Research Article

Electrosynthesis and catalytic activity of PbO_2-fluorinated surfactant composites

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Abstract

BACKGROUND: The effect of the potassium salt of nonafluorobutanesulfonic acid ($C_4F_9SO_3K$) on the kinetic regularities of electrodeposition of lead dioxide (PbO_2) from nitrate electrolytes has been investigated. Obtained results concerning synthesis and physicochemical properties can contribute substantially to a fundamental understanding of the relationship between coating structure and catalytic activity, important to all fields of catalysis.

RESULTS: The introduction of $C_4F_9SO_3K$ into the PbO_2 deposition electrolyte leads to insignificant inhibition of the Pb^{2+} electrooxidation process, whereas the mechanism of the process does not change. Upon deposition of coatings from electrolytes containing surfactants, a composite coating is formed. Depending on the electrolyte composition and electrolysis conditions, the surfactant content in the composite can vary from 2.00 ± 0.05 to 17.00 ± 0.05 wt%. The inclusion of surfactants in the coating composition with subsequent overgrowth with PbO_2 leads to a decrease in the size of PbO_2 crystals and prevents the formation of polycrystalline blocks. The composite material is a PbO_2 matrix with submicron and nanoscale crystals into which surfactant particles are embedded.

CONCLUSION: It was shown that the electrocatalytic activity of composite PbO_2-surfactant materials depends on the nature and content of the latter in the composite. The use of PbO_2 doped with $C_4F_9SO_3K$ as an anode leads to an inhibition of the process of oxygen evolution and an almost three-fold increase in the rate of electrochemical conversion of 4-chlorophenol to aliphatic compounds.
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Keywords: lead dioxide; nitrate electrolyte; surfactant; electrodeposition; 4-chlorophenol

INTRODUCTION

Design and application of various coatings are now employed extensively in modern electrochemical technology.[1–3] Composite coatings, including metal oxide coatings, are one of the most promising issues for modifying the surface properties of various materials.[4,5] A well-known and obvious advantage of composite coatings is that their properties and parameters can be changed directionally by varying the composition of the coating and the ratio of its constituent components.

Electrolysis opens up great opportunities in controlling the structure and the properties of deposited oxide films, accordingly. The development of composite electrochemical coatings based on metal oxides with the inclusion of dopants of various natures, including surfactants should be considered as the one of main directions of electrocatalysis.[6]

Among composite coatings, metal oxide-polymer coatings in which fluorinated compounds are used as a dopant component are of particular interest.[7] The inclusion of fluorinated compounds in the metal-oxide matrix gives antistatic, anti-adhesive and anticorrosion properties while retaining the inherent properties of the metal oxide, including high electrical conductivity, resistance to mechanical wear and good adhesion to the substrate.

Electrodeposited lead dioxide (PbO_2) has a number of valuable benefits that facilitate its use as a platinum (Pt) substitute in a

various processes of electrochemical synthesis.[8] These features include chemical resistance in aggressive solutions, high electrical conductivity of the metal type, the ability to create composite materials and ease of preparation.

The addition of polyelectrolytes (long-chain polymers with charged functional groups) into the electrolyte deposition leads to significant changes in the electrodeposition regularities, the physicochemical properties of oxides and the electrocatalytic activity of the obtained electrode materials.[9,10] As was shown in a number of our previous works, the presence of fluorine (F) ions[11] and the Nafion® polyelectrolyte[12, 13] in the deposition electrolyte affects the properties of the obtained PbO_2, in particular, changing its morphology, texture and electrocatalytic activity in oxygen transfer reactions. From this point of view, investigation of the influence of potassium salt of nonafluorobutanesulfonic acid ($C_4F_9SO_3K$) on the properties of synthesized PbO_2 is of significant interest, because $C_4F_9SO_3K$ is an intermediate surfactant between small fluoride ion and the large polyelectrolyte Nafion®.

