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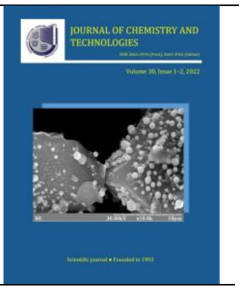

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ELECTROLYTIC GLUCOSE OXIDATION ON COMPOSITE MOLYBDENUM-CONTAINING COBALT COATINGS

Tatiana O. Nenastina,[1*] Mykola D. Sakhnenko,[2] Valeria O. Proskurina[2]

[1]*Kharkiv National Automobile and Highway University, 25 Yaroslava Mudrogo St., 61002, Kharkov, Ukraine*

[2]*National Technical University "Kharkiv Polytechnic Institute", 2 Kyrpychova St., 61002 Kharkiv, Ukraine*

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Abstract

Electrodeposition of refractory metals and zirconium in composite alloys with cobalt allows to obtain coatings with a unique combination of physicochemical properties that are unachievable while using other methods of covering. The coatings deposited by pulsed current can be considered as composite materials the oxide phase for which is formed directly in the electrode process as an intermediate of incomplete reduction of tungstates and hydrolysis of zirconium (IV) salts. It was found that oxygen and carbon are included in the composition of the coatings as well as the main components, thus such systems can be considered as composite. The topography of the films is distinguished by the presence of elliptical and spherical grains with crystallite sizes of 80–180 nm. On the surface of the coatings, there are hills (large grains) with a diameter of 1–3 µm. The anodic glucose oxidation on composite-coated electrodes has been studied and the participation of the intermediate metal oxides in the oxygen transfer has been revealed. Triple cobalt and refractory metal (Mo, W, Zr) alloy coatings were deposited from pyrophosphate –citrate electrolytes in the pulsed mode. Cyclic voltamperograms show that the Co-Mo-ZrO$_2$ alloys are characterized by the highest stability during the anode polarization due to the zirconium and molybdenum oxides added to their composition.

Keywords: composite coatings; electrochemical deposition; cobalt; refractory metals; catalytic materials.

ЕЛЕКТРОЛІТИЧНЕ ОКИСНЕННЯ ГЛЮКОЗИ НА КОМПОЗИЦІЙНИХ МОЛІБДЕНВМІСНИХ ПОКРИТТЯХ КОБАЛЬТУ

Тетяна О. Ненастіна,[1] Микола Д. Сахненко,[2] Валерія О. Проскуріна[2]

[1]*Харківський национальний автомобільно-дорожній університет, вул. Ярослава Мудрого, 25, м. Харків, 61002, Україна*

[2]*Національний технічний університет «Харківський політехнічний інститут», вул. Кірпичова, 2, м. Харків, 61002, Україна*

Анотація

Електроосадження композиційних покриттів кобальтом з тугоплавкими металами дозволяє отримувати покриття з унікальним поєднанням фізико-хімічних властивостей, недосяжних при використанні інших методів нанесення. Покриття, осаджені із застосуванням імпульсного струму, можна вважати композиційними матеріалами, оксидна фаза для яких утворюється безпосередньо в електродному процесі як інтермедіат неповного відновлення вольфраматів та гідролізу солей цирконію. Встановлено, що поряд з основними компонентами до складу покривів включаються оксиґен та карбон, і такі системи можуть розглядатися як композиційні. Топографія плівок відрізняється наявністю зерен еліптичної і сферичної форми з розмірами кристалітів 80–180 нм. На основній поверхні зустрічаються виступи (крупні зерна) діаметром 1–3 мкм. Досліджено анодне окиснення глюкози на електродах з композиційним покриттями і виявлено участь проміжних оксидів металів в перенесенні оксигену. Покриття потрійними сплавами кобальту з тугоплавкими металами (Mo, W, Zr) осаджені з пірофосфатно-цитратних електролітів в імпульсному режимі. Циклічні вольтамперограми показують, що сплави Co-Mo-ZrO$_2$ характеризуються найвищою стабільністю при анодній поляризації завдяки включенню до їх складу оксидів цирконію і молібдену.

Ключові слова: композиційні покриття; електролітічне осадження; кобальт; тугоплавкі метали; каталітичні матеріали.

