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Nanostructured Platinum-Free Catalysts of Oxygen Reduction Based on Metal Chalcogenide Cobalt Clusters

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Abstract—Nanostructured catalysts were synthesized by deposition of cobalt selenide and telluride on highly dispersed carbon black from solutions of corresponding metal chalcogenide clusters. The catalysts were characterized by powder X-ray diffraction, energy dispersive X-ray spectroscopy, and scanning electron microscopy. The electroreduction of oxygen at these catalysts is accompanied by consumption of four electrons. The catalysts were shown to be tolerant to methanol.

Keywords: nanoelectrocatalysts, cobalt chalcogenides, electroreduction
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INTRODUCTION

The use of transition metal chalcogenides as catalysts of oxygen electroreduction for the cathodes of acid electrolyte fuel cells was first mentioned in the literature more than 40 years ago [1], but the interest in these compounds still persists, as indicated by appearance of papers and reviews addressing the latest achievements in this area [2–10]. As methods for preparation of metal chalcogenides, magnetron sputtering of thin films on glassy carbon or deposition of nanoparticles on carbon substrates [2–4] have been described in the literature. In other studies, thermal decomposition of cobalt carbonyl in organic solvents was carried out in the presence of surfactants (to prevent aggregation) giving monodisperse cobalt nanoparticles, which were then reacted with a chalcogen [5–10]. The authors of [11] demonstrated that with porous carbon-supported CoSe nanostructures prepared by the polyol technique, the oxygen reduction currents do not decrease in the presence of 2–10 mol/L of methanol, ethylene glycol, or formic acid. Similar results were reported [12] for glassy carbon-electrodeposited nanostructured Co_7Se_8, the activity of which towards oxygen reduction in the presence of methanol was compared with the activity of a platinum catalyst. Thus, data available from the literature indicate that electrocatalysts based on nanostructured cobalt selenide systems are distinguished by high tolerance to methanol and other alcohols and show rather high activity towards oxygen electroreduction. Meanwhile, the currentless potential of cobalt selenides in a 0.5 M H_2SO_4 solution is 0.5–0.7 V (versus RHE), which is much lower than this potential for Pt electrode [2]. Furthermore, the magnitude and mechanism of observed catalytic effects are determined by not only the nature of the binary catalyst, but also by the catalyst structure and phase composition, which are, in turn, dependent on the preparation procedure. When salts of different metals are reduced together, it is often impossible to obtain a catalyst of a specified composition and structure because of different metal deposition rates. We propose an alternative route to obtain catalysts based on metal chalcogenide clusters in which the metal and chalcogen atoms are directly linked to each other, occur in strict stoichiometric ratio, and are surrounded by organic groups. The organic groups ensure the solubility of the cluster in readily removable inert organic solvents and are themselves readily eliminated during pyrolysis. Having impregnated an appropriate support with a solution of the cluster and having removed the organic surrounding of the metal core via thermal destruction, one can obtain a homogeneous metal chalcogenide coating on the support surface. The metal and chalcogen nature and the component ratio in the precursor core can be varied over fairly broad ranges. A distinctive feature of the catalysts prepared by this method is highly reproducible composition and homogeneous distribution of the catalyst over the carbon support [13–19]. The nanodispersed layers of highly active catalysts (either supported on carbon or not) possess large specific surface

area, which allows considerable decrease in the catalyst loading. The influence of the catalyst preparation method on the structure, formation of surface alloys, oxidation state, and atomic ratio of components, and, as a consequence, on the catalytic activity is a significant problem of electrocatalysis.

This study is an attempt to evaluate the activity of catalysts based on cobalt selenide and telluride towards oxygen electroreduction not only under model conditions, but also directly in a single hydrogen–air fuel cell (HAFC), with chalcogenide being used as the catalytic layer supported on the gas-diffusion layer of an oxygen electrode. To our knowledge, no data on cobalt telluride-based catalyst are available from the literature.

