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ELECTROSYNTHESIS AND CHARACTERIZATION OF LEAD DIOXIDE−PERFLUOROBUTANESULFONATE COMPOSITE

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The effect of potassium perfluorobutanesulfonate on the kinetic features of electrodeposition of lead dioxide from methanesulfonate electrolytes has been investigated. The introduction of $C_4F_9SO_3K$ into the lead dioxide deposition electrolyte leads to insignificant inhibition of the Pb^{2+} electrooxidation process, while the mechanism of the process does not change. A composite coating is formed upon deposition of coatings from electrolytes containing surfactants. The surface of a composite material consists of a mixture of clearly expressed large crystalline blocks with sharp angles and small crystals. Energy dispersive X-ray analysis revealed the satisfactory distribution of modifying elements in the entire sample bulk, and not only on the coating surface. It was shown that the electrocatalytic activity of lead dioxide−perfluorobuthanesulfonate composite differs from the undoped sample. The oxygen evolution reaction slightly decelerates on a $PbO_2−C_4F_9SO_3K$ composite. The Tafel slopes in 1 M $HClO_4$ calculated from these curves plotted in semilogarithmic coordinates are 136 and 145 mV dec^{-1} for undoped sample and lead dioxide-surfactant composite, respectively. The reaction of electrochemical oxidation of p-chlorophenol is characterized by the pseudo-first order kinetics with respect to the initial compound. The use of doped $C_4F_9SO_3K$ lead dioxide as an anode leads to the inhibition of the process of oxygen evolution and an almost one and a half higher rate of electrochemical conversion of 4-chlorophenol to aliphatic compounds.

Keywords: lead dioxide, methanesulfonate electrolyte, surfactant, electrodeposition, 4-chlorophenol.

Introduction

Development of methods for direct synthesis of new materials with predicted properties is one of the priority challenges of modern electrochemistry [1]. It should be noted that the fabrication of composite materials is recognized to be the most promising method due to possibility to change the functional properties in a wide range by variations in the nature of dispersed phase [2]. Despite the large number of methods for the synthesis of composite materials, electrochemical ones are considered the most promising due to the simplicity of their implementation and relatively small energy losses as compared with sol-gel method and other techniques [3]. This method opens wide opportunities for influencing the composition and properties of materials by changing the conditions of electrolysis and electrolyte composition. Lead (IV) and manganese (IV) oxides are known as typical representatives of such materials, which due to the simplicity of their electrochemical synthesis, high corrosion resistance and relatively low cost are widely used in electrocatalysis, electroplating and electrochemical energy, lead-acid batteries, flowing redox energy storage devices, asymmetric supercapacitors, and primary and secondary current sources [4]. The inclusion of fluorinated compounds in the metal-oxide matrix ensures anti-static, anti-adhesive, and anti-corrosion properties and at the same time, they retain the following properties of the metal-oxide: high electrical conductivity, resistance to mechanical wear and good adhesion to the substrate.

Per- and polyfluoroalkyl substances are synthetic organofluorine chemical compounds that have several fluorine atoms attached to an alkyl chain.

As such, they contain at least one perfluoroalkyl moiety, $C_nF_{2n}-$ [5]. Fluorinated surfactants can reduce the surface tension of water to a value that is half that which can be obtained using hydrocarbon surfactants [6]. This ability is due to the lipophobic nature of fluorocarbons, since fluorinated surfactants tend to concentrate at the liquid−air interface [7]. They are not as sensitive to London dispersion force, which contributes to lipophilicity, since the electronegativity of fluorine reduces the polarizability of surfactants with a fluorinated surface.

However, in nitrate electrolytes it is not possible to produce coatings with a thickness of over 100 μm, which possess a satisfactory mechanical stability. In this regard, in the present paper, the possibility of electrodeposition of PbO_2-fluorinated surfactant composites from methanesulfonate electrolytes has been considered. Methanesulfonic acid is a green acid with a remarkably high solubility of majority of metals including lead, making it an interesting leaching agent for metals. It is safer and less toxic than the mineral acids (HCl, H_2SO_4, HNO_3) and intensively employed for leaching metals from primary and secondary sources [8]. It has previously been shown [9], that PbO_2 coatings up to 2 mm thick with satisfactory mechanical properties can be prepared in these media.

Therefore, in this work, we studied the kinetics of electrodeposition of lead dioxide in the presence of potassium perfluorobutanesulfonate as a dopant in methanesulfonate electrolyte and determined the electrocatalytic activity of the fabricated oxide materials.