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For polyelectrolytes, in particular for Nafion®,[12] significant changes were observed both in the electrodeposition regularities and in the electrocatalytic activity of the resulting electrode materials. It is obvious that modification with surfactants, because some of them are monomers of polyelectrolytes, also should lead to a change in the kinetics of deposition, and, as a consequence, to a change in their properties.

Herein we used $C_4F_9SO_3K$ as an additive in the PbO_2 deposition electrolyte. We chose a surfactant containing F and a fluorosulfonic acid residue as substituents. This surfactant contains substituents similar to Nafion®, and, in fact, is its monomer. The oxidation of compounds of this type at high anodic potentials is practically excluded. Because the selected additive is an anionic surfactant, then most likely it will be adsorbed on the positively charged surface of the growing oxide. It should be noted that in the literature there is practically no information on the effect of surfactants on the electrodeposition regularities of metal oxides.[14] Therefore, in this work, we studied the regularities of electrodeposition of PbO_2 in the presence of nonafluorobutanesulfonic acid in the potassium salt solution as a modifying additive, as well as the electrocatalytic activity of the obtained oxide materials.

The obtained results concerning synthesis and physicochemical properties can contribute substantially to a fundamental understanding of the relationship between the coating composition, structure and catalytic activity, important to all fields of catalysis.

MATERIALS AND METHODS

All chemicals were reagent grade. Electrodeposition kinetics of doped PbO_2 were 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 1–100 mV s⁻¹ depending on the purposes of the experiments. Before each experiment, the electrode surface was treated with a freshly prepared mixture (1:1) of concentrated sulfuric acid (H_2SO_4) and hydrogen peroxide (H_2O_2).[15] This preliminary treatment technique permits the stabilization of the electrode surface and determines the reproducibility of cyclic voltammograms in the background electrolyte (0.1 mol L⁻¹ HNO₃). Voltammetry measurements were carried out in a standard temperature-controlled three-electrode cell. Temperature was maintained at 298 ± 1 K. All potentials were recorded and reported *versus* silver/silver/potassium chloride [Ag/AgCl/KCl (sat.)].

Electrodeposition was studied in 0.1 mol L⁻¹ nitric acid (HNO₃) + 0.01 mol L⁻¹ lead nitrate [Pb(NO₃)₂]. Surfactant was added into the deposition electrolyte as an aqueous solutions with 0.003 mol L⁻¹ concentration. Because at low concentrations of surfactant, the composition of the electrolyte will significantly change during deposition, a concentration was chosen at which, according to the adsorption isotherm, one can obtain 100% surface filling, when the electrolyte composition will not change if the surfactant has been consumed.

The determination of current efficiency and partial current of PbO_2 deposition [$I_{Pb(II)}$] was done according to the method described in detail previously.[16]

Becuase PbO_2 electrodeposition proceeds simultaneously with an oxygen evolution reaction, for determination of partial PbO_2 electrodeposition current [$I_{Pb(II)}$] and current efficiency [CE_{PbO_2}] of the PbO_2 total charge and charge that passed on the reduction of obtained deposit were measured[16]:

$$CE_{PbO_2} = Q_{red}/Q$$
$$I_{PbO_2} = Q_{red}/\tau,$$

where Q and Q_{red} are charges passed through the electrolytic cell and passed on the reduction of PbO_2 coating, respectively, and τ is electrolysis time upon state potential.

For finding out the surfactant influence on PbO_2 electrodeposition kinetics values of the apparent heterogeneous rate constants (k) for anodic Pb(II) oxidation were calculated according to the Koutecky–Levich equation:

$$\frac{1}{I} = \frac{1}{nkFSc_0} + \frac{1}{0.62nFSD^{2/3}\nu^{-1/6}c_0} \cdot \frac{1}{\varpi^{1/2}},$$

where n is the number of electrons transferred in the half reaction, S is the electrode area (cm²), ω is the angular velocity of electrode rotation (rad s⁻¹), ν is the solution kinematic viscosity (Pa s) and other terms have their conventional electrochemical significance.[17]

The surface morphology of the PbO_2 anodes was studied by scanning electron microscopy (SEM) with a Leica/Cambridge Stereoscan 440 LEO microscope/ UK.

