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THE SYNTHESIS AND ELECTROCATALYTIC ACTIVITY OF PbO_2-POLYELECTROLYTE AND PbO_2-SURFACTANT COMPOSITE COATINGS

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Abstract

The regularities of the PbO_2-polyelectrolyte and PbO_2-surfactant composite coatings deposition have been investigated. On a cyclic voltammogram (CV) several characteristic areas can be distinguished: at the anode region of the CV at potentials higher than 1.4 V, the anode current is growing exponentially due to the simultaneous reactions of Pb(II) oxidation and the evolution of oxygen. At the cathodic branch of a CV, a current maximum is observed at potentials of 1.0–1.2 V, corresponding to the reaction of the reduction of lead dioxide. If the polyaminoguanidine hydrochloride is present in the electrolyte, the electrodeposition of lead dioxide is inhibited. If the anionic polymer additive Nafion® is in the electrolyte, one can see an increase in the peak of cathodic reduction of lead dioxide, which indicates an increase in the formation rate of PbO_2. The addition to the electrolyte of anionic surfactants leads to a slight inhibition of the process of deposition of PbO_2. As one can see from the experimental data, the adsorption of anionic surfactants is described satisfactorily by the Langmuir isotherm. Values of the limiting adsorption and the adsorption equilibrium constant were calculated. According to the results obtained, the anionic surfactants, cationic polyelectrolyte polyaminoguanidine hydrochloride and anionic polyelectrolyte Nafion® can be used as additives to the electrolyte during the deposition of the lead dioxide. It has been established, that they are being included into the growing deposit by forming the composite coatings with different composition and various electrocatalytic activity in the reaction of the evolution of oxygen. The content of organic compound in the oxide can vary from 2 to 16 w.%, a surfactant–oxide and polyelectrolyte–oxide composite coating is formed. The overpotential of the oxygen evolution decreases in the line $C_4F_9SO_3K > C_{12}H_{25}O_4SNa > C_{16}H_{29}O_6SNa$. It should be noted that the energy of adsorption on PbO_2 increases in the same line.

Keywords: polyelectrolyte; surfactant; lead dioxide; nitrate electrolyte; oxygen evolution reaction.

СИНТЕЗ ТА ЕЛЕКТРОКАТАЛІТИЧНА АКТИВНІСТЬ PbO_2-ПОЛІЕЛЕКТРОЛІТ ТА PbO_2-ПОВЕРХНЕВО-АКТИВНА РЕЧОВИНА КОМПОЗИЦИЙНИХ ПОКРИТТІВ

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Анотація

Досліджено закономірності електроосадження композиційних покриттів PbO_2-поліелектроліт і PbO_2-поверхнево-активна речовина. На циклічній вольтамперограмі можна виділити кілька характерних областей: на анодній гілці за потенціалів вище 1,4 В струм зростає експоненціально через одночасний перебіг реакцій окиснення Pb(II) та виділення кисню. На катодній гілці вольтамперограми спостерігається максимум струму за потенціалів 1,0-1,2 В, відповідно до реакції відновлення плюмбум(IV) оксиду. За наявності гідрохлориду поліаміногуанідіну в розчині, електроосадження плюмбум(IV) оксиду інгібується, тоді як наявність аніонної полімерної добавки Nafion® приводить до збільшення піку катодного відновлення плюмбум(IV) оксиду, що вказує на збільшення швидкості утворення PbO_2. Додавання в електроліт аніонних поверхнево-активних речовин приводить до незначного пригнічення процесу осадження PbO_2. Як видно з експериментальних даних, адсорбція аніонних ПАР задовільно описується ізотермою Ленгмюра. Були розраховані значення граничної адсорбції та константи адсорбційної рівноваги. Згідно з отриманими результатами, аніонні поверхнево-активні речовини, катіонний поліелектроліт поліаміногуанідін гідрохлорид і аніонний поліелектроліт Nafion® можуть використовуватися в якості добавок до електроліту осадження плюмбум(IV) оксиду. Встановлено, що вони включаються в оксид, утворюючи композиційні покриття з різним складом і електрокаталітичною активністю в реакції виділення кисню. Вміст органічної сполуки в оксиді може варіюватися від 2 до 16 мас.%, утворюючи композиційне покриття ПАР-оксид і поліелектроліт-оксид. Перенапруга виділення кисню зменшується в ряду $C_4F_9SO_3K > C_{12}H_{25}O_4SNa > C_{16}H_{29}O_6SNa$. Слід зазначити, що енергія адсорбційної взаємодії з PbO_2 збільшується в тому ж ряду.

Ключові слова: поліелектроліт; поверхнево-активна речовина; плюмбум діоксид; нітратний електроліт.

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СИНТЕЗ И ЭЛЕКТРОКАТАЛИТИЧЕСКАЯ АКТИВНОСТЬ PbO_2-ПОЛИЭЛЕКТРОЛИТ И PbO_2-ПОВЕРХНОСТНО-АКТИВНОЕ ВЕЩЕСТВО КОМПОЗИЦИОННЫХ ПОКРЫТИЙ