Materials and methods

All chemicals were reagent grade. Kinetics of electrodeposition of doped lead dioxide was studied on a Pt rotating disk electrode (Pt−RDE, 0.19 cm²) by steady-state voltammetry and chronoamperometry. For the RDE experiments, the voltammetry system SVA−1BM was used. The potential scan rate was varied within the range of 1 to 100 mV s⁻¹ depending on purposes of the experiments. Before each experiment, the electrode surface was treated with a freshly prepared mixture (1:1) of concentrated H_2SO_4 and H_2O_2 [9]. Such preliminary treatment technique permits to stabilize the electrode surface and provides the reproducibility of cyclic voltammograms in a supporting electrolyte (0.11 M CH_3SO_3H). Voltammetry measurements were carried out in a standard temperature-controlled three-electrode cell. Temperature was maintained at 25±1⁰C. All potentials were recorded and reported vs. Ag/AgCl/KCl(sat.) reference electrode.

Electrodeposition was studied in 0.11 M CH_3SO_3H+0.01 M $Pb(CH_3SO_3)_2$ solution. Surfactant was added into the deposition electrolyte as aqueous solutions (0.0003 M). Due to low concentrations of surfactant, the composition of the electrolyte may significantly change during deposition; therefore, the concentration of surfactant was chosen at which, according to the adsorption isotherm, a 100% degree of surface filling is observed, which ensures that the electrolyte composition will not significantly change even if the surfactant is consumed.

The current efficiency and partial current of lead dioxide deposition ($I_{Pb(II)}$) were determined according to method described in detail previously [10].

Surface morphology of lead dioxide anodes was studied by scanning electron microscopy (SEM) with Stereoscan 440 LEO microscope. X-ray powder diffraction (XRPD) data were collected in the transmission mode on a STOE STADI P diffractometer with the following setup: Cu $K_{α1}$-radiation, curved Ge (1 1 1) monochromator on primary beam, $2θ/ω$-scan, angular range for data collection of 20.000−110.225⁰ $2θ$ with increment of 0.015, linear position sensitive detector with the step of recording of 0.480⁰ $2q$ and times per step of 130−250 s, U=40 kV, I=30 mA, and T=294 K. A calibration procedure was performed utilizing SRM 640b (Si) and SRM 676 (Al_2O_3) NIST standards. Preliminary data processing and X-ray qualitative phase analysis were performed using STOE WinXPOW and PowderCell program packages. Crystal structures of the phases were refined by the Rietveld method with the program FullProf.2k, using a pseudo-Voigt profile function and isotropic approximation for the atomic displacement parameters, together with quantitative phase analysis. Microstructural parameters (i.e., size of coherently diffracting domains accepted as average apparent crystallite size D, and average maximum strain ε) were identified by isotropic line broadening analysis using simplified integral breadth methods for reflections with maximal intensities: (110) for $α$-PbO_2 and (111) for $β$-PbO_2.

The determination of the concentration of surfactant in aqueous solutions was conducted according to the procedure described elsewhere [10]. Adsorption measurements were carried out using 0.5 g of PbO_2 powder (Merck) in 0.1 M HCl solutions containing various amounts of additive. The measurements were performed in the presence of an indifferent electrolyte (0.1 M KCl), which screened the electrostatic field of the oxide surface. The time to establish the adsorption equilibrium was 24 hours. Adsorption parameters were calculated using the

Frumkin equation [11].

Platinized titanium was used as a sheet during investigation of electrocatalytic activity of materials. It was treated accordingly before platinum layer depositing [9].

Oxygen evolution reaction was investigated by steady-state polarization on computer controlled EG & G Princeton Applied Research potentiostat model 273A in 1 M H_2SO_4.

The electrooxidation of organic compounds was carried out in a divided cell at $j_a=50$ mA cm^{-2}. The volume of anolyte was 130 cm^3. Solution containing phosphate buffer (0.25 M Na_2HPO_4+0.1 M KH_2PO_4)+2·10^{-4} M organic compound (pH 6.55) was used as anolyte; phosphate buffer served as catholyte. Stainless steel was used as cathode. Composite PbO_2−surfactant electrodes were used as anodes. Electrode surface area was 2.5 cm^2.

The change of the concentration of the organic substance during the electrolysis was measured by sampling (volume of 5 cm^3) at regular intervals and measuring the absorbance of the solution in the ultraviolet and visible region (the wavelength range of 200−350 nm) using a Kontron Uvikon 940 spectrometer.

Analyses of the reaction products were conducted by high performance liquid chromatography (HPLC) using a Shimadzu RF-10A xL instrument equipped with an Ultraviolet SPD-20AV detector and a 30 cm Discovery® C18 column.

Results and discussion

The introduction of $C_4F_9SO_3K$ into the lead dioxide deposition electrolyte leads to insignificant inhibition of the Pb^{2+} electrooxidation process, while the mechanism of the process does not change. This mechanism was described and discussed in detail in our previous publication [10], where lead dioxide−surfactant composites were deposited from a nitrate medium.