EXPERIMENTAL

Preparation of cobalt telluride and cobalt selenide catalysts supported on Vulcan XC-72 carbon black. The cluster $Co_3(PhTe)_5(CO)_4$ (synthesized by the procedure described in [20], but with the reaction being conducted in heptane instead of benzene) and the cluster $[(CH_3)_4C_5H]_2Co_3(PhSe)_6$ (synthesized by the procedure used in [21], but without carborane addition) were used as metal chalcogenide precursors. The highly dispersed Vulcan XC-72 carbon black (specific surface area of 250–300 $m^2 g^{-1}$) to be used for catalyst preparation was pretreated by ultrasonication in benzene or dichloromethane, and then solutions of precursors in benzene or dichloromethane were added dropwise. Then the reaction mixture was sonicated again, the solvent was evaporated, the residue was dried in a vacuum at 100°C, then the temperature was raised to 450°C, and heating in a hydrogen atmosphere was continued for 45 min. After cooling in a high-purity argon atmosphere, the catalysts thus obtained contained 30 wt % metals and 70 wt % carbon black. The metal to chalcogen atomic ratio was determined by energy dispersive X-ray spectroscopy (EDX).

The geometric parameters and the structure of the catalysts were studied using a Quanta 650 FEG scanning electron microscope with a field effect cathode (FEI, the Netherlands). The energy-dispersive X-ray detector present in the instrument kit allowed conducting EDX analysis of the samples.

Powder X-ray diffraction (PXRD) analysis was carried out on an Empyrean (Panalytical) diffractometer using filtered CuK_α radiation. The measurements were carried out in the standard Bragg–Brentano (reflection) geometry. The samples were studied without binders.

The activities of the CoTe/C and CoSe/C cluster catalysts under model conditions were evaluated using the thin-film rotating disk electrode method, which has been used previously to determine the kinetic parameters of hydrogen oxidation and oxygen reduction on dispersed platinum catalysts immobilized on carbon supports [13, 17]. The kinetics of molecular oxygen reduction was studied in the 0.2–0.9 V range of potentials (here and below the potentials are given versus a hydrogen electrode in the same solution).

Electrochemical measurements were carried out in a standard undivided three-electrode glass cell. A platinum grid of ~10 cm^2 area was used as the auxiliary electrode and Hg/Hg_2SO_4/0.5 M H_2SO_4 served as the reference electrode. A rotating glassy carbon disk (S = 0.196 cm^2) served as the working electrode; prior to deposition of a catalyst layer, the electrode was polished and washed with a hot alkaline solution and water. A portion of the synthesized catalyst was mixed with water, and a Nafion solution (Aldrich sol. 5%) was added in an amount of 15% relative to the catalyst weight. The resulting suspension was sonicated, and an aliquot portion of this suspension was applied with a pipette on a glassy carbon disk (to chalcogenide content of 100–200 μg cm^{-2}) and dried in air at 60°C. A 0.5 M solution of H_2SO_4 prepared from special purity grade H_2SO_4 and deionized water served as the electrolyte. The solution was purged with argon or saturated with oxygen using the gases from gas cylinders. All measurements were carried out at room temperature.

The kinetics of electroreduction of molecular oxygen was studied by cyclic voltammetry in the potential range of 0.9–0.2 V at a 5 mV s^{-1} sweep rate with the electrode rotating at 600 to 2500 rpm. All electrochemical measurements were carried out using an EL-02.06 automated potentiostat connected to a PC.

The membrane electrode assemblies (MEAs) were tested in a single HAFC using ElectroChem (US) test fuel cell with a working area of 5 cm^2 on a G40 test bench (Hydrogenics, Canada) and an Elins potentiostat.

Oxygen was fed from the cathode side at a flow rate of 200 mL min^{-1} without additional moisturizing or excessive pressure, and hydrogen was fed from the anode side at a rate of 200 mL min^{-1} at 25°C. The electrode preparation details are presented in the relevant section. The discharge characteristics of the HAFC were estimated in the cyclic voltammetry (CV) mode. Cyclic voltammograms were measured in the range from the open circuit voltage (OCV) to 0 V at a sweep rate of 2.5 mV s^{-1}. The MEA discharge characteristics were measured when stable operating mode has been reached after prolonged cycling in the voltage range from the OCV to 0 V.

