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Nanoscale Catalysts Based on Platinum–Ruthenium and Platinum–Ruthenium–Tin Alloys: Synthesis from Appropriate Metal Complexes and the Use in Direct Methanol Electrooxidation

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Abstract—Bi- and trimetallic platinum–ruthenium and platinum–ruthenium–tin catalysts with different atomic ratios of the metals in the surface layer were obtained by deposition of appropriate metal complexes onto highly dispersed carbon black and characterized by X-ray powder diffraction, energy-dispersive X-ray spectroscopy, and transmission electron microscopy. Voltammetric measurements showed that the catalyst PtRu(3 : 1)/C provides the highest current densities of methanol oxidation, in agreement with the structural data as well as with the electrochemical and power characteristics of the membrane electrode assemblies tested in single direct-methanol fuel cells.

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INTRODUCTION

Alcohol-fuelled direct oxidation fuel cells (DAFCs), which involve no external reforming, are very attractive because of their considerably simplified design; this is one of the key factors when developing an efficient power source for portable devices. The catalytic activity of highly dispersed PtRu alloys for the synthesis of active anodic catalysts for methanol oxidation is widely covered in the literature [1–7]. The factors affecting the activity of PtRu/C catalysts include the alloy composition [2, 8], the even distribution of its constituents [8], the particle morphology and size [9], the electronic state [10–12], the presence of impurities crucial for the parameters of these catalysts, and the properties of carbon supports, which are important for characterization of bimetallic PtRu particles [13, 14]. Some researchers have noted the maximum catalytic activity in methanol oxidation for an equiatomic ratio of platinum and ruthenium [2]; according to other data, the catalyst is most active when its platinum content is 20–25 at % [15].

The current methods of coreduction or carbonylation of salts containing platinum and another metal not always enable these elements to be reliably combined because of their different reduction rates. An alternative method used by us involves the synthesis of precursors from so-called heterometallic clusters in which the platinum and another metal atoms surrounded by organic groups are in rigorous stoichiometric ratios and are either connected by a metal–metal bond or linked by bridging groups. Such clusters are prepared by so-called chemical assembly when, e.g., a dinuclear complex of one metal—the "unit" that comprises sulfur or phosphorus atoms bearing lone electron pairs—serves as a metal-containing ligand to an electron-deficient fragment ML_n (where M is another metal), which can be generated when low-valence transition metal complexes with cyclopentadienyl or carbonyl ligands are heated or exposed to UV light. In principle, this method can be useful in the synthesis of clusters with a widely varied set of framework metals.

Transmetalation of electron-saturated or electron-rich homonuclear clusters can be another promising approach that involves the replacement of isoelectronic metal-containing fragments to form a new heterometallic sulfide framework. For instance, the clusters $L_2PtFe_2S_2(CO)_6$ (where L is triphenylphosphine, cyclooctadiene, or dicyclopentadiene) have been obtained earlier in this way from L_2PtCl_2 and $Fe_3S_2(CO)_9$, and structurally characterized [16]. These clusters are soluble in organic solvents. Thermolysis of such compounds results in elimination of all the organic groups, leaving an inorganic heterometallic chalcogenide product. Its preset composition corresponds to the inorganic framework of the cluster.

Therefore, by impregnating an appropriate support material with a solution of a heterometallic cluster and by removing the organic environment of the metal framework by thermolysis under argon or in a reducing hydrogen atmosphere, one can obtain as homogeneous heterometallic particles as possible on the surface of the support. The Pt : M ratio in the metal framework of the cluster precursor, which can be widely varied, is retained in the final thermolysis product. The course of the thermolysis can be monitored using differential thermal analysis, thermogravimetry, and differential scanning calorimetry.

According to Adams et al. [17], the bimetallic nanoelectrocatalyst Pt–Ru obtained by pyrolysis of the cluster complex $Pt_2Ru_4(CO)_{18}$ shows high catalytic activity (five times that of the commercial Pt–Ru catalyst E-TEK) in methanol oxidation, with the platinum amount lowered by half [17]. Paillaud et al. have described bimetallic cluster precursors to Pd–Mo–P nanoparticles and demonstrated that mesoporous support materials are preferred for the formation of homogeneous nanoparticles [18].