Chronoamperograms were obtained on a Pt disk electrode in order to investigate the initial stages of deposition of lead dioxide in the presence of perfluorobutanesulfonate in solution. A typical j−t curve of PbO_2 deposition can be characterized by

several features and fully consistent with the transients recorded and described in detail by Abyaneh et al. [12] during the electrocrystallization of PbO_2 onto a vitreous carbon electrode from nitrate solutios and in our previous paper [13] concerning the initial stages of lead dioxide nucleation. The electrocrystallization model proposed by Abyaneh and Gonzalez-Garcia [12] was selected as appropriate one for investigation of initial stages of the formation of a new PbO_2 phase. This model gives a rather complete description and provides means for understanding phase formation, in the sense that it allows determining kinetic parameters of nucleation for both α- and β-phases from an analysis of current−time transients. It was previously shown that such model is appropriable for both methanesulfonate and nitrate electrolytes [13]. The main parameters of lead dioxide crystallization from methanesulfonate electrolyte (Table 1) were calculated based on the model [12] for progressive mechanism with simultaneous formation of α- and β-phases of PbO_2.

In accordance to [13], one can observe either the predominance of one phase over another or ingesting of growing centers of one phase by another, depending on the composition of electrolyte. The formation of one phase is noticeably lagged behind the other. In present work, there is a slight predominance of the growth of β-phase of PbO_2 both for undoped sample and for lead dioxide−surfactant composite. Phase growth is inhibited by a surfactant due to surface blocking, which does not contradict existing models of electrocrystallization [13].

On the one hand, the mechanism of electrodeposition can be adequately described using the classical four-stage scheme of electrodeposition [9,10], according to which surfactant adsorption occurs on the surface of growing PbO_2, and the change in the surfactant content in the coating can be caused by two factors: (i) heterogeneous and (ii) migratory. On the other hand, we cannot exclude that not only crystallization occurs from a supersaturated solution bulk, but also colloidal particles are formed which adhere to the surface of growing crystals. It should be noted that it is possible

Table 1

Parameters of initial stages of lead dioxide electrocrystallization*

Deposition electrolyte	t_α / s	K_α / mol m^{-2} s^{-1}	t_β / s	K_β / mol m^{-2} s^{-1}
0.1 M Pb^{2+}+0.1 M CH_3SO_3H	0.54	3.40·10^{-5}	1.65	1.02·10^{-4}
0.1 M Pb^{2+}+0.1 M CH_3SO_3H+3·10^{-4} $C_4F_9SO_3K$	0.57	4.46·10^{-5}	1.88	0.82·10^{-4}

Note: K_α is the rate constant of growth of α-phase crystals in a direction perpendicular to the electrode surface; t_α is time corresponding to the beginning of α-phase formation; K_β is the rate constant of growth of β-phase crystals in a direction perpendicular to the electrode surface; t_β is the time corresponding to the beginning of β-phase formation.

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that all the described effects can be realized simultaneously with different contributions. All these hypotheses do not contradict the obtained experimental data.

Adsorption measurements were performed on a lead dioxide powder at zero charge potential [14]. The adsorption of surfactant is satisfactorily described by the Frumkin isotherm (correlation factor 0.996). The value of interaction parameter calculated from above mentioned dependence is unity, which evidences a slight interaction between adsorbed molecules. The value of the energy of adsorption interaction ($-\Delta G$) is 33.2 kJ mol^{-1}, indicating the specific character of adsorption. The adsorption of $C_4F_9SO_3K$ on PbO_2 is accompanied by a shift of pH_0 (zero charge pH) of the oxide to a region of higher value: from 7.4 for naked PbO_2 to 7.6 for PbO_2-2 wt.% $C_4F_9SO_3K$, which was discussed in detail in our previous publication [10].
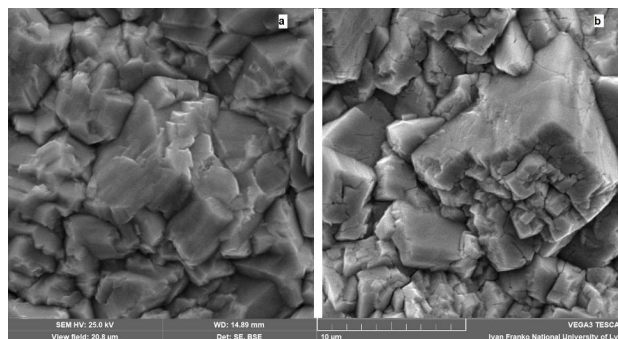
The effect of deposition conditions (current