**Corresponding author: e-mail address: nenastina@ukr.net*

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Introduction

The monosaccharide oxidation reaction is the bedrock of the contemporary methods that are used for the formation of many biologically active compounds. For example, the gluconic acid is formed by the D-glucose oxidation. The gluconic acid is attributed to the group of aldol acids and it is used by pharmaceutical and food industries. The food industry registered gluconic acid as a food additive E574, as a pH adjusting agent and the leaven. In addition, it is used as the acidifying agent, complexing agent and the antioxidant action booster. Gluconic acids are successfully used by the pharmaceutical industry to synthesize such important preparations as sodium-, calcium-, and iron gluconates and also glucono-d-lactone.

Gluconic acid can be formed using the method of chemical or electrochemical glucose oxidation (33 %), however, exactly microbiological methods (67 %) of its production are used on an industrial scale [1].

Actually, the microbiological method provides the softest monosaccharide oxidation. For these purposes, different strains of microorganisms and the enzymes extracted from them are used [2–6]. The drawbacks of this method are a high cost of the enzymes, the time-consuming process and the sensitivity of the microorganisms and enzymes to a change in the environmental factors that result in their inactivation [7].

Chemical oxidation of glucose has many drawbacks and specific features; in particular the outputs of desired product are rather moderate in most cases. It requires the use of special equipment and an ample amount of oxidizing agents that have an unfavorable effect on the environment.

In comparison to the chemical oxidation, the electrochemical method of the glucose oxidation is the most promising. The enzyme-free electrolytic method presupposes the electrocatalytic oxidation of glucose on modified electrodes to get gluconic acid. The electrochemical technologies are also among the methods that are widely used for the glucose oxidation and these are considered to be the most promising, because these exclude the use of the corrosive and toxic oxidizing and reducing agents and are relatively waste-free. The selectivity of the process of electrochemical oxidation is defined by the applied potential, the electrode nature [8-10] and modifying agents. Many scientific papers delve into the processes of the electrolytic oxidation of alcohols on composite coatings [11; 12], however, the processes that occur in glucose solutions have been studied insufficiently.

The purpose of this scientific paper was to study the anodic behavior of the composite electrolytic Co-Mo-WO_x and Co-Mo-ZrO_2 coatings in the alkaline medium in the presence of glucose.

Experimental procedure

Composite electrolytic Co-Mo-WO_x and Co-Mo-ZrO_2 coatings of at least 10 μm thick were deposited from biligand pyrophosphate citrate electrolytes [13] onto the steel substrate St.20 that was preliminary treated using the standard technique [14]. The compositions and the concentrations of the electrolytes are given in Table 1.

The electroplating of composite coatings with cobalt-based alloys was carried out in the pulsed current mode with the density of $i = 4$ A/dm^2 using the potentiostat PI-50-1.1 with the programmer PR-8 (table 1). The content of oxygen in deposited coatings, wt.%: Co-Mo-W – 12–15; Co-Mo-Zr – 10–12; due to incomplete reduction of oxometalates and incorporation of intermediate oxides in the alloys matrix. The electrolysis was conducted in the glass cell using parallel insoluble anodes made of stainless steel of a X18H10T grade and the volume current density was maintained at the level of 2 A/dm^3. The electrolyte temperature was maintained at the level of T = 22 °C.

The chemical composition of the obtained coatings was determined by a SPRUT spectrometer. The analysis was handled at least at 3 points, followed by averaging of the obtained values. The elemental composition and surface morphology of the coatings were analyzed on a ZEISS EVO 40XVP scanning electron microscope (SEM). Images were obtained by recording secondary electrons by scanning with an electron beam, which made it possible to study topography with high resolution and contrast. The error in content of the components measuring was ± 1 wt. %.

Cyclic voltamperograms were recorded for the platinum Co-Mo-WO_x and Co-Mo-ZrO_2 –coated electrode using the potentiostat PI-50-1.1 and the programmer PR-8, equipped with the special circuit board designed for the digital data recording. The measurements were taken using the standard three-electrode cell YASE-2, the auxiliary electrode in the form platinum spiral and the reference electrode i.e. the chloride silver half-cell. The electrooxidation processes were studied in alkaline water-glucose solutions that were prepared using analytically pure reagents with the distilled water.