In this study, we developed an approach to the synthesis of bi- and trimetallic electrocatalysts by thermolysis of individual Pt clusters, Ru complexes, and anhydrous tin chloride on highly dispersed carbon supports in a hydrogen atmosphere at 500°C. Earlier, it has been found that such catalysts are highly reproducible in composition and feature an even distribution over the carbon support, which provides the constancy and reproducibility of their characteristics [19–23].

EXPERIMENTAL

Synthesis of platinum–ruthenium and platinum–ruthenium–tin catalysts supported on Ketjenblack carbon black. (Ethoxydicyclopentadiene)platinum ethoxide $(C_{10}H_{12}OC_2H_5)_2Pt_3(OC_2H_5)_4$ was used as a starting platinum reagent for the synthesis of a heterometallic organic precursor. The ruthenium arene complex, namely, the (cymene)ruthenium dichloride dimer $[(CH_3)_3C_7H_5RuCl_2]_2$, and anhydrous tin(II) chloride were employed as its reaction partners. The first step of catalyst preparation involved ultrasonication of highly dispersed Ketjenblack carbon black (specific surface area 600 $m^2\ g^{-1}$) in CH_2Cl_2, whereupon appropriate mixed solutions of the precursors in CH_2Cl_2 (for the platinum and ruthenium complexes) or THF (for the former two + $SnCl_2$) were added dropwise. The solution turned almost colorless because of the adsorption of the complexes on carbon black. The reaction mixture was again exposed to ultrasound and evaporated to dryness *in vacuo* at 100°C. The resulting powder was placed in a quartz tube and heated in a hydrogen atmosphere at 500°C for 45 min. The catalysts obtained were cooled under hydrogen, which then was replaced by high-purity argon. The metal content of the catalysts was 30 wt % for binary systems and 32.8 wt % for ternary systems. Carbon black accounts for the balance (70 and 67.2 wt %, respectively). The atomic Pt : Ru ratio in the binary systems was 1 : 1 or 3 : 1; the ratio of the metals in the ternary system Pt–Ru–Sn was nearly 3 : 1 : 1.

The geometrical parameters and structures of the as-prepared catalysts and those exposed to electrochemical polarization were examined through a scanning electron microscope (SEM) with a Quanta 650 FEG field emission gun (FEI, the Netherlands). This instrument is fitted with an energy-dispersive X-ray detector (EDX) for chemical microanalysis of the objects under study.

X-ray powder diffraction was carried out on an Empyrean diffractometer (Panalytical) (filtered CuK_α radiation, standard Bragg–Brentano reflection geometry, no binder used).

Small-angle X-ray scattering (SAXS) studies were performed on a SAXSess diffractometer (Anton Paar). Samples in a nondissipative polymer envelope were examined at room temperature using a transmission geometry. The chamber with a sample inside was evacuated; Imaging plates were used as a detector. Experimental curves were normalized for sample absorption; a collimation correction was applied according to standard procedures. The size distribution of particles was calculated after subtracting the scattering curve of the initial carbon support using the Tikhonov regularization method (the GNOM program) [24].

The average particle size and the size distribution were also determined by transmission electron microscopy (TEM) on a Philips EM-301 instrument (accelerating voltage 80 kV).

Electrochemical measurements were carried out in a temperature-controlled standard three-electrode glass cell with a glassy carbon disk electrode (S = 0.07 cm^2) as a working electrode. Prior to the deposition of a catalyst, the working electrode was polished and washed with hot alkaline solution and water. A catalyst was deposited in a thin dispersed layer as follows. A weighed sample of the catalyst was mixed with water or aqueous ethanol, depending on the wettability. The resulting suspension was exposed to ultrasound, and then its aliquot was placed through a micropipette on the glassy carbon disk so that the total amount of platinum and ruthenium on the electrode was 2 μg. The suspension was dried in air at 60°C, and the catalyst was fixed on the electrode surface with a layer of liquid Nafion. For this purpose, the initial 5% Nafion solution (Aldrich) was diluted with water in a ratio of 1 : 100 and applied over the catalyst in an amount sufficient to form a film ~0.2 μm thick.