Fig. 1. SEM images of composite surfaces obtained from the following solutions: a − 0.1 M $Pb(CH_3SO_3)_2$+0.11 M CH_3SO_3H; b − 0.1 M $Pb(CH_3SO_3)_2$+0.11 M CH_3SO_3H+0.0003 M $C_4F_9SO_3K$

density, temperature, and concentration of dopants in the electrolyte) on the composition of lead dioxide−surfactant composites, fluorine-containing surfactants in particular were investigated in works
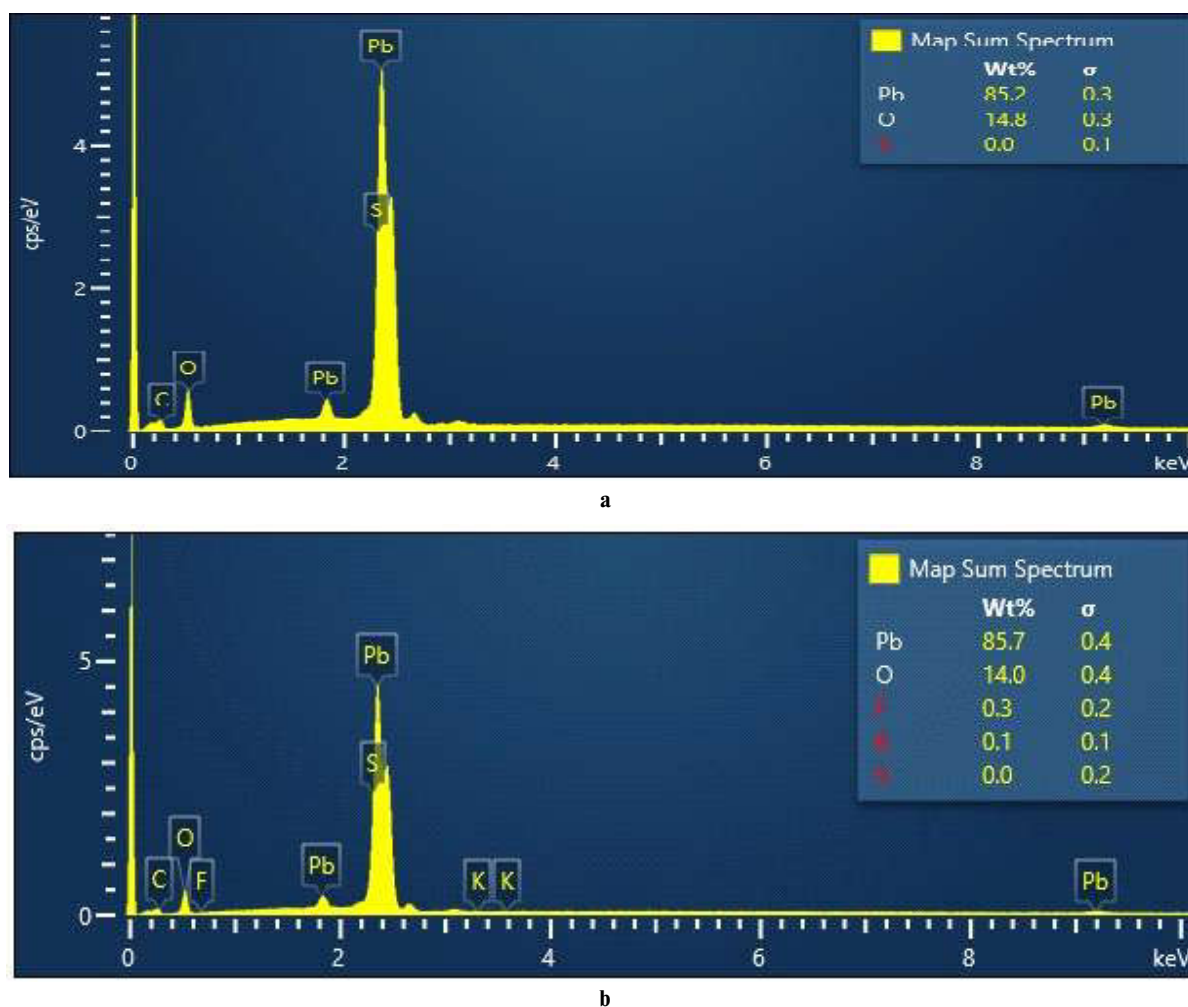

Fig. 2. EDX spectra of composites obtained from the following solutions: a − 0.1 M $Pb(CH_3SO_3)_2$+0.11 M CH_3SO_3H; b − 0.1 M $Pb(CH_3SO_3)_2$+0.11 M CH_3SO_3H+0.0003 M $C_4F_9SO_3K$

[9,10]. It was found that the surfactant content in the composite weakly depends on its concentration in the deposition electrolyte. At high surfactant concentrations in the electrolyte, the active centers of oxide are blocked by the surfactant, which leads to a decrease in electrical conductivity and deterioration of the mechanical properties. Low surfactant concentrations in the electrolyte deposition have weak effect on the catalytic activity of the coating. Having in mind these effects, the optimal concentration of perfluorobutanesulfonate in solution was chosen. At this concentration, the content of surfactant in the resulting coating was 2 wt.%.