RESULTS AND DISCUSSION

According to EDX analysis data (typical spectra for CoTe/C and CoSe/C catalyst samples are shown in Fig. 1), the CoTe/C catalyst initially (i.e., before electrochemical testing) contained 3.01 at % Co and

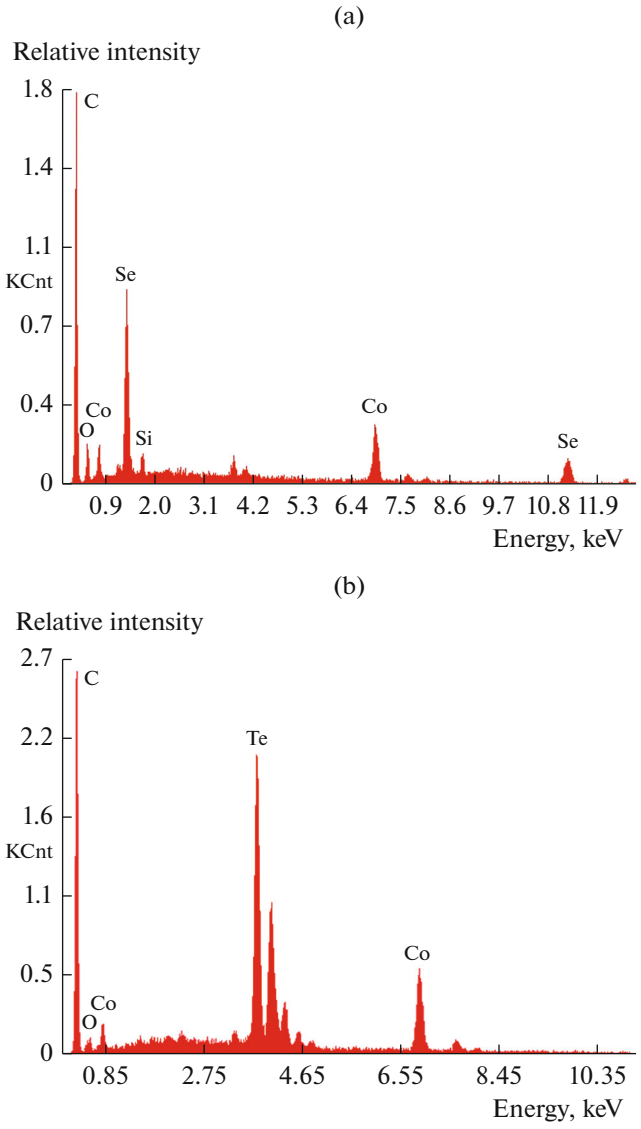

Fig. 1. Typical EDX spectra of (a) CoTe/C and (b) CoSe/C catalysts.

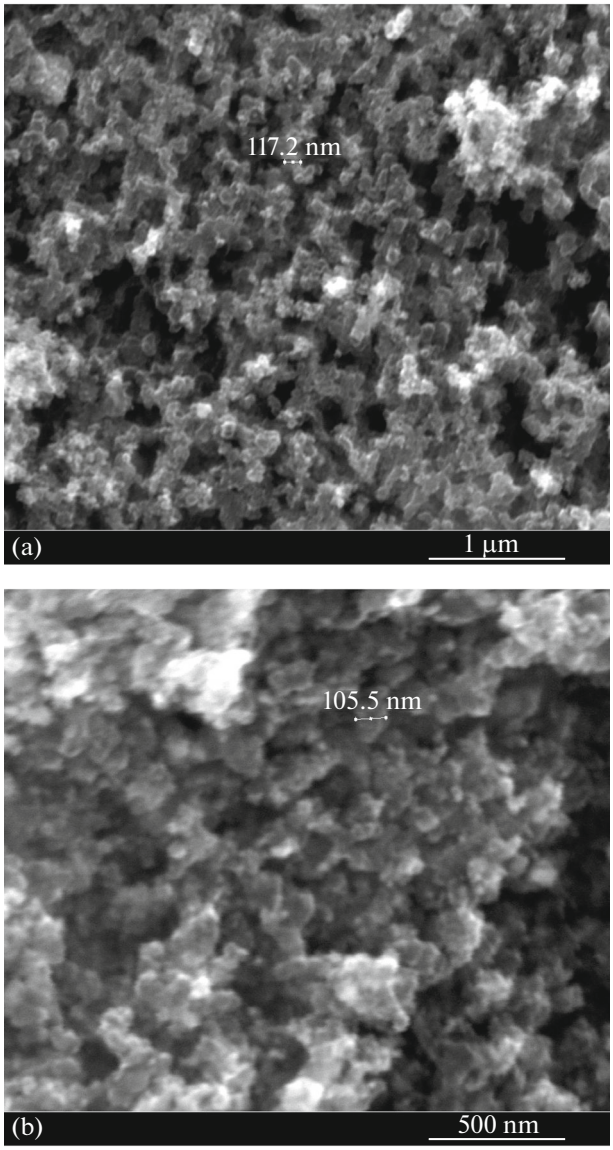

Fig. 2. Micrographs of (a) CoTe/C and (b) CoSe/C samples.