Table 1

Composition of the electrolytes used for the deposition of composite cobalt coatings

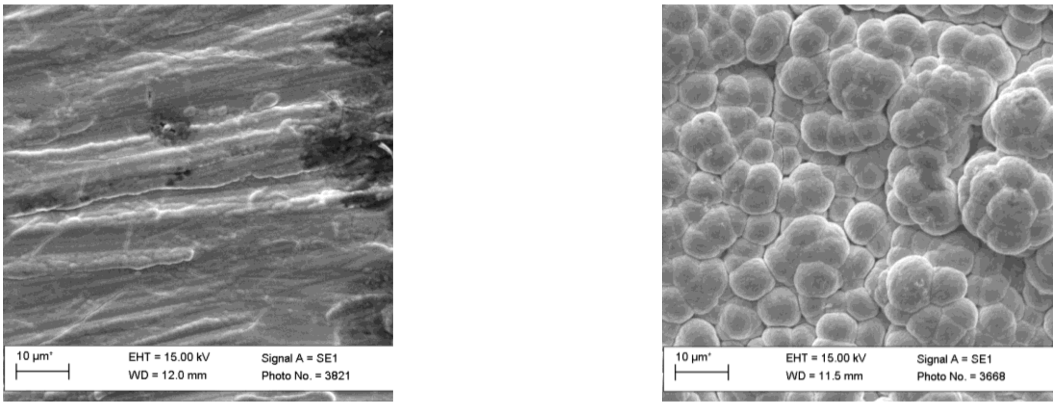
Electrolyte composition, mol/dm^3	Coating	
	Co-Mo-WO$_x$	Co-Mo-ZrO$_2$
$CoSO_4 \cdot 7H_2O$	0.2	0.15
$Na_2MoO_4 \cdot 2H_2O$	0.16	0.06
$Na_2WO_4 \cdot 2H_2O$	0.08	-
$Zr(SO_4)_2 \cdot 4H_2O$	-	0.05
$Na_3C_6H_5O_7 \cdot 2H_2O$	0.2	0.2
$K_4P_2O_7$	0.4	0.2
Na_2SO_4	0.5	0.5
pH	9–10	9–10
Composition (in the terms of metal)*, wt.%	Co –59.9; Mo –23.3; W – 16.8	Co – 62.1; Mo – 33.3; Zr – 4.6

The surface topology was analyzed using the scanning atomic force probe microscope (AFM) NT-206, by the contact method with the use of the probe CSC-37, cantilever B with the lateral solving capacity with the resolution of 3 nm. The scan area was fixed within 0.0×20.0µm and the surface relief height was fixed with the resolution of 256×256 pixels. The results were visualized through the relief reconstruction in the form of 2D and 3D topographic maps (the height is shown by color). The obtained AFM images were processed using programming product Explorer Software and analyzing the statistically average amplitude parameters of the surface coarseness in compliance with international standards, arithmetic-mean Ra (ISO 4287/1) that determines the surface roughness in the form of the two-dimensional arithmetic value and the root-mean-square value Rq (ISO 4287/1), that is the defining characteristic of the surface roughness. Based on the analysis data of the surface profile that was constructed along the section on topographic maps we defined the size and shape of the grains and the availability of the anisotropy of the properties All the structures showed the identity of surface characteristics for different scan sections that enabled the extrapolation of data to the characteristics of the test specimen on the whole.