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Аннотация

Исследованы закономерности электроосаждения композиционных покрытий PbO_2-полиэлектролит и PbO_2-поверхностно-активное вещество. На циклической вольтамперограмме можно выделить несколько характерных областей: на анодной ветви при потенциалах выше 1,4 В ток растет экспоненциально из-за одновременных реакций окисления Pb(II) и выделения кислорода. На катодной ветви вольтамперограммы наблюдается максимум тока при потенциалах 1,0–1,2 В, соответствующий реакции восстановления диоксида свинца. При наличии гидрохлорида полиаминогуанидина в растворе, электроосаждение диоксида свинца ингибируется, тогда как наличие анионной полимерной добавки Nafion® приводит к увеличению пика катодного восстановления диоксида свинца, что указывает на увеличение скорости образования PbO_2. Добавление в электролит анионных поверхностно-активных веществ приводит к незначительному ингибированию процесса осаждения PbO_2. Как видно из экспериментальных данных, адсорбция анионных ПАВ удовлетворительно описывается изотермой Ленгмюра. Были рассчитаны значения предельной адсорбции и константы адсорбционного равновесия. Согласно полученным результатам, анионные поверхностно-активные вещества, катионный полиэлектролит полиаминогуанидин гидрохлорид и анионный полиэлектролит Nafion® могут использоваться в качестве добавок к электролиту осаждения диоксида свинца. Установлено, что они включаются в растущий осадок, образуя композиционные покрытия с различным составом и электрокаталитической активностью в реакции выделения кислорода. Содержание органического соединения в оксиде может варьироваться от 2 до 16 мас.%, образуя композиционное покрытие ПАВ-оксид и полиэлектролит-оксид. Перенапряжение выделения кислорода уменьшается в ряду $C_4F_9SO_3K$> $C_{12}H_{25}O_4SNa$> $C_{16}H_{29}O_6SNa$. Следует отметить, что энергия адсорбционного взаимодействия с PbO_2 увеличивается в том же ряду.

Ключевые слова: полиэлектролит; поверхностно-активное вещество; диоксид свинца; нитратный электролит.

Introduction

Lead dioxide electrodes are of considerable interest in their use at high anodic polarizations [1–3]. They can be obtained by electrodeposition from aqueous solutions and are characterized by high electrical conductivity, low cost, suitable corrosion resistance and high electrocatalytic activity in reactions proceeding at high anodic potentials with the participation of oxygen-containing radicals [1; 4; 5]. At the same time, lead dioxide-based materials have not yet had wide practical application, because of unsuitable mechanical properties, which are manifested when the composite metal-based dimensionally-stable anodes are being created, such as the bad adhesion of the active layer to the substrate, in particular. In this case, the rate of mechanical destruction of the oxide layer of a dimensionally-stable anode is proportional to the intensity of the evolution of oxygen. One of the ways to solve this problem is the surface treatment, the creation of a transition layer, the deposition of a catalyst on the another type of substrate, for example Ebonex® [6]. Another way is to create a composite material that would not be inferior in its properties to the base oxide, but at the same time will have lower internal stresses [7–11].

It is widely recognized, that the presence in the solutions for the deposition of various additives of ions and oxides of other metals has a significant effect on the composition, physico-chemical properties and electrocatalytic activity of the obtained lead dioxide based materials [7; 12–15]. At the same time, in contrast to metal coatings, the effect of organic additives on the regularities of PbO_2 electrodeposition and the properties of resulting materials remains virtually uninvestigated. Since the electrodeposition of lead dioxide is carried out at high anodic potentials, at which most organic compounds oxidize at a sufficiently high rate, the choice of additives is a significant problem. Based on the general considerations, water-soluble polymers (polyelectrolytes) may have value for its usage as an additive to the deposition electrolyte. The long polymer chain and high molecular weight of the polyelectrolytes would ensure the stability of this class of compounds in the range of PbO_2 electrodeposition potentials. In this paper, we investigated the effect of a polymer additive on the electrodeposition of lead dioxide, the composition and the properties of the materials obtained.

Experimental and Methods

All chemicals were of the class of reagents. Lead dioxide was electrodeposited from the nitrate electrolytes which contained 0.1 M HNO_3, 0.1 M $Pb(NO_3)_2$.

Platinized titanium was used as a sheet. It was treated as described in [7] before the platinum layer was deposited. The content of organic compounds varied within: $1\cdot10^{-6}$ to 0.01 M, depending on the purposes of the experiment. Electrolyte compositions and conditions of the deposition of composite coatings were selected in such a way that in all cases the current efficiency of lead dioxide deposition was about 100%.

Electrodeposition regularities of doped lead dioxide were studied on a Pt rotating disk electrode (Pt-RDE, 0.19 cm^2) by steady-state voltammetry, chronoamperometry. For the RDE experiments the voltammetry system SVA-1BM was used. The rate of the scanning potential was varied within 1÷100 mV/s depending on purposes of the experiments. Before an each experiment, the electrode surface was treated with freshly prepared mixture (1:1) of concentrated H_2SO_4 and H_2O_2 [7]. This preliminary treatment technique permits to stabilize the electrode surface, which is oxidized to a certain state under the action of strong oxidizing medium (the phase and chemical composition of the oxides on the surface is defined), which determines the favourable reproducibility in obtaining the cyclic voltammograms in the background electrolyte (0.1 M HNO_3). Voltammetry measurements were carried out in a standard temperature-controlled three-electrode cell.

The reaction of the evolution of oxygen was investigated by steady-state polarization on a computer controlled EG & G Princeton Applied Research potentiostat model 273A in 1M H_2SO_4. All potentials were recorded and reported vs. Ag / AgCl / KCl $_{(sat.)}$.

Adsorption measurements were carried out in 0.5 g of PbO_2 powder in 0.1 M HCl solutions containing various amounts of additive. It should be noted that the measurements were carried out with the presence of the indifferent electrolyte (0.1 M KCl), which shielded the electrostatic field of the oxide surface. The time for establishing the adsorption equilibrium was 24 hours. The content of organic substance was determined by the photocolorimetrical measurements after the extraction of ionic associate with chloroform.

Results and Discussion

The development of a technology sets the task of creating new composite polymer coatings or films that combine both metal and / or oxide properties and polymer properties (high elasticity and strength). The electrodeposition method has been well studied for the preparation of polymer films [16–19]. Electrodeposition is also an effective method in the manufacture of ceramic materials, as well as organoceramic films [20–22]. Electrodeposition of ceramic materials can be performed both in cathodic and anodic ways. At the same time the nanostructured ceramic films are formed. The main component of the formation of films is one that is used for the electrophoresis – a process in which the charged ceramic particles, which are dispersed in a solution, migrate in an electric field to the electrode. The formation of the composite occurs by coagulation of particles on the surface of the electrode. For a more successful deposition of ceramic films the electrolytes include various additives, such as polymers, which influence the formation of colloidal particles [23].