5.82 at % Te (Co : Te = 1 : 1.93). The synthesized CoSe/C catalyst contained 2.48 at % Co and 3.09 at % Se (Co : Se = 1 : 1.25).

According to scanning electron microscopy (SEM) data, the particle size in the CoTe/C and CoSe/C samples varied over a rather broad range from 20 nm (single particles) to 117 nm (particle aggregates), with larger particles predominating. The micrographs of the CoTe/C and CoSe/C samples are presented in Fig. 2.

The phase composition of the CoTe/C and CoSe/C metal chalcogenide catalysts was determined by PXRD. According to the results, the X-ray diffraction-based composition of CoTe/C is a mixture of approximately equal amounts of $Co_{1.11}Te_2$ (hexagonal phase, ICDD No. 01-089-4061) and $CoTe_2$ (orthorhombic phase, mattagamite, ICDD No. 01-089-2091) (Fig. 3a). The size of $CoTe_2$ crystallites calculated by the Scherrer formula is ~20 nm.

The composition of the CoSe/C catalyst is described as the $Co_{6.84}Se_8$ (or $Co_{6.8}Se_8$) phase, possibly, with some Co_3Se_4 (all phases are monoclinic, ICDD No. 01-074-4768, 01-074-4769, and 01-074-4766) (Fig. 3b). An unambiguous phase identification for this sample is substantially complicated by the existence of quite a number of cobalt selenides with different element ratios but similar X-ray diffraction patterns and X-ray diffraction peak broadening caused by small size of crystallites.

The cobalt selenide crystallite size in the CoSe/C catalyst is 17–22 nm; considerable lattice strain was

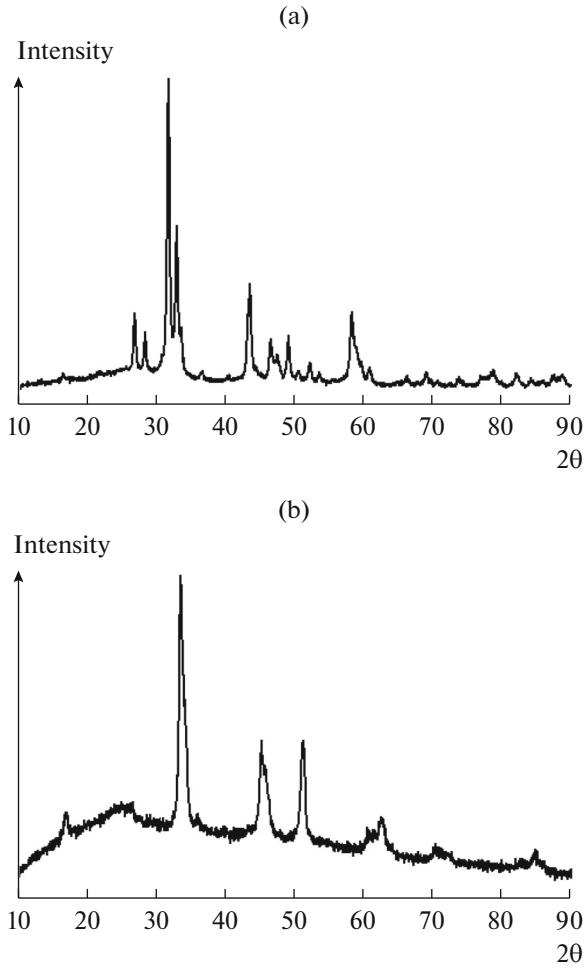

Fig. 3. X-ray diffraction patterns of (a) CoTe/C and (b) CoSe/C catalyst samples.