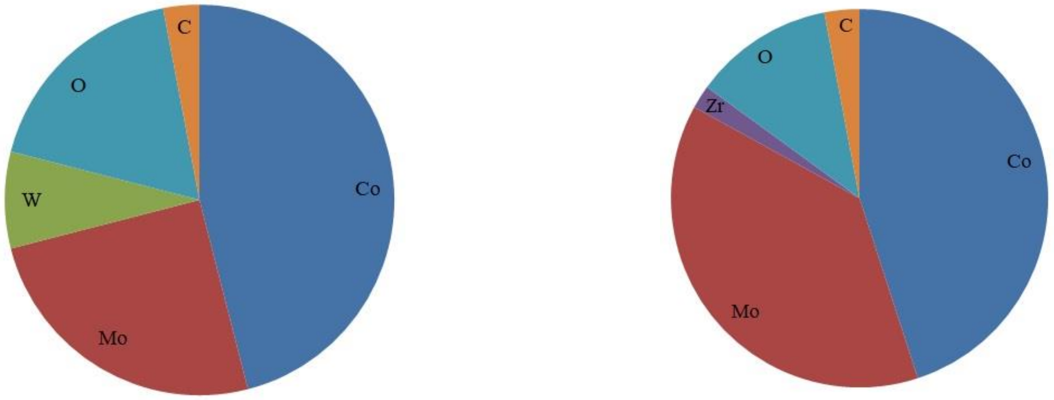
Results and discussion

The material science treats the roughness as a surface quality characteristic and it depends on the method of the material treatment. In the case of the deposition of galvanic coatings, this parameter reflects the substrate roughness degree and it depends on the method of the coating crystal formation, subsequent crystal growth and the speed ratio of these processes and simultaneously with the morphology it can be an additional indicator of the degree of the surface development [15; 16] that in its turn has an effect on the catalytic activity.

The analysis data of the surface morphology and its composition obtained for the specimens with cobalt-based composite coatings are indicative of the fact that a definite amount of carbon and oxygen was detected in addition to basic components, i.e. cobalt, molybdenum, tungsten and zirconium (Fig. 1).



a *b*

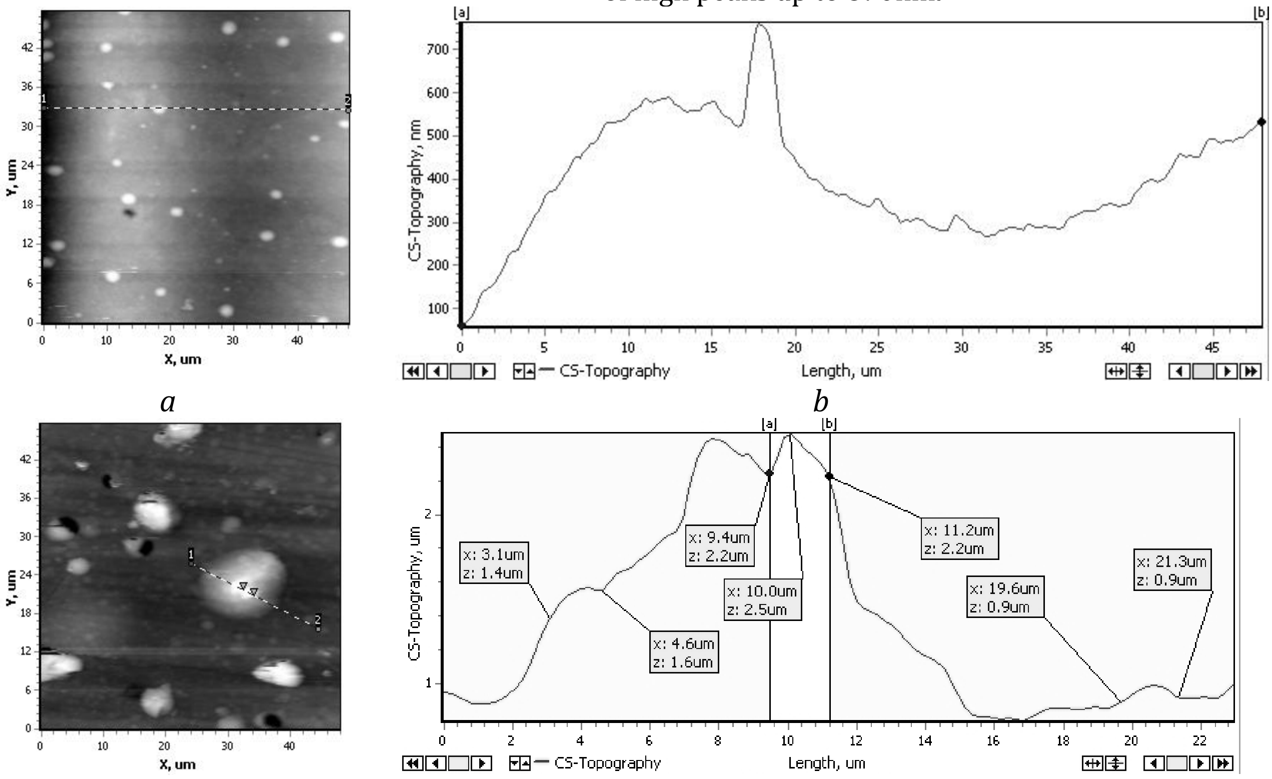


c *d*

Fig. 1. Morphology (a, b,) and composition (c, d) of composite coatings Co-Mo-WO$_x$ (a, c), Co-Mo-ZrO$_2$ (b, d)
Рис. 1. Морфологія (a, b) і склад (c, d) композиційних покриттів Co-Mo-WO$_x$ (a, c), Co-Mo-ZrO$_2$ (b, d)