It should be noted that there are no data in the literature discribing the effect of polyelectrolytes on the regularities of electrodeposition and the physico-chemical properties of oxide materials, lead dioxide in particular.

In some cases, small amounts of ionic additives are included in the growing oxide, forming the micromodified materials based on lead dioxide [7; 12]. On this basis, it should be assumed that the addition of organic substances will also affect the electrodeposition, composition and the properties of the oxide materials.

At the beginning of investigation, polyelectrolytes and surfactants of various classes were selected.

Polyelectrolytes:

i) cationic

polyaminoguanidine hydrochloride;

acrylamide based polymer Magnafloc (Ciba);

ii) anionic

perfluorinated ionite Nafion® (Du pont).

Surfactants:

i) cationic

aethonium (1,2-ethylene-bis-(N-decyloxycarbonylmethyl-N, N-dimethylammonium) dichloride);

ii) anionic

potassium nonafluoro-1-butanesulfonate ($C_4F_9SO_3K$);

sodium dodecyl sulfate (SDS, $C_{12}H_{25}SO_4Na$);

sodium laureth sulfate (SLES, $C_{16}H_{29}SO_6Na$);

iii) non-ionic

nonoxynol-3 (monoalkyl ether of polyethylene glycol based on primary fatty alcohols).

Since the organic additives must be adsorbed on the surface of the oxide, the adsorprion of the compounds included in the PbO_2 has been investigated.

It was established that the adsorption of Nafion® (Fig. 1) and polyaminoguanidine hydrochloride (Fig. 2) on the surface of lead dioxide is described by an isotherm, similar to the Langmuir isotherm. The nature of the adsorption isotherm shows the high affinity of the adsorbate to the surface. Even at low concentrations, the magnitude of adsorption increases sharply and quickly reaches an almost constant value. As a result of potentiometric measurements, it was established that the adsorption of Nafion® on PbO_2 is accompanied by a shift of the zero charge point of the oxide to a region of higher pH. This suggests that the adsorption of polyelectrolyte at $pH < pH_0$ is caused by not only the electrostatic attraction of the polyanion to the positively charged surface of lead dioxide, but also, apparently, as a result of some specific interaction. This assumption is well-supported by the data on the adsorption material balance [24]. It was established that the adsorption of the polymer is accompanied by the release of OH^- ions. If we assume that the adsorption is carried out with the participation of the SO_3^- groups of the polymer, the release of hydroxide ions can be explained by the coordinating interaction of the polyanion with the lead surface cations on the surface of PbO_2:

$$\equiv PbOH + R_n(SO_3^-)_m \rightarrow \equiv Pb(SO_3^-)R_n(SO_3^-)_{m-1} + OH^- \quad (1).$$

With a decrease of the pH of the solution, the adsorption of Nafion® on PbO_2 increases significantly (see Fig. 1), which can be associated with both the increasing role of the electrostatic factor, caused by the increase in the positive charge of the oxide, and the transition of the polymer to the protonated form.

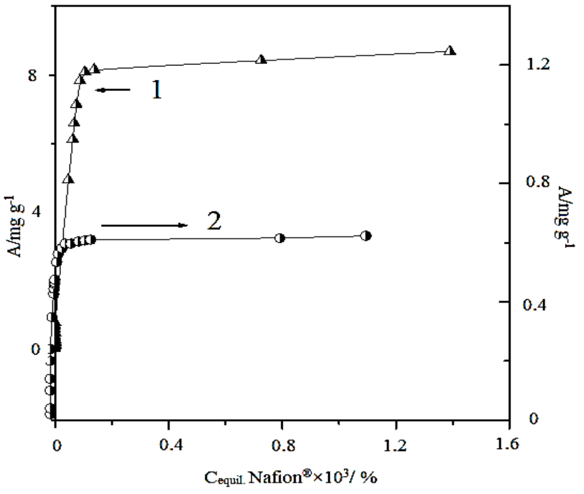

Fig. 1. The adsorption of anionic polyelectrolyte Nafion® on the lead dioxide in 0.1 M HCl (1) and H_2O (2)

The adsorption of Magnafloc is also specific, and its basic regularities are similar to those previously described for Nafion®.

As one can see from the experimental data, the adsorption of anionic surfactants is described satisfactorily by the Langmuir isotherm (Fig. 3).

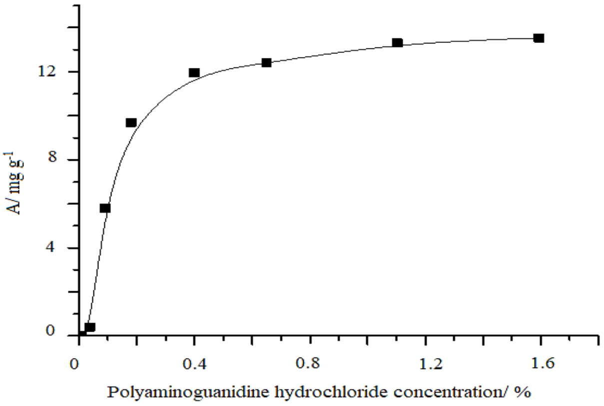

Fig. 2. The adsorption of cationic polyelectrolyte polyaminoguanidine hydrochloride on the lead dioxide in H_2O

In coordinates $A^{-1}=f(C^{-1})$, a linear dependence is observed (correlation factor 0.998), from which the values of the limiting adsorption and the adsorption equilibrium constant were calculated (Table 1).