The inclusion of surfactants in a growing coating led to a change in the texture and structure of the resulting film [10]. Surface morphology of the investigated samples is depicted in Fig. 1.

As can be seen, large crystalline blocks with sharp angles and small crystals are clearly expressed in the case of lead dioxide−perfluorobutanesulfonate
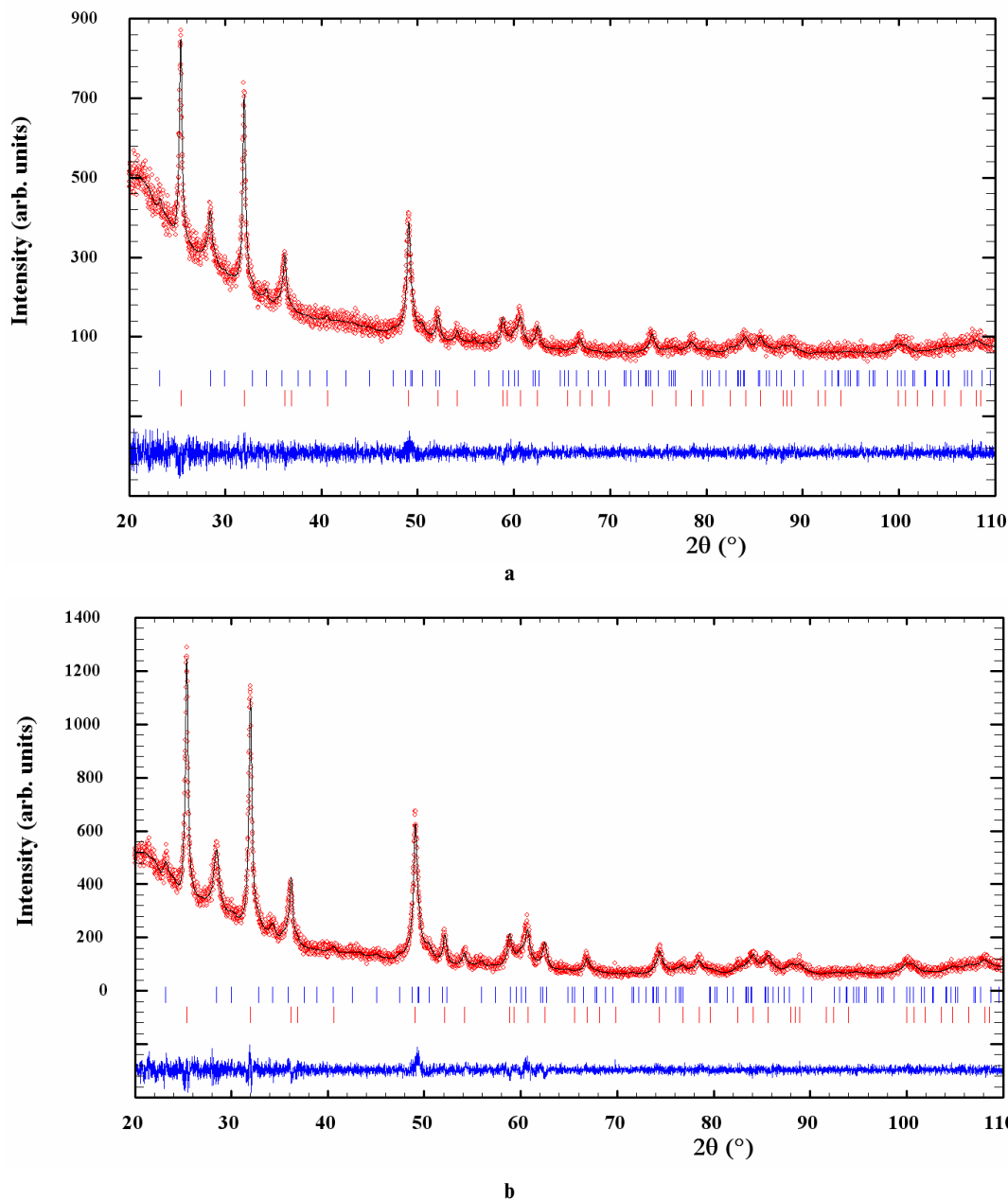

Fig. 3. Observed and calculated X-ray powder profiles for composite surfaces obtained from the following solutions: a − 0.1 M $Pb(CH_3SO_3)_2$+0.11 M CH_3SO_3H; b − 0.1 M $Pb(CH_3SO_3)_2$+0.11 M CH_3SO_3H+0.0003 M $C_4F_9SO_3K$. Experimental data (circles) and calculated profile (solid line through the circles) are presented together with the calculated Bragg positions (vertical ticks) and difference curve (bottom solid line). Upper ticks: α-PbO_2, bottom ticks: β-PbO_2

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composite, which is typical of lead dioxide−surfactant coatings deposited from nitrate electrolytes [10] (Fig. 1,b). The surface of the unmodified sample is more ordered, large and small crystals are evenly distributed (Fig. 1,a).