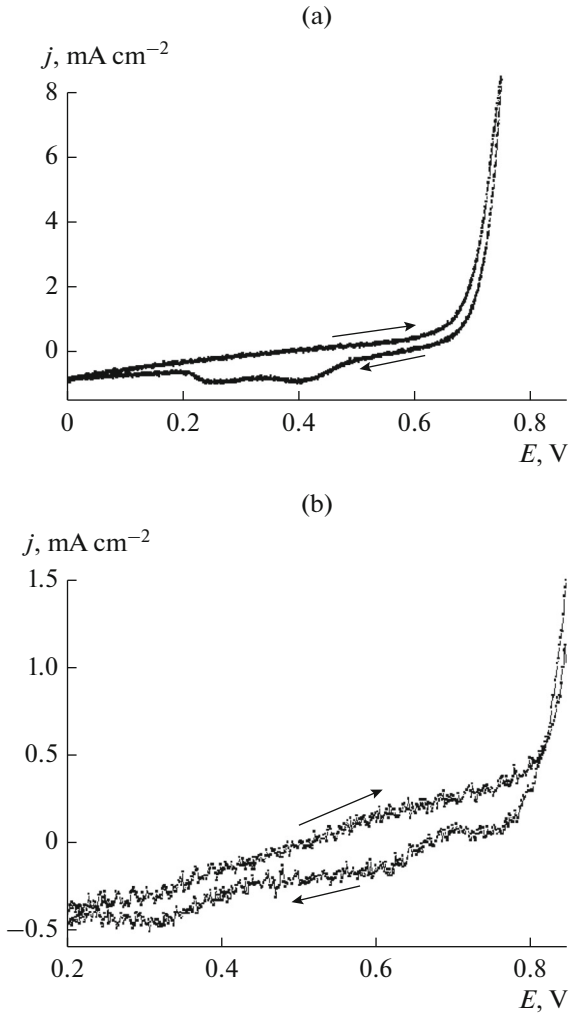

Fig. 4. CV curves of (a) CoTe/C and (b) CoSe/C samples in 0.5 M H_2SO_4. The potential sweep rate is 10 mV s^{-1}.

detected (Scherrer and Williamson–Hall calculations). It should be noted that the powder X-ray diffraction pattern of the CoSe/C sample synthesized here coincides with that of the CoSe/C catalyst obtained in [11] by the polyol method.

The grain size and composition determined by X-ray diffraction and electron microscopy were noted to coincide, which is indicative of predominance of monodomain selenide nanoparticles.

Figure 4 presents typical CV curves recorded in 0.5 M H_2SO_4 (argon-purged) in the 0–0.8 V potential range for the samples of CoTe/C and CoSe/C catalysts (chalcogenide content was 180 μg cm^{-2} in both cases). In the case of cobalt telluride (Fig. 4a) and selenide (Fig. 4b), the shift of the electrode potential to anodic region more positive than 0.7–0.8 V gave rise to increasing anodic currents, caused apparently by the dissolution of cobalt in the supporting electrolyte solution.

The cathodic part of the curve shows two clear-cut reduction peaks for the oxidation products at 0.4 and 0.25 V for cobalt telluride and at 0.6 and 0.32 V for cobalt selenide. A similar behavior of the nanostructured Co_7Se_8 catalyst has been noted in [12].

Figure 5 shows the voltammograms of oxygen reduction catalyzed by CoTe/C and CoSe/C measured on a rotating disk electrode in oxygen-saturated 0.5 M H_2SO_4 at atmospheric pressure and different electrode rotation rates. For both catalysts, the dependence of the current density on the electrode potential in the 0.85–0.2 V range has a typical shape observed for oxygen electroreduction in the presence of other metal catalysts, which is under kinetic control in the initial section and mixed activation-diffusion control at lower potentials. The oxygen reduction onset potentials are similar for both catalysts and are 0.79–0.81 V.

The plots for measured current densities (j) vs. the electrode rotation rate (w) in the Koutecky–Levich coordinates (shown in the insets of Figs. 5a and 5b) for the 0.2–0.5 V range are shaped as nearly parallel straight lines with a slope close to the theoretical value calculated