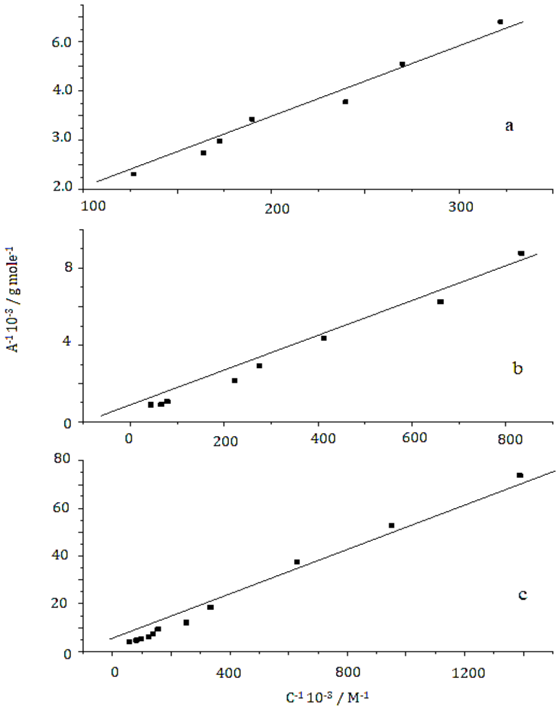

Fig. 3. The Langmuir isotherm of SDS (a), SLES (b) and potassium nonafluoro-1-butanesulfonate (c) on PbO_2 in linear coordinates

The values of the energy of adsorption interaction (–ΔG) are changed in line $C_{16}H_{29}O_6SNa$> $C_{12}H_{25}O_4SNa$ > $C_4F_9O_3SK$ and are 35.0; 34.1 and 31.5 kJ mol^{-1}, respectively. The obtained values indicate the electrostatic adsorption of anionic surfactants on the lead dioxide. This is also confirmed by a slight shift of the pH_0 of the oxide, which is 0.71±0.1 V in 0.1 M HNO_3 [7; 24].

Table 1

Adsorption parameters of anionic surfactants

Surfactant	Limiting adsorption A_∞ 10^3, mole g^{-1}	Adsorption equilibrium constant
$C_4F_9SO_3K$	3.07	6022.1
$C_{12}H_{25}SO_4Na$	3.72	17162.4
$C_{16}H_{29}SO_6Na$	4.15	24638.4

Non-ionic and cationic surfactants are not adsorbed on the positively charged PbO_2 surface.

The next step was to investigate the electrochemical stability of the organic additives which have an impact on the PbO_2 deposition potentials.

Cyclic voltammograms (CV) were taken on a Pt-electrode in a 0.1 M HNO_3 background electrolyte with the included additives (potential scan range 0–1.8 V). It was found that the cationic polyelectrolyte Magnafloc shows an electrochemical activity, forming a phase film on the electrode. In this regard, this polyelectrolyte is not of our interest in further research. The remaining additives, selected by the adsorption, did not show an electrochemical activity in the potential range under study. Thus, anionic polyelectrolyte Nafion®, cationic polyelectrolyte polyaminoguanidine hydrochloride and anionic surfactants can be used as additives to the lead dioxide deposition electrolyte.

To determine the effect of organic additives on electrodeposition of lead dioxide qualitatively, the cyclic voltammograms were obtained on a platinum electrode. On the CV (potential scan range 0.8–1.6 V) several characteristic areas can be distinguished [7, 25] (Fig. 4). At the anode region of the CV at potentials higher than 1.4 V, an anode current is growing exponentially due to the simultaneous reactions of Pb(II) oxidation and oxygen evolution. At the cathodic branch of the CV, a current maximum is observed at the potentials of 1.0–1.2 V, corresponding to the reaction of the reduction of lead dioxide:

$$PbO_2 + 4H^+ \rightarrow Pb^{2+} + 2H_2O + 2e^- \qquad (2)$$

As it was established earlier [7; 25], the area and size of the cathode peak characterizes the amount of oxide formed on the electrode surface, that allows one to use these parameters for a qualitative assessment of the PbO_2 electrodeposition rate.

The addition of polyelectrolytes into the deposition electrolyte affects the oxidation process of Pb^{2+} (Fig. 4). At the same time, the nature of the substance plays a significant role. When polyaminoguanidine hydrochloride is present in the electrolyte, the electrodeposition of lead dioxide is inhibited. With the presence of anionic polymer additive Nafion® in the electrolyte, one can see an increase in the peak of cathodic reduction of lead dioxide on the CV (see Fig. 4), which indicates an increase in the formation rate of PbO_2.

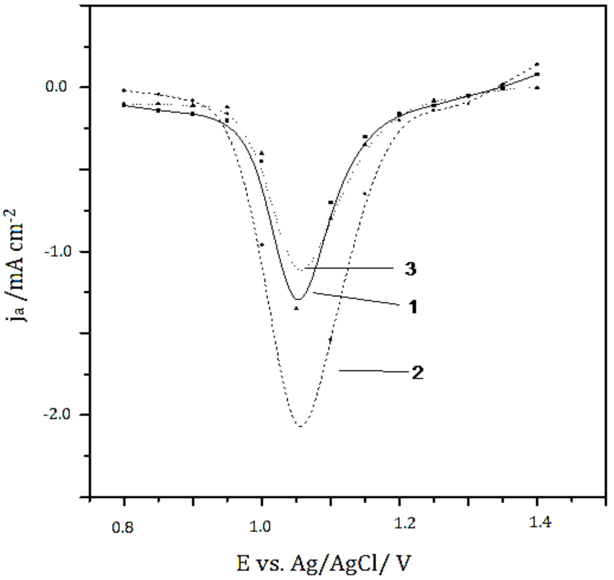

Fig. 4. Cyclic voltammograms cathodic branches (scan range 0.8 to 1.6 V) on Pt-DE in solutions containing 0.01 M $Pb(NO_3)_2$+0.1 M HNO_3 (1) + 0.2% Nafion® (2) or 0.2% of polyaminoguanidine hydrochloride. v=100 mV/s.

The addition to the deposition electrolyte of anionic surfactants leads to a slight inhibition of the process of deposition of PbO_2 (Fig. 5).