SEM/EDAX experiments (Fig. 2) were performed to evaluate the amount and distribution of chemical elements in a electrodeposited composite. Low peaks corresponding to O and F indicate a satisfactory distribution of modifying elements in the entire sample bulk, and not only on the coating surface. In addition, it was not possible to detect the sulfur peak due to proximity of the very intense lead peak.

All investigated samples contain two phases (as detected by XRPD): α-PbO$_2$ (structure type Fe$_2$N$_{0.94}$, space group *Pbcn*) and β-PbO$_2$ (structure type TiO$_2$ rutile, space group *P*4$_2$/*mnm*). The difference is observed only in the ratio of these two phases and also in the degree of crystallinity (Fig. 3, Table 2).

As one can see, both investigated samples have the higher β-phase amount, which is twice bigger than α-phase amount. The presence of surfactant leads to small fluctuations in the phase composition of the resulting coatings.

It is widely recognized [15] that oxide surface consists of crystal (PbO$_2$) and hydrated [PbO(OH)$_2$] zones which are in equilibrium, and the latter is a rather open structure which can exchange cations and anions. From the point of view of the phase composition, no obvious changes are observed in the crystalline zone of the oxide, but this does not exclude changes in the composition of the oxide in the hydrated zone, which could explain the electrocatalytic activity of the coatings involved. Such phase composition (as XPRD investigation provides information about crystal phase) is an indirect confirmation that the main changes in the composition occur in the hydrated zone of the oxide.

The electrocatalytic activity of lead dioxide deposited from a methanesulfonic solution containing surfactant was studied both in the oxygen evolution

Table 2

Phase composition, crystallographic data and microstructural parameters of the investigated samples

Sample description	Phase	Content (wt.%)	Lattice parameters, Å			Unit cell volume, Å^3	Reliability factors R_I/R_P, R_{WP}, R_{EXP}, χ^2	D, Å/ε^*
			a	b	c	V		
PbO$_2$	α-PbO$_2$	33(6)	4.997(4)	5.963(5)	5.457(4)	162.6(2)	0.0613	184/0.0085
	β-PbO$_2$	67(4)	4.9588(10)	–	3.3862(7)	83.27(3)	0.0356/0.0615, 0.0812, 0.0839, 0.94	247/0.0071
PbO$_2$–C$_4$F$_9$KO$_3$S	α-PbO$_2$	38(7)	5.000(3)	5.955(4)	5.453(3)	162.38(18)	0.0308	131/0.0120
	β-PbO$_2$	62(4)	4.9578(6)	–	3.3847(5)	83.195(19)	0.0229/0.0589, 0.0773, 0.0773, 1.0	227/0.0077

Note: meaning of parameters see in Materials and methods section.