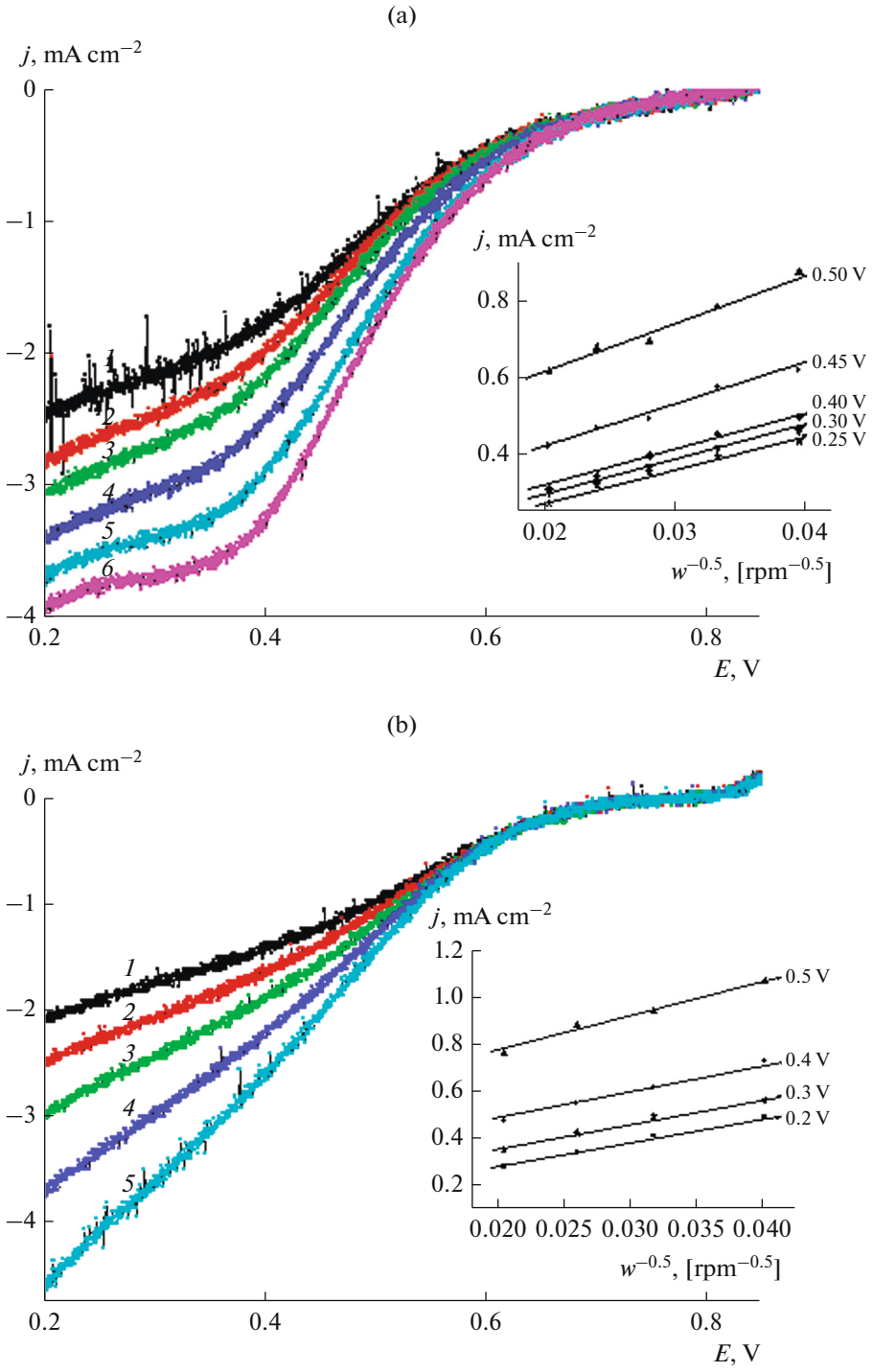

Fig. 5. Voltammograms of oxygen reduction at (a) CoTe/C and (b) CoSe/C in oxygen-saturated 0.5 M H_2SO_4 at electrode rotation rate (rpm): (a) (*1*) 325, (*2*) 620, (*3*) 1100, (*4*) 1400, (*5*) 2000, (*6*) 2500; (b) (*1*) 620; (*2*) 1100; (*3*) 1400; (*4*) 2000; (*5*) 2500. The potential sweep rate is 5 mV s^{-1}.

for a four-electron oxygen reduction to water, as was observed in [11, 12] for the CoSe/C catalyst.