A platinum grid ~10 cm^2 in area served as an auxiliary electrode; the potentials were measured versus Hg/Hg_2SO_4/0.5 M H_2SO_4 as a reference electrode. The working electrolyte (1 M methanol in 0.5 M H_2SO_4) was prepared from H_2SO_4 (special purity grade), methanol (high-purity grade), and twice-distilled water. The operating temperature of the electrolyte was 50°C. The electrolyte was stirred with argon flow. All potentials are cited versus a hydrogen electrode in the same electrolyte.

During our studies, we noticed that prolonged cycling of the synthesized catalysts and a commercial PtRu(1 : 1)/C (used for comparison) reaction at anodic potentials results in their decreased tin and ruthenium contents because of a very small amount of the catalyst on the electrode. For this reason, the working electrode with the deposited catalyst was purified electrochemically by alternating application of three to five short pulses with potentials of 0.02 and 1.0 V. Then a voltammogram was recorded at a scan rate of 5×10^{-4} V s^{-1} from 0.2 to 0.9 V in the argon-stirred electrolyte. To estimate the free currents of methanol oxidation under conditions simulating the operating conditions for the anodes of fuel cells, we measured the current transients at a working electrode potential of 0.5 V. The true surface areas of the deposited catalysts were estimated by anodic oxidation of the monolayer of adsorbed carbon monoxide [25].

Electrochemical measurements were carried out on an EL-02.06 automated potentiostat connected to a personal computer. The experimental data were processed using standard software.

To study the activity of the catalysts obtained in methanol oxidation reaction under simulated conditions and in membrane electrode assemblies (MEAs) on their basis, we employed nanoscale catalysts of the formulas PtRu(1 : 1)/C, PtRu(3 : 1)/C, and PtRuSn(3 : 1 : 1)/C prepared as described above by deposition of appropriate metal complex precursors onto the Ketjenblack surface. The commercial 30% platinum–ruthenium catalyst PtRu(1 : 1)/C E-TEK was used for comparative estimation of the characteristics of these catalyst samples.

Membrane electrode assemblies were tested in dummy direct methanol fuel cells (DMFCs) using ElectroChem test fuel cells (USA) 5 cm^2 in working area on the TS-200-02 test stand. Atmospheric-pressure air with a natural moisture content was pumped on the cathode side at a rate of 100 mL min^{-1}. On the anode side, 1.5 M aqueous methanol was pumped by a flexible-hose pump at a rate of 10 mL min^{-1} at 40°C. The details of the electrode preparation are given in [26]. The discharge characteristics of DMFCs were estimated using cyclic voltammetry (CV); CV curves were recorded from the open-circuit voltage (OCV) to 0 V at a scan rate of 10 mV s^{-1} on an IPC-PRO potentiostat designed and manufactured at the Frumkin Institute of Physical Chemistry and Electrochemistry of the Russian Academy of Sciences. The discharge characteristics of MEAs were measured after their operating performance had been achieved through a great number of cycles in a potential range from OCV to 0 V.

The metal contents of the surface layers of the initial catalysts

Catalyst	Metal	Weight percent	Atomic percent
PtRu/C	Pt	14.73	1.15
	Ru	8.1	1.22
3PtRu/C	Pt	14.63	1.08
	Ru	2.79	0.4
3PtRuSn/C	Pt	18.93	1.59
	Ru	4.79	0.78
	Sn	4.47	0.62

RESULTS AND DISCUSSION

The surface compositions of the catalysts obtained in the initial state (i.e., before electrochemical tests) were calculated from energy-dispersive X-ray data and are summarized in table.

It should be noted that according to the EDX data (Fig. 1), the atomic ratio of the main components in the catalysts PtRu(1 : 1) and PtRu(3 : 1) vary in the surface layer from 1 : 1.06 to 1 : 1.65 and from 2.71 : 1 to 1.59 : 1, respectively; in the catalyst PtRuSn(3 : 1 : 1), the ratio of the main components varies as follows: (2.56–2.12) : (1.14–1.35) : 1. Therefore, the surface layer of the first catalyst is enriched in ruthenium, while the second catalyst has both regions with a nearly stoichiometric platinum content and platinum-depleted regions. The third catalyst shows a lower platinum content and a higher ruthenium content with respect to the third component (tin). Apparently, the aforementioned variation in the contents of the main components over the surface layer of the catalysts is due to the mutual diffusion of the components during the synthesis of the catalysts. At the same time, the empirical formulas of these three catalysts correspond to the following atomic ratios: Pt : Ru = 1 : 1, Pt : Ru =