It should be noted that the oxygen content is increased with an increase in the content of refractory components in the coatings. An increased content of molybdenum in the Co-Mo-ZrO$_2$ coating contributes to the formation of the uniform microglobular surface and the availability of zirconium provides a decreased cracking of the coatings (Fig.1 b). Such systems are viewed as composite electrolytic Co-Mo-ZrO$_2$ and Co-Mo-WO$_x$ coatings due to a considerable amount of oxygen in the composition that is related to the incomplete reduction of tungstate-ions and zirconium hydrolysis (IV) and also the nonuniform distribution of alloy components on the surface.

Composite Co-Mo-WO$_x$ coatings (Fig.2a, b) are characterized by the uniformly developed globular surface with the relief that differs essentially from that of the substrate. The studies of the topography of the coating surface using the AFM enabled the estimation of the grain size and the structure homogeneity of surface layers. Fig.2 shows that the coating consists of the grains of a spherical shape and it is characterized by a rather high structure density, homogeneity and uniformity with the availability of a small number of high peaks up to 870nm.



a *b*

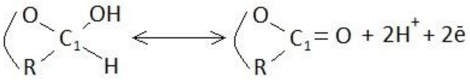
c *d*

Fig. 2. The 2D map of the surface (a, c), the intersection profile between the markers 1 and 2 (b, d) of the composite electrolytic Co-Mo-WO$_x$ (a, b) and Co-Mo-ZrO$_2$ (c, d) coatings. The scan area is 48x48 μm.

It was discovered earlier [17; 18] that the formation of the spheroid structure of the surface is conditioned exactly by the presence of refractory metals in composite electrolytic coatings (CEC).

The surface map of the Co-Mo-ZrO_2 [19], coating differs by more developed surface both in the case of the substrate and composite electrolytic Co-Mo-WO_x coating. The surface consists of uniformly distributed conic associates with the diameter of 5 to 7 μm (Fig. 3c, d) whose sizes exceed the indices of the Co-Mo-WO_x coating by 1.5 to 2.5 times. The analysis data of the surface intersection profile in the interval between the markers 1 and 2 are indicative of the formation of the small-size conically shaped grains of 0.3 to 0.3 μm and their aggregation into the crystallites with their size varying in the range of 1.5 to 3.5 μm.

The glucose oxidation mechanism consists [20] of the following stages: glucose in the form of a closed ring (α- or β- modifications) is subjected to the oxidation with the formation of glucono- β-lactone by the 2-electron reaction [21]:



Thereafter, glucono-β-lactone is hydrolyzed with the formation of gluconic acid. In addition to gluconic acid that is the basic product of the glucose oxidation glutaric acid, tartaric acid, glyoxalic, oxalic and methanoic acids are formed [22; 23]. The end oxidation products are CO_2 and water [23].