It is noteworthy that in the presence of oxygen in the electrolyte, polarization of the CoTe/C catalyst to 0.9–1.0 V did not induce anodic currents of cobalt dissolution, although in the argon-purged electrolyte, noticeable oxidation currents were detected even at lower potentials (Fig. 4a). Probably, the oxides formed on the CoTe/C surface prevent its further corrosion (as opposed to CoSe/C for which anodic currents are

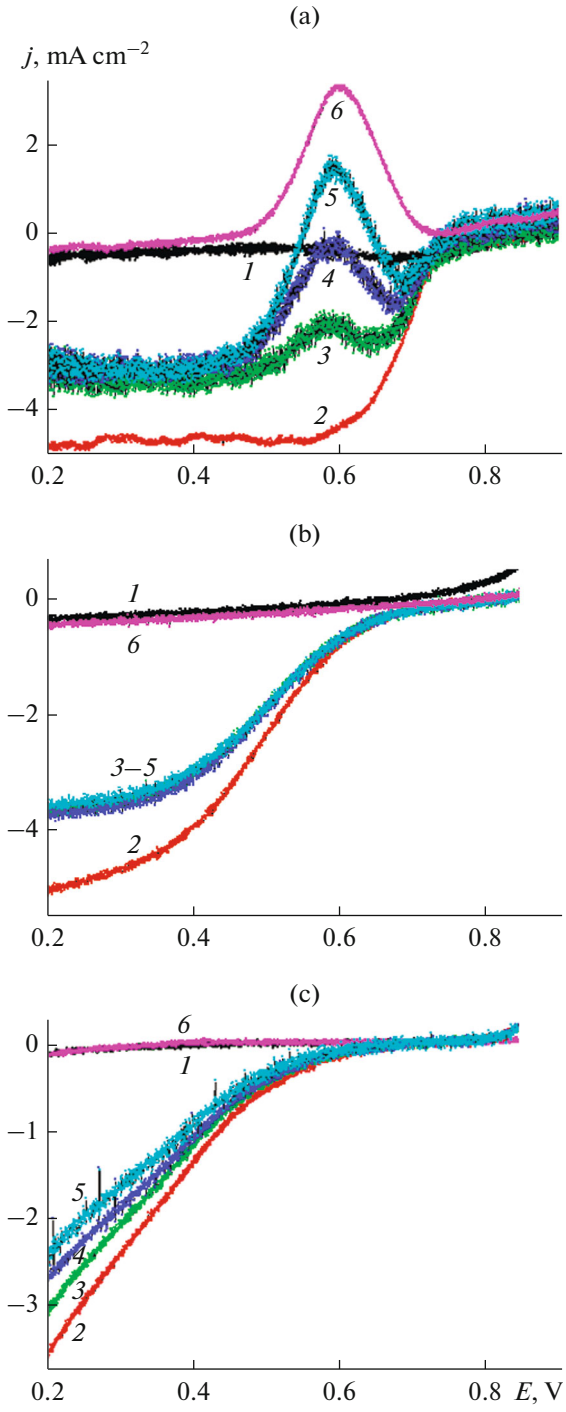

Fig. 6. Voltammograms measured on (a) Pt/C, (b) CoTe/C, (c) CoSe/C electrodes in 0.5 M H_2SO_4, (*1*, *6*) purged with argon and (*2*–*5*) saturated with oxygen under atmospheric pressure in the presence of methanol (mol L^{-1}): (a) (*1*, *2*) 0; (*3*) 0.05; (*4*) 0.1; (*5*, *6*) 0.2; (b) (*1*, *2*) 0; (*3*) 0.05; (*4*) 0.1; (*5*) 0.2; (*6*) 1; (c) (*1*, *2*) 0; (*3*) 0.1; (*4*) 0.2; (*5*, *6*) 1. The electrode rotation rate is 1800 rpm.

detected at potentials more positive than 0.8 V both in the absence and in the presence of oxygen), which may provide preservation of the catalyst activity during long-term operation.

Figure 6 shows the voltammograms of oxygen electroreduction at CoTe/C and CoSe/C catalysts measured in the electrolyte containing methanol in different concentrations. For comparison, Fig. 6a presents similar voltammograms for Pt/C (platinum loading at the electrode of 28 μg cm^{-2}). The presence of methanol in the solution leads to decreasing oxygen reduction currents at the platinum electrode. The higher the methanol concentration, the more pronounced this decrease, because of the competing methanol oxidation reaction proceeding in parallel (Fig. 6a, *6*). Unlike platinum, in the case of cobalt chalcogenides, no methanol oxidation takes place, and the potential of the onset of oxygen reduction does not change even at a considerably higher concentration of methanol in the solution (Figs. 6b and 6c, *6*). Some decrease in the oxygen reduction currents (most pronounced in the 0.2–0.4 V potential range and detected also at a Pt electrode) may be attributable to some other factors rather than the catalyst nature (for example, surface blockage by methanol as a result of adsorption, change in the oxygen near-electrode concentration and/or diffusion coefficient in aqueous alcohol and so on). However, it can be stated that CoTe/C and CoSe/C catalysts, although less active than the traditional catalysts, are highly tolerant to the presence of methanol (and, udging by the published data [11, 12], for a number of other low-molecular organic compounds). In view of the much lower cost of the catalysts based on cobalt chalcogenides compared with commonly used platinum catalysts, they can be considered as rather promising candidates for the application in direct oxidation fuel cells using organic fuels.

