; doi: 10.3390/catal5031507
[8] Poplavsky V.V., Dorozhko A.V., and Matys V.G., *J. Surf. Invest.: X-ray, Synchrotron and Neutron Tech.*, **12**, 1314, 2019; doi: 10.1134/S102745101905032X