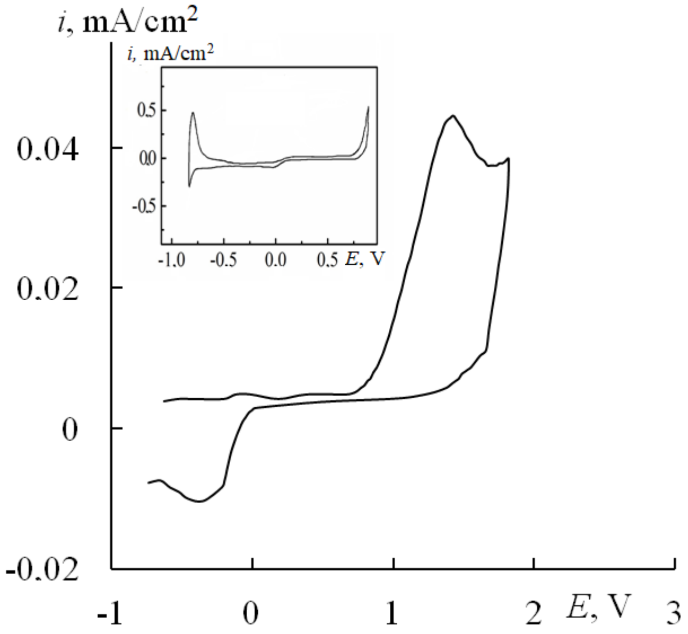
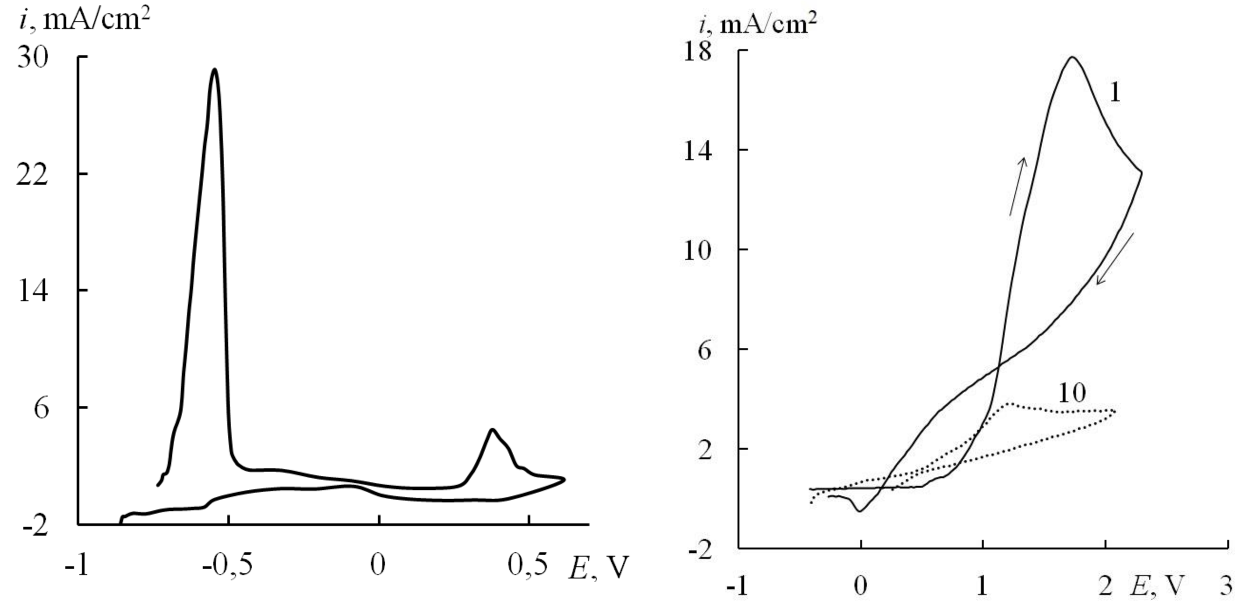


Fig. 3. Cyclic voltamperogram for the electrooxidation of the platinum electrode in the 1M $C_6H_{12}O_6$+ 0.1 M NaOH electrolyte, the framing insert is for the 0.1 M NaOH._*s* = 0,01 V/s

The electrocatalytic properties of the Co-Mo-WO_x and Co-Mo-ZrO_2 [24; 25] coated electrodes were studied in the model reaction of the glucose oxidation in the 1 M $C_6H_{12}O_6$ solution against the background of 0.1 M NaOH using the method of the cyclic voltamperometry (CVA) and these were compared with the electrochemical behavior of the platinum electrode in the analogous solution (Fig. 3).

The CVA of the platinum electrode gives us an opportunity to visualize one peak of the glucose oxidation with the half-peak potential $E_{pa/2}$ 1.1 V, and the current peak $i_{p/2}$ is equal to 0.023 mA/cm^2, while the reverse peak is five times less than the direct anode current peak. The potential difference of oxidation half-peaks $E_{pa}/2$ and the reverse half-peaks $E_{pc/2}$ exceeds 30 mV that is indicative of the irreversible behavior of the electrochemical reaction.