It was established that the additives chosen for further studies (anionic surfactants, polyaminoguanidine hydrochloride and Nafion®) are being included in the growing lead dioxide. The content of organic compound in the oxide can vary from 2 to 16 w.%, the surfactant–oxide and polyelectrolyte–oxide composite coating is formed (Table 2).

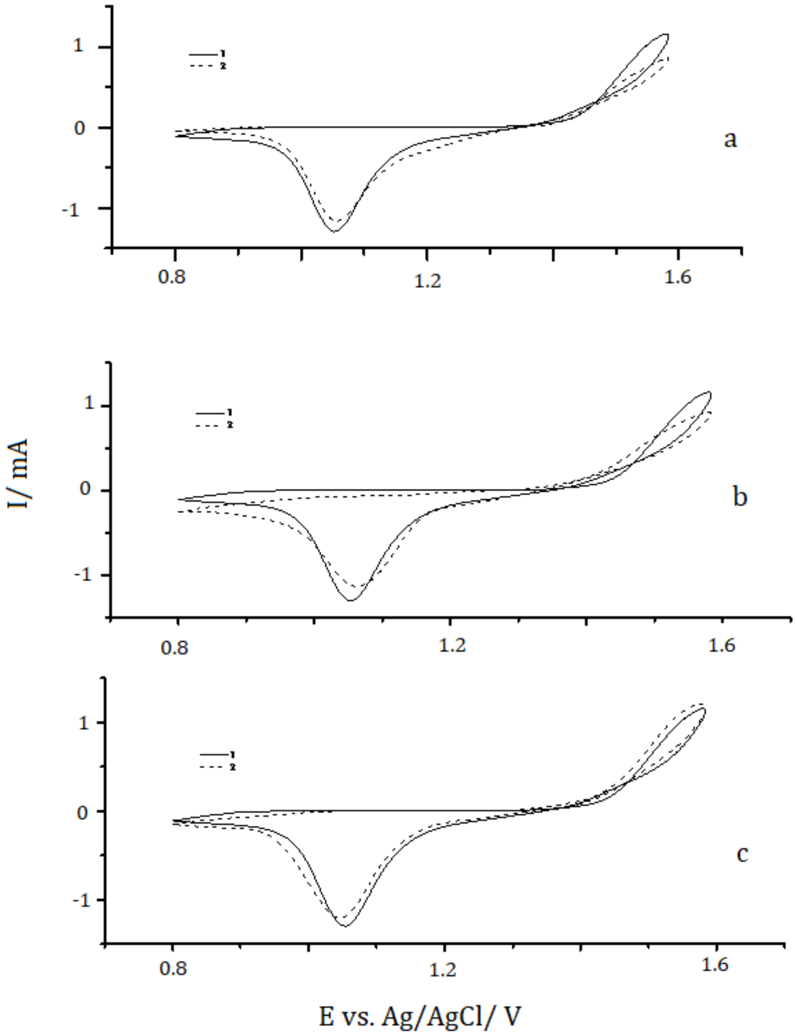

Fig. 5. Cyclic voltammograms (scan range 0.8 to 1.6 V) on Pt-DE in solutions containing 0.01 M $Pb(NO_3)_2$ + 0.1 M HNO_3 + 0.0003 M SDS (a); SLES (b); $C_4F_9SO_3K$ (c). v=100 mV/s.

Table 2

The content of polyelectrolytes anf surfactants in PbO_2-anodes due to deposition conditions

Solution, j_a= 4 mA cm^{-2}	w.%
0.1M HNO_3 + 0.1M $Pb(NO_3)_2$ + 0.02% polyaminoguanidine hydrochloride	1.9
0.1M HNO_3+ 0.1 M $Pb(NO_3)_2$+0.05% Nafion®	7.6
1M HNO_3+ 0.1 M $Pb(NO_3)_2$+ 0.005 M $C_4F_9O_3S$	16.2
0.1M HNO_3+ 0.1 M $Pb(NO_3)_2$+ 0.0007 M $C_{12}H_2$	4.2
0.5M HNO_3+ 0.1 M $Pb(NO_3)_2$+ 0.007 M $C_{16}H_{29}$	4.8

The inclusion of organic additives into the coating (like the ionic additives [12, 25]) can have a significant impact on physico-chemical properties of obtained materials, for example, on their morphology and structure.

It should also be assumed that the composite oxide-surfactant and oxide-polyelectrolyte materials will differ significantly in their electrocatalytic activity from lead dioxide. Since the vast majority of electrochemical processes at high anodic potentials occur with the participation of oxygen-containing particles which are adsorbed on the electrode (so-called oxygen transfer reactions), it is convenient to evaluate the nature of effects by changing the reaction rate of the evolution of the oxygen.

The rate of the process of the evolution of oxygen on composite materials depends on both the nature and the content of the additive in the oxide (Fig. 6). Thus, the overpotential for the evolution of oxygen decreases in the line $C_4F_9SO_3K$> $C_{12}H_{25}O_4SNa$> $C_{16}H_{29}O_6SNa$. It should be noted that the adsorption energy on PbO_2 increases in the same row. The nature and content of polyelectrolytes in lead dioxide also have a significant effect on the reaction of the evolution of oxygen (Fig. 7).