For the fabrication and testing of the MEA based on the Nafion XL membrane, we used 30% cobalt chalcogenide at the cathode and commercial 20% PtRu (1 : 1)/C catalyst at the anode. The MEA was a compact assembly incorporating a Nafion XL membrane (28 μm thick) sandwiched between the cathode and anode gas diffusion (GD) layers supporting the cathode and anode catalyst, respectively. The GD cathode and anode were fabricated by depositing the catalytic layer on a Sigracet 30BC GD layer (SGL Group, Germany) using the catalytic ink printing technique. The catalytic ink for the cathode was prepared from the catalyst based on the synthesized cobalt telluride, while the anode catalytic ink was based on commercial 20% PtRu (1 : 1) catalyst supported on the XC-72 carbon black (Cabot).

The following ink composition was employed to prepare GD cathodes: CoTe/C catalyst (94 mg), Nafion polymeric electrolyte (DuPont) as a solution in aqueous alcohol with a 15 wt % concentration and 0.86 g cm^{-3} density (0.51 mL), deionized water (2 mL), and isopropyl alcohol (4 mL). The mixture of these reagents was sonicated for 30 min in a Sonorex digital 10P bath, Bandelin; this gave a stable suspension, which was deposited with a spray gun on a 5 ×

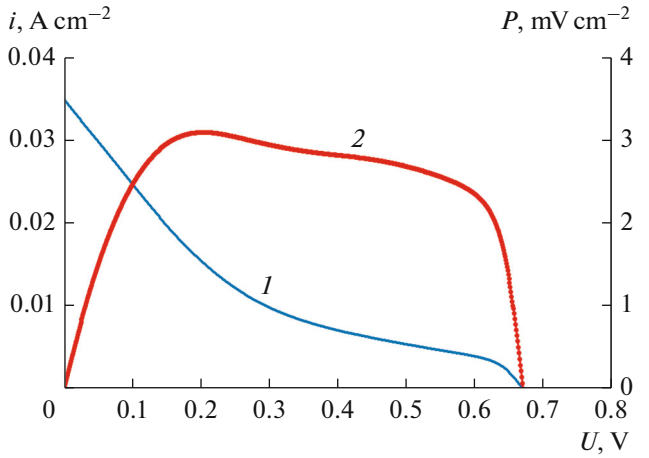

Fig. 7. (*1*) Current and (*2*) power density characteristics of the MEA with a CoTe/C-based cathode.

2.5 cm GD layer. The catalyst loading on the electrode was determined by weighing. The GD cathode contained the CoTe/C catalyst (5.1 mg cm^{-2}) and Nafion ionomer (3.5 mg cm^{-2}). The GD anode containing PtRu/C (1.25 mg cm^{-2}) and Nafion ionomer (3.5 mg cm^{-2}) was prepared in a similar way.

The MEA was formed by hot pressing of the gas diffusion anode and cathode to a proton-conducting membrane using a Carver semi-automatic press (USA) with heated plates at a pressure on gas diffusion electrodes of 50 kg cm^{-2} and a temperatuere of 135°C for 3 min. The MEA was tested using an Electrochem. Corp. test cell (5 cm^2 working surface area).

Figure 7 shows the current–voltage and power characteristics of MEA with the above-indicated catalytic and GD layers at hydrogen and oxygen pumping rates of 200 mL min^{-1}. The implemented specific power is rather stable over a broad range of fuel cell voltages (0.6 to 0.15 V) and is 2.5–3.25 mW cm^{-2}, reaching the maximum value at 0.2 V.

Thus, the results of testing of a single FC with a cobalt telluride-based cathode are consistent with the data obtained for the CoTe/C catalyst under model conditions. Although the specific characteristics of the tested FC are markedly inferior to those for FC based on the traditional platinum catalysts, it was demonstrated that platinum-free materials, in particular, cobalt chalcogenides, can be used in real fuel cells.

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