In contrast to platinum, the behavior of the Co-Mo-WO_x (Fig. 4*b*) and Co-Mo-ZrO_2-(Fig. 5*b*) coated electrodes has a different character, the anodic current peak is observed at more positive potentials of 1.6 V and 1.9 V, accordingly. The peak current of Co-Mo-ZrO_2-coated electrodes is within 31 mA/cm^2 (Fig. 5*b*) and it exceeds the Co-Mo-WO_x oxidation current peak and that of the platinum electrode by one order of magnitude (Fig. 4*b*).

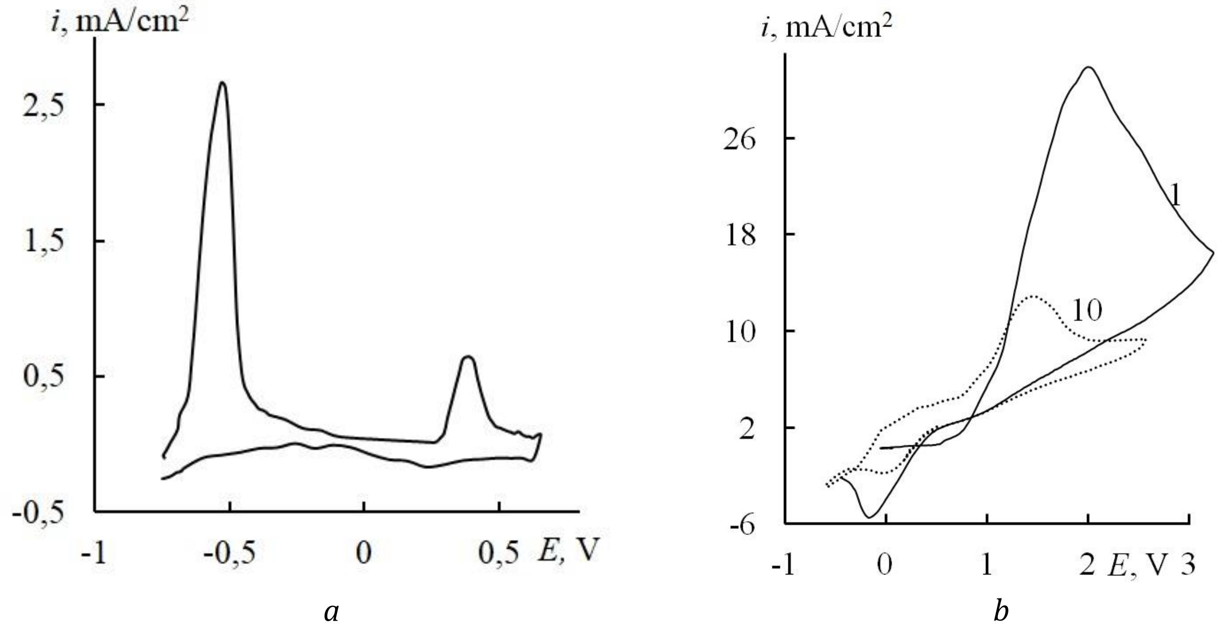


a *b*

Fig. 4. Cyclic voltamperogram for the electrooxidation of the composite Co-Mo-WO$_x$ coating in the0.1 M NaOH (*a*) and in the 1M $C_6H_{12}O_6$+ 0.1 M NaOH (*b*) electrolyte, *s* = 0,01 V/s

The availability of peak at E > 0.6 V (normal hydrogen electrode) is indicative of the fact that the adsorbed dehydrated glucose is oxidized with the formation of glucono-δ-lactone resulting in no breakdown of the C-O-C bond. Glucono-δ-lactone is slowly desorbed and with time it turns to glaconate due to the hydrolysis in the alkaline solution.

The analysis of cyclic voltamperograms in the 10th cycle is indicative of the fact that glucose and the products of its oxidation block the active centers on the electrode surface reducing thus the electrochemical activity of the electrode and it results in the reduced velocity of its oxidation.



a *b*

Conclusions

It was established that the refractory metal oxides that are formed on the surface of composite coatings are the catalytic centers in the glucose oxidation reaction. Such catalytic properties can be explained by a higher degree of the surface branching, and synergetic effect of cobalt, molybdenum, and zirconium, which are characterized by variable oxidation states and oxygen affinity.

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