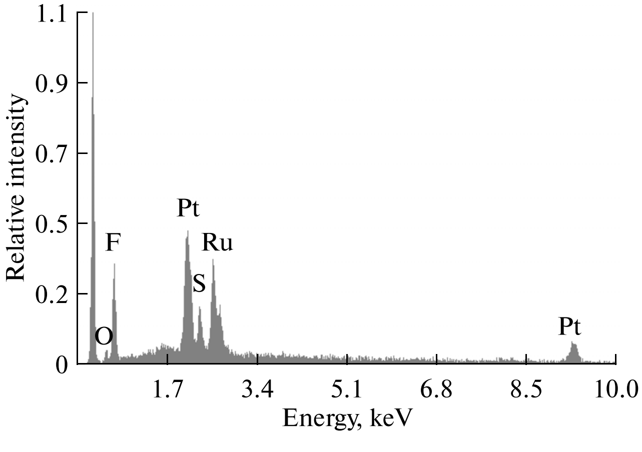

Fig. 1. Typical EDX spectrum of the catalyst PtRu/C.

3 : 1, and Pt : Ru : Sn = 3 : 1 : 1, respectively (MALDI MS data, an EMAL-2 instrument, ion photodetection, sensitivity level 10^{-4}–10^{-5} at %), which agree well with the stoichiometric amounts of the components used in the synthesis of the bimetallic and trimetallic catalysts. Similar enrichment of the surface layer in a less noble component has been observed earlier for alloys dispersed on carbon black [23].

The X-ray powder diffraction data for the catalysts PtRu/C, 3PtRu/C, and 3PtRuSn/C are shown in Fig. 2. The catalyst PtRu/C is most ordered and seems to be a solid Pt–Ru solution with a nearly equal atomic ratio of the components [27]. No individual ruthenium phase was detected in this sample. Unfortunately, it is difficult to draw definite conclusions about the phase compositions of the other two catalysts from the data obtained, probably because of the very small size or semiamorphous state of the particles under consideration.

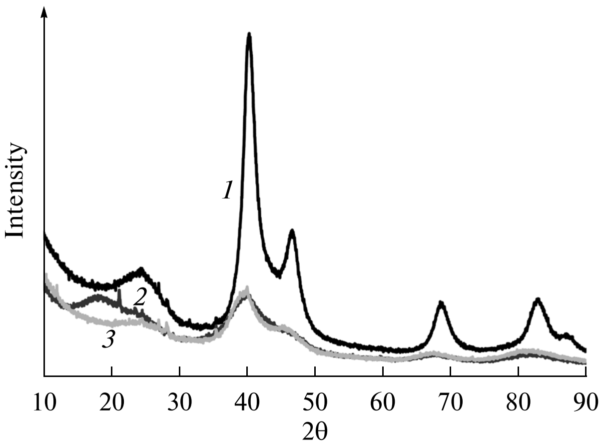

Fig. 2. X-ray powder diffraction spectra of the binary catalysts PtRu/C (*1*) and 3PtRu/C (*2*) and the ternary catalyst 3PtRuSn/C (*3*).