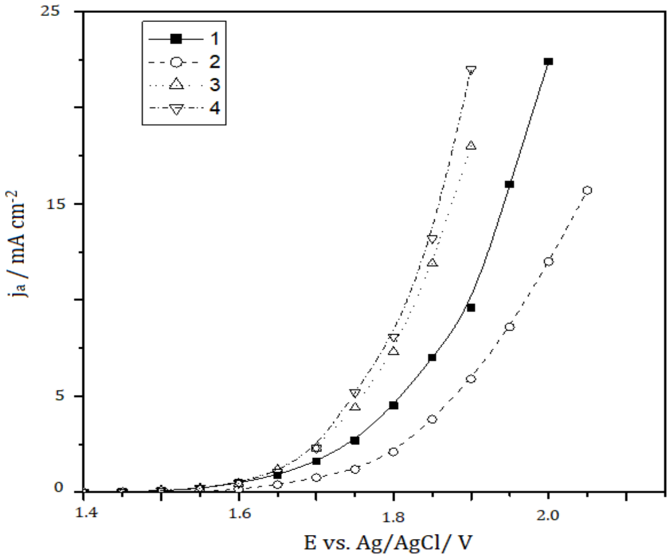

Fig. 6. Steady-state polarization curves of the evolution of oxygen in 1 M H_2SO_4 on the next electrodes: PbO_2 (1); PbO_2-2% $C_4F_9SO_3K$ (2); PbO_2-2.2 % $C_{12}H_{25}O_4SNa$ (3); PbO_2-2.4 % $C_{16}H_{29}O_6SNa$ (4).

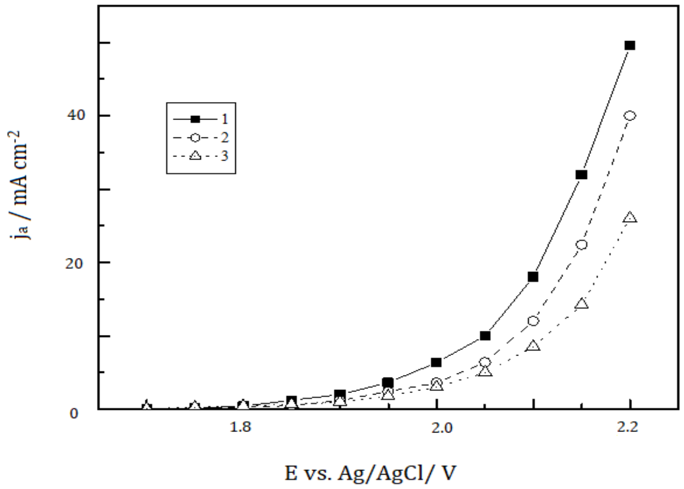

Fig. 7. Steady-state polarization curves of the evolution of oxygen in 1 M H_2SO_4 on the next electrodes: PbO_2 (1); PbO_2-2% polyaminoguanidine hydrochloride (2); PbO_2-6.6 % Nafion® (3)

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Conclusions

Thus, according to the results obtained, anionic surfactants, cationic polyelectrolyte polyaminoguanidine hydrochloride and anionic polyelectrolyte Nafion® can be used as additives to the electrolyte during the deposition of the lead dioxide. It has been established, that they are included into the growing deposit and form the composite coatings with different composition and various electrocatalytic activity in the reaction of the evolution of oxygen. The content of organic compound in the oxide can vary from 2 to 16 w.% and the composite surfactant–oxide and polyelectrolyte–oxide coating is formed. The overpotential for the evolution of oxygen decreases in the line $C_4F_9SO_3K$> $C_{12}H_{25}O_4SNa$> $C_{16}H_{29}O_6SNa$. It should be noted that the adsorption energy on PbO_2 increases in the same line.

Бібліографічні посилання

[1] Electrochemical oxygen transfer reactions: electrode materials, surface processes, kinetic models, linear free energy correlations, and perspectives. A review / R. Vargas, C. Borras, D. Mendez [et al.] // J. Solid State Electrochem. – 2016. – Vol. 20. – P. 875–893.

[2] evelopments in soluble lead flow batteries and remaining challenges: An illustrated review / M. Krishna, E. J. Fraser, R. G. A. Wills [et al.] // J. Energy Storage. – 2018. – Vol. 15. – P. 69–90.

[3] Electrocatalytic processes on PbO_2 electrodes at high anodic potentials / O. B. Shmychkova, V. A. Knysh, T. V. Luk'yanenko [et al.] // Surf. Engin. Appl. Electrochem. – 2018. – Vol. 54(1). – P. 38–46.

[4] Wu W. Recent development of mixed metal oxide anodes for electrochemical oxidation of organic

pollutants in water / W. Wu, Z.-H. Huang, T.-T. Lim // Appl. Catal., A. – 2014. –Vol. 480. – P. 58–78.

[5] Application of TiO2-nanotubes/PbO_2 as an anode for the electrochemical elimination of Acid Red 1 dye / J. E. L. Santos, D. C. de Moura, D. R. da Silva [et al.] // J. Solid State Electrochem. – 2019. – Vol. 23. – P. 351–360.

[6] Electrochemical properties of thermally treated platinized Ebonex® with low content of Pt / O. I. Kasian, T. V. Luk’yanenko, P. Yu. Demchenko [et al.] // Electrochim. Acta. – 2013. – Vol. 109. – P. 630–637.

[7] Electrodeposition of composite PbO_2-TiO_2 materials from colloidal methanesulfonate electrolytes / V. Knysh, T. Luk’yanenko, O. Shmychkova [et al.] // J. Solid State Electrochem. – 2017. – Vol. 21. – P. 537–544.

[8] Study of the mechanisms underlying the effects of composite intermediate layers on the performance of Ti/SnO_2 -Sb-La electrodes / Q. Bi, W. Guan, Y. Gao [et al.] // Electrochim. Acta. – 2019. – Vol. 306. – P. 667–679.

[9] Fabrication of Ga_2O_3 –PbO_2 electrode and its performance in electrochemical advanced oxidation processes / H. Du, G. Duan, N. Vang [et al.] // J. Solid State Electrochem. – 2018. – Vol. 22(12). – P. 3799–3806.

[10] Hydrogel-graphene oxide nanocomposites as electrochemical platform to simultaneously determine dopamine in presence of ascorbic acid using an unmodified glassy carbon electrode / J. Pereyra, M. V. Martinez, C. Barbero [et al.] // J. Compos. Sci. – 2019. – Vol. 3. –P. 1–14.