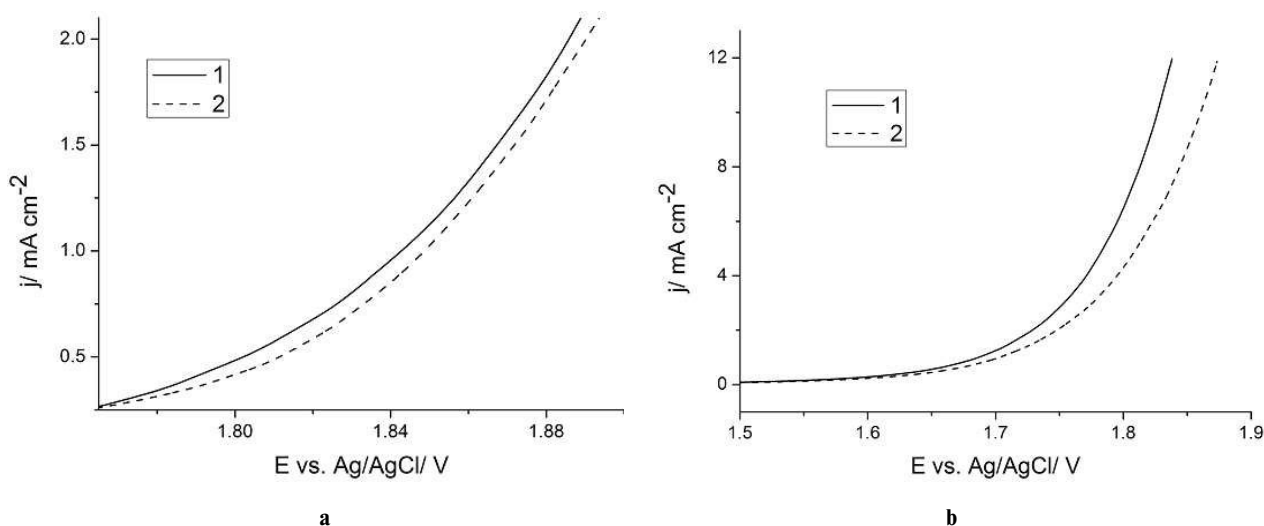**a**   **b**

Fig. 4. Steady state polarization curves of oxygen evolution in 1 M HClO$_4$ (a) and phosphate buffer (b) (scan rate 1 mV s^{-1}, t=25^{0}C) on PbO$_2$ electrodes deposited from the following solutions: 0.1 M Pb(CH$_3$SO$_3$)$_2$+0.11 M CH$_3$SO$_3$H (1); 0.1 M Pb(CH$_3$SO$_3$)$_2$+0.11 M CH$_3$SO$_3$H+0.0003 M C$_4$F$_9$SO$_3$K (2). Coating were electrodeposited on Ti/Pt sheet

reaction and in the oxidation of 4-chlorophenol. As follows from the steady state polarization curves (Fig. 4), the oxygen evolution reaction slightly decelerates on a $PbO_2-C_4F_9SO_3K$ composite. The Tafel slopes were calculated from these curves plotted in semilogarithmic coordinates: they are 136 and 145 mV dec^{-1} for undoped sample and lead dioxide–surfactant composite in 1 M HClO$_4$, respectively; and 140 and 157 mV dec^{-1} in phosphate buffer, respectively.

Two processes occur in the investigated solutions: (i) oxygen evolution and (ii) oxidation of the organic compound, which proceeds at the limiting current density due to a relatively low concentration of 4-chlorophenol. The oxygen evolution is an undesirable side process; so one should be interested in the factors inhibiting this process. The kinetics of oxygen evolution on lead dioxide has been well studied by Pavlov et al. [15]. In order to increase the selectivity of the target process (oxidation of 4-chlorophenol), it is necessary to increase the Tafel slope of the oxygen evolution process, since this process is limited by the charge transfer stage, and the target oxidation process of the organic compound is controlled by diffusion kinetics. This effect can be achieved by modifying the lead dioxide surface with perfluorobutanesulfonate.

The inhibition of oxygen evolution and an increase in the Tafel slope in the case of a lead dioxide–perfluorobuthanesulfonate sample is probably due to the blocking of the surface by the surfactant, as is observed in sulfate solutions. The shift of the oxygen evolution potential to the region of lower potentials on both samples in a buffer solution is associated with a change in the electrolyte pH.
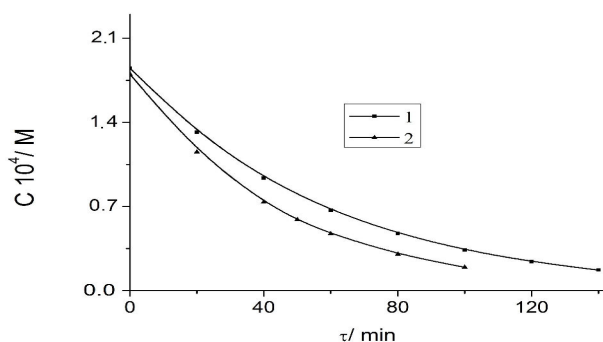

Fig. 5. Time dependences of 4-chlorophenol concentration during the electrochemical oxidation on the following electrodes: 1 − PbO$_2$; 2 − PbO$_2$−C$_4$F$_9$SO$_3$K

Fig. 5 shows dependences concentration of 4-chlorophenol versus time during the electrochemical oxidation. Plotting them in the corresponding coordinates reveals the pseudo first order of the reaction with respect to the initial compound.

As it was established earlier, the rate of oxidation of organic compounds increases significantly in the case of modification of lead dioxide with a fluorinated surfactant [10] or a polymer [9]. The same effect is observed in the present work. Thus, the conversion rate of 4-chlorophenol on lead dioxide–perfluorobuthanesulfonate composite is 1.3 times higher than on unmodified sample (Table 3).

Table 3

The rate of 4-chlorophenol oxidation on the composites involved

Anode	Apparent heterogeneous rate constant $\times 10^2$ min^{-1}
PbO$_2$	1.7
PbO$_2$−C$_4$F$_9$SO$_3$K	2.2

HPLC data indicated that the aromatic compounds are completely destroyed with the formation of only aliphatic electrolysis products (in particular, maleic acid) after 2 hours of electrolysis on an unmodified PbO$_2$-anode. It should be noted that even using the unmodified film synthesized from methanesulfonic medium allows destroying the 4-chlorophenol 2 times faster than in the case of coating synthesized from nitrate medium [10].