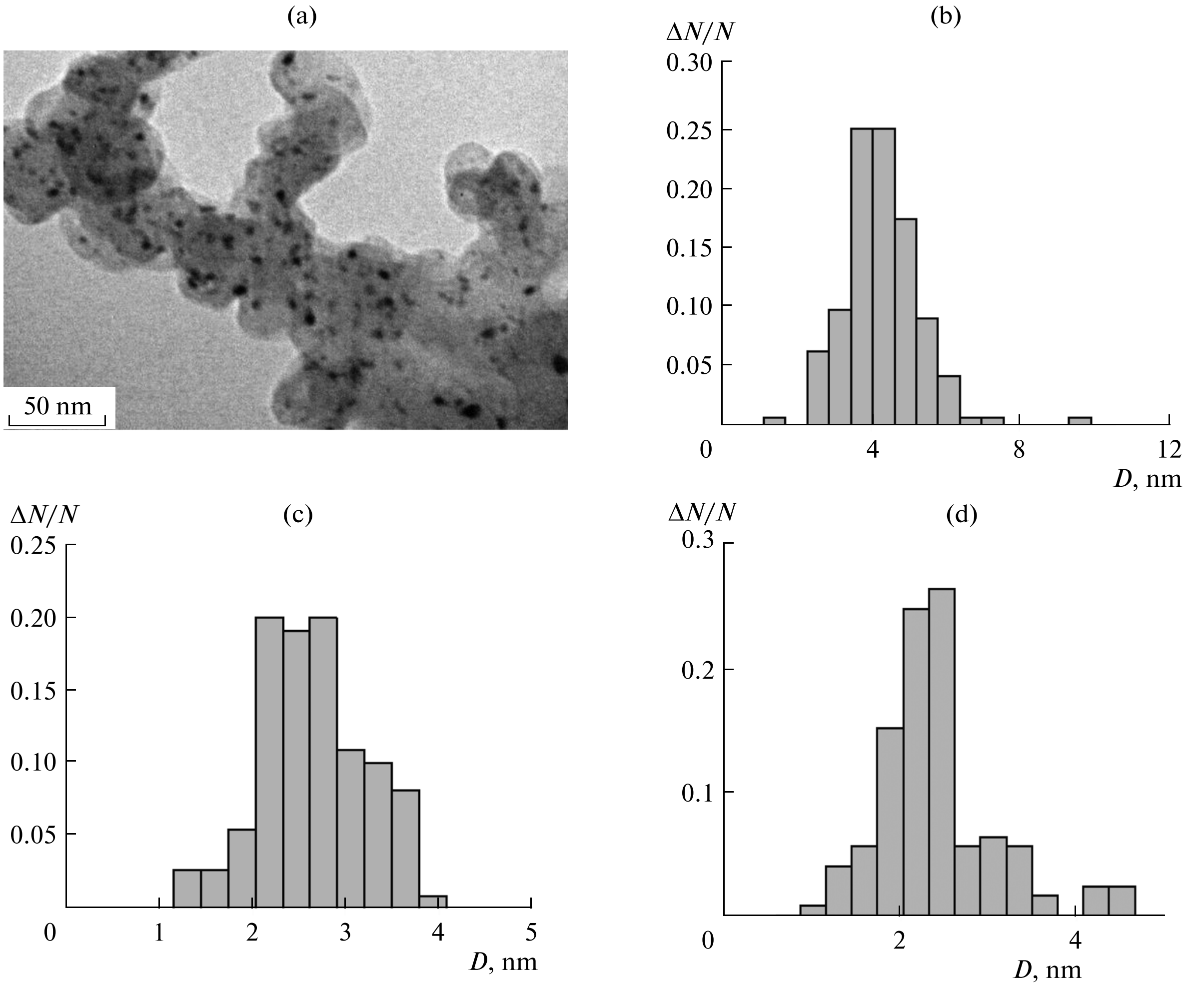

Fig. 3. Micrograph of the catalyst PtRu/C (a) and the bar charts showing the particle size distribution in the catalysts PtRu/C (b), 3PtRu/C (c), and 3PtRuSn/C (d).