[11] Pouladvand I. Characterization and electrochemical behavior of Ti/TiO_2–RuO_2–IrO_2–SnO_2 anodes prepared by sol–gel process / I. Pouladvand, S. K. Asl, M. G. Hoseini, M. Rezvani // J. Sol-Gel Sci. Technol. – 2019. – Vol. 89. – P. 553–561.

[12] Shmychkova O. Physico-chemical properties of PbO_2-anodes doped with Sn^{4+} and complex ions / O. Shmychkova, T. Luk'yanenko, R. Amadelli, A. Velichenko // J. Electroanal. Chem. – 2014. – Vol. 717–718. – P. 196–201.

[13] Li X. Effects of twelve sodium dodecyl sulfate (SDS) on electro-catalytic performance and stability of PbO2electrode / X. Li, H. Xu, W. Yan // J. Alloy Compd. – 2017. – Vol. 718. – P. 386–395.

[14] Shmychkova O. Electrodeposition of Ni^{2+}-doped PbO_2 and physicochemical properties of the coating / O. Shmychkova, T. Luk'yanenko, R. Amadelli, A. Velichenko // J. Electroanal. Chem. – 2016. – Vol. 774. – P. 88–94.

[15] The electrochemical oxidation of salicylic acid and its derivatives on modified PbO_2-electrodes / O. Shmychkova, T. Luk’yanenko, R. Amadelli [et al.] // Bull. Dnipr. Univ. Ser. Chem. – 2017. – Vol. 25 (2). – P. 57–61.

[16] Walsh F. C. Developments in electrode design: structure, decoration and applications of electrodes for electrochemical technology / F. C. Walsh, L. F. Arenas, C. Ponce de Leon // J. Chem. Tech. Biotechnol. – 2018. – Vol. 93(11). – P. 3073–3090.

[17] Ratcliff E. R. Directed electrodeposition of polymer films using spatially controllable electric field gradients / E. R. Ratcliff, A. C. Hillier // Langmuir. – 2007. – Vol. 23. – P. 9905–9910.

[18] Darmanin T. Electrodeposited polymer films with both superhydrophobicity and superoleophilicity / T. Darmanin, M. Nicolas, F. Guittard // Phys. Chem. Chem. Phys. – 2008. – Vol. 10. – P. 4322–4326.

[19] Electrodeposition of insulating poly(phenylene oxide) films with variable thickness / M. Y. Timmermans, F. Mattelaer, S. Moitzheim [et al.] J. Appl. Polym. Sci. – 2917. – Vol. 134. – P. 44533–44540.

[20] Zhitomirsky I. The electrodeposition of ceramic and organoceramic films for fuel cells I. Zhitomirsky, A. Petric // JOM. – 2001. – Vol. 53. – P. 48–50.

[21] Recent advances in complex functional materials: from design to application L. E. La Porta, F. de Almeida (Eds.) Springer Int. Publ., 2017.

[22] Tian Q. Electrophoretic deposition and characterization of nanocomposites and nanoparticles on magnesium substrates / Q. Tian, H. Liu // Nanotechnology. – 2015. – Vol. 26. – P. 175102–175108.

[23] Electrodeposited Ni-based magnetic mesoporous films as smart surfaces for atomic layer deposition: an "all-chemical" deposition approach toward 3D nanoengineered composite layers / J. Zhang, A. Quintana, E. Menendez [et al.] // ACS Appl. Mater. Interfaces. – 2018. – Vol. 10(17). – P. 14877–14885.

[24] Nafion effect on the lead dioxide electrodeposition kinetics / A. B. Velichenko, T. V. Luk'yanenko, N. V. Nikolenko [et al.] // Russ. J. Electrochem. – 2007. – Vol. 43. – P. 118–120.

[25] Bi-doped PbO_2 anodes: electrodeposition and physico-chemical properties / O. Shmychkova, T. Luk'yanenko, A. Velichenko [et. al.] // Electrochim. Acta. – 2013. – Vol. 111. – P. 332–338.

References

[1] Vargas, R., Borras, C., Mendez, D., Mostany, J., Scharifker, B.R. (2016). Electrochemical oxygen transfer reactions: electrode materials, surface processes, kinetic models, linear free energy correlations, and perspectives. A review. *J. Solid State Electrochem*., *20*, 875–893. doi:10.1007/s10008-015-2984-7.

[2] Krishna, M., Fraser, E. J., Wills, R. G. A., Walsh, F. C. (2018). Developments in soluble lead flow batteries and remaining challenges: An illustrated review. *J. Energy Storage*, 15, 69-90. doi: 10.1016/j.est.2017.10.020.

[3] Shmychkova, O. B., Knysh, V. A., Luk’yanenko, T. V., Amadelli, R., Velichenko, A. B. (2018). Electrocatalytic processes on PbO_2 electrodes at high anodic potentials. *Surf. Engin. Applied Electrochem.*, 54(1), 38-46. doi: 10.3103/S1068375518010143.

[4] Wu, W., Huang, Z.-H., Lim, T.-T. (2014). Recent development of mixed metal oxide anodes for electrochemical oxidation of organic pollutants in water. *Appl. Catal., A*, 480, 58-78. doi: 10.1016/j.apcata.2014.04.035.

[5] Santos, J. E. L., de Moura, D. C., da Silva, D. R., Panizza, M., Martinez-Huitle, C. A. (2019). Application of TiO_2-nanotubes/PbO_2 as an anode for the electrochemical elimination of Acid Red 1 dye. *J. Solid State Electrochem.*, 23, 351–360. doi: 10.1007/s10008-018-4134-5.

[6] Kasian, O. I., Luk’yanenko, T. V., Demchenko, P. Yu., Gladyshevskii, R. E., Amadelli, R., Velichenko, A. B. (2013). Electrochemical properties of thermally treated platinized Ebonex® with low content of Pt *Electrochim. Acta*, 109, 630–637. doi: 10.1016/j.electacta.2013.07.162.