Conclusions

The kinetics of lead dioxide electrodeposition from a methanesulfonate medium does not differ from that observed obtained in a nitrate medium. As concern the nucleation of coatings, there is a slight predominance of the growth of β-phase of PbO$_2$ both for undoped sample and for lead dioxide surfactant composite. Phase growth is inhibited by surfactant due to surface blocking, which does not contradict existing models of electrocrystallization. The adsorption of surfactant is satisfactorily described by the Frumkin isotherm and is accompanied by a shift of the zero-charge pH of the oxide to a region of higher values. The morphology of the composites involved differs when the perfluorobuthanesulfonate is added to the deposition electrolyte. Thus, large crystalline blocks with sharp angles and small crystals are clearly expressed on the surface of lead dioxide–perfluorobuthanesulfonate composite. It has been observed that both investigated samples have the higher β-phase amount, which is twice bigger than α-phase amount. The presence of surfactant leads to small fluctuations in the phase composition of the resulting coatings. The oxygen evolution potential on lead dioxide–surfactant composite is higher than

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on undoped film. It was established that apparent heterogeneous rate constant of 4-chlorophenol on lead dioxide−perfluorobuthanesulfonate composite is 1.3 times higher than on unmodified sample.

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ЕЛЕКТРОСИНТЕЗ І ХАРАКТЕРИСТИКА КОМПОЗИТУ СВИНЕЦЬ(IV) ОКСИД−ПЕРФТОРБУТАНСУЛЬФОНАТ

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Досліджено вплив калій перфлуоробутансульфонату на кінетичні закономірності електроосадження свинець(IV) оксиду з метансульфонатних електролітів. Введення C$_4$F$_9$SO$_3$K в електроліт осадження свинець(IV) оксиду приводить до незначного пригнічення процесу електроокислення Pb^{2+}, при цьому механізм процесу не змінюється. З електролітів, що містять поверхнево-активну речовину, утворюється композитне покриття. Поверхня композитного матеріалу складається з суміші чітко виражених великих кристалічних блоків із гострими кутами та дрібних кристалів. Енергодисперсійний рентгенівський аналіз показав задовільний розподіл модифікуючих елементів у всьому об'ємі зразка, а не тільки на поверхні покриття. Показано, що електрокаталітична активність композиту свинець(IV) оксид−перфлуоробутансульфонат відрізняється від немодифікованого зразка. На композиті PbO$_2$−C$_4$F$_9$SO$_3$K реакція виділення кисню трохи сповільнюється. Тафелівські нахили в 1 M HClO$_4$, розраховані за цими кривими, побудованим в логарифмічних координатах, становлять 136 і 145 мВ/дек для немодифікованого зразка і композиту, відповідно. Реакція електрохімічного окислення п-хлорфенолу характеризується кінетикою псевдопершого порядку за вихідною сполукою. Використання модифікованого C$_4$F$_9$SO$_3$K свинець(IV) оксиду як анода приводить до пригнічення процесу виділення кисню і в півтора рази вищого значення швидкості електрохімічного перетворення 4-хлорфенолу в аліфатичні сполуки.

Ключові слова: свинець(IV) оксид, метансульфонатний електроліт, поверхнево-активна речовина, електроосадження, 4-хлорфенол.

ELECTROSYNTHESIS AND CHARACTERIZATION OF LEAD DIOXIDE−PERFLUOROBUTANESULFONATE COMPOSITE

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The effect of potassium perfluorobutanesulfonate on the kinetic features of electrodeposition of lead dioxide from methanesulfonate electrolytes has been investigated. The introduction of $C_4F_9SO_3K$ into the lead dioxide deposition electrolyte leads to insignificant inhibition of the Pb^{2+} electrooxidation process, while the mechanism of the process does not change. A composite coating is formed upon deposition of coatings from electrolytes containing surfactants. The surface of a composite material consists of a mixture of clearly expressed large crystalline blocks with sharp angles and small crystals. Energy dispersive X-ray analysis revealed the satisfactory distribution of modifying elements in the entire sample bulk, and not only on the coating surface. It was shown that the electrocatalytic activity of lead dioxide−perfluorobutanesulfonate composite differs from the undoped sample. The oxygen evolution reaction slightly decelerates on a $PbO_2−C_4F_9SO_3K$ composite. The Tafel slopes in 1 M $HClO_4$ calculated from these curves plotted in semilogarithmic coordinates are 136 and 145 mV dec^{-1} for undoped sample and lead dioxide-surfactant composite, respectively. The reaction of electrochemical oxidation of p-chlorophenol is characterized by the pseudo-first order kinetics with respect to the initial compound. The use of doped $C_4F_9SO_3K$ lead dioxide as an anode leads to the inhibition of the process of oxygen evolution and an almost one and a half higher rate of electrochemical conversion of 4-chlorophenol to aliphatic compounds.

Keywords: lead dioxide; methanesulfonate electrolyte; surfactant; electrodeposition; 4-chlorophenol.

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