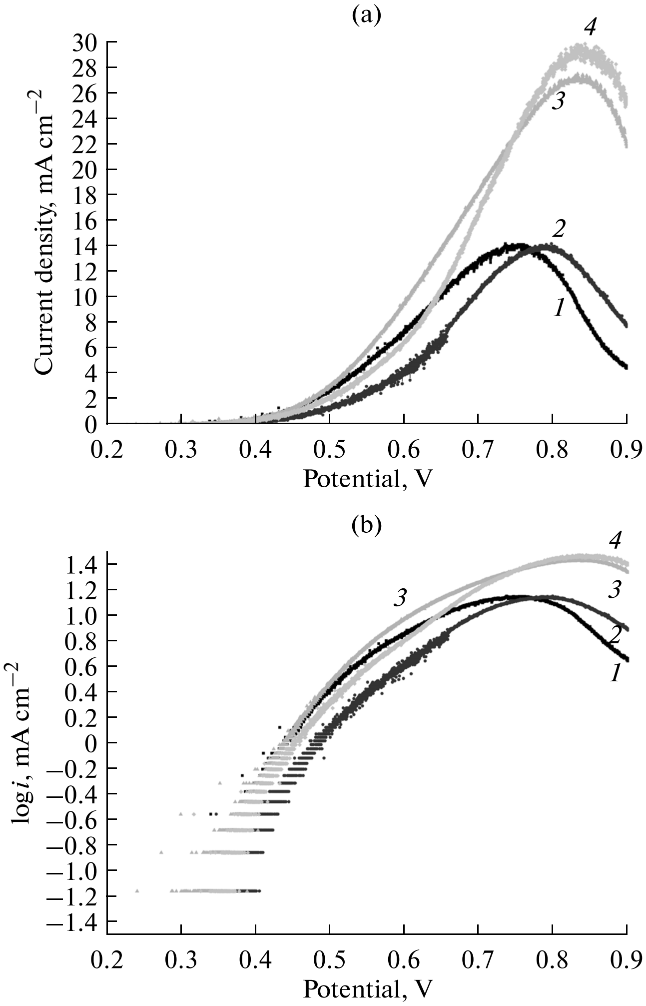

Fig. 4. Voltammograms (a) and the Tafel plots (b) for the oxidation of methanol at the commercial catalyst PtRu/C E-TEK (*1*) and at the synthesized catalysts PtRu/C (*2*), 3PtRu/C (*3*), and 3PtRuSn/C (*4*) in argon-stirred 1 M MeOH at 50°C. The supporting electrolyte is 0.5 M H_2SO_4; the scan rate is 5×10^{-4} V s^{-1}.

The phase composition of the PtRu/C sample was determined by comparison of its reflection range with the JCPDS–ICDD[1] database and the literature data.

The TEM data for the platinum–ruthenium and platinum–ruthenium–tin catalysts obtained are shown in Figs. 3a–3d. As can be seen in the micrograph and bar charts, the average particle size of the catalyst 3PtRu/C is 2.5 nm. In addition, a few particles are three to four nanometers in size. For the catalyst PtRu/C, the average particle size is 4 nm; some of its particles are as large as five to ten nanometers. The average particle size of the catalyst 3PtRuSn/C is 2.5 nm, with some larger particles present (up to 4.5 nm).

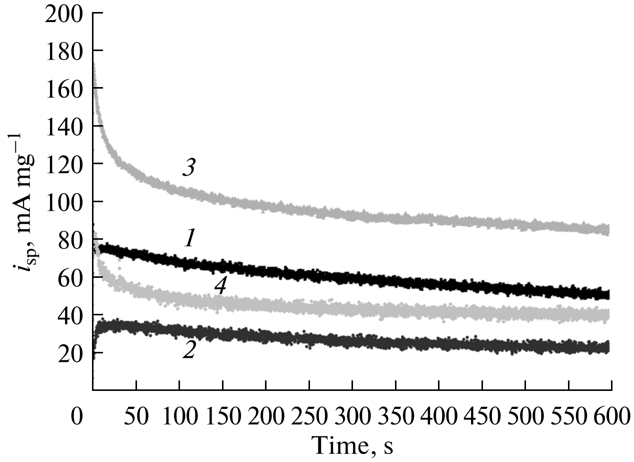

Fig. 5. Current transients of methanol oxidation at the dispersed catalysts PtRu/C E-TEK (*1*), PtRu/C (*2*), 3PtRu/C (*3*), and 3PtRuSn/C (*4*) in argon-stirred 1 M MeOH at 50°C. The supporting electrolyte is 0.5 M H_2SO_4; the electrode potential is 0.5 V.

Typical voltammograms of methanol oxidation in the presence of the catalysts studied are shown in Figs. 4a and 4b. It can be seen that the voltammograms are similar for all the catalysts. A distinction is that the ascending region of the voltammograms for the synthesized nanoscale catalysts is somewhat longer than that for the commercial catalyst. The nearly equal Tafel slopes (Fig. 4b) suggest that the electrochemical processes occurring at all the catalysts follow the same mechanism.