[7] Knysh, V., Luk’yanenko, T., Shmychkova, O., Amadelli, R., Velichenko, A. (2017). Electrodeposition of composite PbO_2-TiO_2 materials from colloidal methanesulfonate electrolytes, *J. Solid State*

Electrochem., 21, 537-544. doi: 10.1007/s10008-016-3394-1.

[8] Bi, Q., Guan, W., Gao, Y., Cui, Y., Ma, S., Xue, J. (2019). Study of the mechanisms underlying the effects of composite intermediate layers on the performance of Ti/SnO_2-Sb-La electrodes, *Electrochim. Acta*, 306, 667-679. doi: 10.1016/j.electacta.2019.03.122.

[9] Du, H., Duan, G., Vang, N., Liu, J., Tang, Y., Pang, R., Chen, Y., Wan, P. (2018). Fabrication of Ga_2O_3 – PbO_2 electrode and its performance in electrochemical advanced oxidation processes, *J. Solid State Electrochem.*, 22(12), 3799-3806. doi: 10.1007/s10008-018-4082-0.

[10] Pereyra, J., Martinez, M. V., Barbero, C., Bruno, M., Acevedo, D. (2019). Hydrogel-graphene oxide nanocomposites as electrochemical platform to simultaneously determine dopamine in presence of ascorbic acid using an unmodified glassy carbon electrode, *J. Compos. Sci.*, 3, 1-14. doi: 10.3390/jcs3010014.

[11] Pouladvand, I., Asl, S. K., Hoseini, M. G., Rezvani, M. (2019). Characterization and electrochemical behavior of Ti/TiO_2–RuO_2–IrO_2–SnO_2 anodes prepared by sol–gel process, *J. Sol-Gel Sci. Technol.*, 89, 553–561. doi: 10.1007/s10971-018-4887-4.

[12] Shmychkova, O., Luk'yanenko, T., Amadelli, R., Velichenko, A. (2014). Physico-chemical properties of PbO_2-anodes doped with Sn^{4+} and complex ions. *J. Electroanal. Chem.*, *717-718*, 196-201. http://www.sciencedirect.com /science/article/pii/S1572665714000502.

[13] Li, X., Xu, H., Yan, W. (2016). Effects of twelve sodium dodecyl sulfate (SDS) on electro-catalytic performance and stability of PbO_2 electrode, *J. Alloy Compd.*, 718, 386–395. doi: 10.1016/j.jallcom.2017.05.147.

[14] Shmychkova, O., Luk'yanenko, T., Amadelli, R., Velichenko, A. (2016). Electrodeposition of Ni^{2+}-doped PbO_2 and physicochemical properties of the coating, *J. Electroanal. Chem.*, 774, 88–94. doi: 10.1016/j.jelechem.2016.05.017.

[15] Shmychkova, O., Luk'yanenko, T., Amadelli, R., Dmitrikova, L., Velichenko, A. (2017). The electrochemical oxidation of salicylic acid and its derivatives on modified PbO_2-electrodes, *Bull. Dnipr. Univ. Ser. Chem.*, 25 (2), 57–61. doi:10.15421/081706.

[16] Walsh, F. C., Arenas, L. F., Ponce de Leon, C. (2018). Developments in electrode design: structure, decoration and applications of electrodes for electrochemical technology, *J. Chem. Tech. Biotechnol.*, 93(11), 3073-3090. doi: 10.1002/jctb.5706.

[17] Ratcliff, E. R., Hillier, A. C. (2007). Directed electrodeposition of polymer films using spatially controllable electric field gradients, *Langmuir*, **23**, 9905–9910. doi: 10.1021/la700827w.

[18] Darmanin, T., Nicolas, M., Guittard, F. (2008). Electrodeposited polymer films with both superhydrophobicity and superoleophilicity, *Phys. Chem. Chem. Phys.*, 10, 4322-4326. doi: 10.1039/B804617D.

[19] Timmermans, M. Y., Mattelaer, F., Moitzheim, S., Clerckx, N., Sepulveda, A., Deheryan, S., Detavernier, Ch., Vereecken, P. M. (2017), Electrodeposition of insulating poly(phenylene oxide) films with variable thickness, *J. Appl. Polym. Sci.*, 134, 44533-44540. doi: 10.1002/app.44533.

[20] Zhitomirsky, I. Petric, A. (2001). The electrodeposition of ceramic and organoceramic films for fuel cells, *JOM*, 53, 48-50. doi: 10.1007/s11837-001-0071-2.

[21] *Recent advances in complex functional materials: from design to application*, L. E. La Porta, F. de Almeida (Eds.), 2017, Springer Int. Publ. doi: 10.1007/978-3-319-53898-3 9.

[22] Tian, Q., Liu, H. (2015). Electrophoretic deposition and characterization of nanocomposites and nanoparticles on magnesium substrates, *Nanotechnology*, 26, 175102–175108. doi: 10.1088/0957-4484/26/17/175102.

[23] Zhang, J., Quintana, A., Menendez, E.,Coll, M., Pellicer, E, Sort, J. (2018). Electrodeposited Ni-based magnetic mesoporous films as smart surfaces for atomic layer deposition: an "all-chemical" deposition approach toward 3D nanoengineered composite layers, *ACS Appl. Mater. Interfaces*, 10(17), 14877–14885. doi: 10.1021/acsami.8b01626.

[24] Velichenko, A. B., Luk'yanenko, T. V., Nikolenko, N.V., Amadelli, R., Danilov, F. I. (2007). Nafion effect on the lead dioxide electrodeposition kinetics, *Russ. J. Electrochem.*, 43, 118–120. doi: 10.1134/S102319350701017X.

[25] Shmychkova, O., Luk'yanenko, T., Velichenko, A., Meda, L., Amadelli, R. (2013). Bi-doped PbO_2 anodes: electrodeposition and physico-chemical properties. *Electrochim. Acta*, *111*, 332–338. http://www.sciencedirect.com/science/article/pii/S0013468613016125.