The current transients of methanol oxidation at the catalysts studied are shown in Fig. 5. They were recorded in an argon-stirred electrolyte at a constant potential of the working electrode (0.5 V). All plots are similar: an initial abrupt drop of the current is followed by a plateau. The highest current densities of methanol oxidation were observed for the catalyst 3PtRu/C, in agreement with the X-ray diffraction data: this catalyst has the smallest particles, which ensures the larger area of the electrochemically active surface and, accordingly, higher currents. The higher activity of this catalyst can also be due to a better wettability of its surface as compared to two other catalysts synthesized: the catalyst 3PtRu/C as well as the commercial catalyst PtRu/C E-TEK forms a stable suspension in water, while the other catalysts need aqueous ethanol to produce sufficiently stable suspensions. The insufficient wettability of a catalyst operating in an aqueous electrolyte may preclude full contact of a reactant with the catalytically active component, thus lowering the current of a reaction under study.

The aforementioned tests of the catalysts based on the platinum–ruthenium and platinum–ruthenium–tin alloys under simulated conditions revealed that the catalyst 3PtRu/C exhibits the highest electrocatalytic activity in methanol oxidation. For this reason, this

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[1] The Joint Committee on Powder Diffraction Standards–International Center for Diffraction Data (1999).

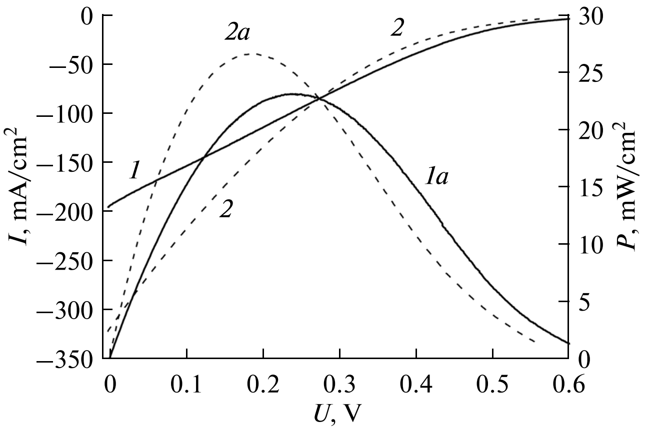

Fig. 6. Current (*1, 2*) and power densities (*1a, 2a*) in the discharge of the unit DMFCs on the base of the Nafion 117 membrane with the anode made up of the commercial catalyst PtRu/C (2 mg cm^{-2}; Cabot, USA) (*1, 1a*, solid lines) or the synthesized catalyst 3PtRu/C (2 mg cm^{-2}) (*2, 2a*, dashed lines). In both cases, 20% Pt/C (E-TEK, 2.5 mg cm^{-2}) was used as the cathode. The working solution was 1.5 M aqueous MeOH ($T = 40°C$).

catalyst was chosen as an anodic one when preparing a MEA on the base of a commercial membrane Nafion 117 (the commercial Pt(20%)/C E-TEK was used as a cathodic catalyst) tested in a unit DMFC. For comparison, we assembled and tested an analogous MEA containing a commercial anodic catalyst PtRu/C (Cabot, USA). The results obtained are shown in Fig. 6 as the plots of the current and power densities versus the voltage of the unit DMFC. It can be seen that the DMFC based on the synthesized anodic catalyst 3PtRu/C is similar in current and power characteristics to the DMFC containing the commercial anodic catalyst and is even superior to the latter at fuel cell voltages of 0.3–0.1 V.

To sum up, we obtained bi- and trimetallic nanoelectrocatalysts of the platinum–ruthenium and platinum–ruthenium–tin systems with different ratios of the metals. The synthesis involved deposition of appropriate metal complexes from their solutions onto highly dispersed carbon black followed by pyrolysis in a hydrogen atmosphere. We studied the electrooxidation of methanol at these catalysts and demonstrated that the catalyst 3PtRu/C is superior in specific activity to the bimetallic catalyst PtRu/C, the trimetallic platinum–ruthenium–tin electrocatalyst, and the commercial catalyst PtRu/C (E-TEK). The testing of a MEA containing the catalyst 3PtRu/C in a unit DMFC also revealed its high specific characteristics. Therefore, the catalyst 3PtRu/C obtained from platinum and ruthenium cluster complexes can be regarded as a promising anodic material for use in DMFCs.

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