The method for the determination of high molecular weight aliphatic acids[18] was adapted for the determination of the concentration of surfactant in aqueous solutions. This method involves the formation of an associate of a high-molecular anion and a dye, followed by extraction into a nonaqueous medium. The content of organic substance was determined photocolorimetrically after extraction of the ionic associate with chloroform. Ten millilitres of distilled water were placed in a separatory funnel and 2 mL of 0.1% aqueous solution of methylene blue was injected. Then, 1 mL of the test solution was injected and shaken for 2 min with 15 mL chloroform. The organic phase was filtered through cotton wool and the optical density measured at 650 nm using a CPC-2 colorimeter/ Sergiev Posad/ Russian Federation. To determine surfactants in composite coatings of known mass, the latter were cathodically dissolved at a current density of 2 mA cm⁻² in 30 mL of 0.1 mol L⁻¹ HCl. Then the concentration of additives was determined in solution by the above method.

Adsorption measurements were carried out on 0.5 g PbO_2 powder (Merck) in 0.1 mol L⁻¹ hydrochloric acid (HCl) solutions containing various amounts of additive. The measurements were carried out in the presence of an indifferent electrolyte (0.1 mol L⁻¹ KCl), which screened the electrostatic field of the oxide surface. The time to establish the adsorption equilibrium was 24 h.

Adsorption parameters were calculated using the Frumkin equation[19]:

$$Bc = \frac{\theta}{1-\theta}\exp(-2\alpha\theta),$$

where B is the adsorption constant, θ is the surface coverage, α is an interaction parameter and c is the equilibrium concentration.

For aqueous solutions, when the concentration of solute is small and is expressed in mol L⁻¹,

$B = 0, 018\exp(-\Delta G/RT)$, where ΔG is free adsorption energy.

The surface tension of surfactant solutions was measured by the method of maximum pressure in a gas bubble.[20] Platinized titanium was used as a sheet during investigation of the

electrocatalytic activity of materials. It was treated accordingly before Pt layer deposition.[21]

The O_2 evolution reaction was investigated by steady-state polarization on a computer-controlled EG & G Princeton Applied Research potentiostat model 273A/ Ametek/UK in 1 mol L^{-1} H_2SO_4.

The electro-oxidation of organic compounds was carried out in divided cell at $j_a = 50$ mA cm^{-2}. The volume of anolyte was 130 cm^3. Solution containing phosphate buffer (0.25 mol L^{-1} Na_2HPO_4 + 0.1 mol L^{-1} KH_2PO_4) + 10^{-4} mol L^{-1} organic compound (pH = 6.55) was used as anolyte; phosphate buffer was the catholyte with a stainless steel cathode. Composite PbO_2-surfactant electrodes were used as anodes. The electrode surface area was 2.5 cm^2.

The changing concentration of the organic substance during electrolysis was measured by sampling (5 cm^3 volumes) at regular intervals and measuring the optical density of the solution in the UV-visible region (wavelength range 200–350 nm) using a Kontron Uvikon 940 spectrometer/ Kontron Instruments/ Plaisir/ France.

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

All of the experiments were repeated twice at least in order to achieve satisfactory reproducibility. All instruments had normalized metrological characteristics and were calibrated. The data for the linearized plots were processed using the least squares method, which requires that the sum of the squared deviations of the experimental points from the curve be the smallest. For straight lines, equations were found from which constants were determined. Reliable data were considered for which the correlation factor was >0.99. Calibration plots were processed by a data processing program for calibration plots. The results were processed using mathematical statistics methods in order to determine the required number of measurements and assess the reliability of the obtained experimental data. The reliability of the results and the validity of the conclusions were confirmed by the integrated use of a set of modern techniques, reproducibility of experimental material.

RESULTS AND DISCUSSIONS

Several characteristic regions could be distinguished in cyclic voltammograms (CV, potential scan area 0.9–1.6 V; Fig. 1). An exponential increase in the anode current was observed in the anode region at potentials from 1.4 V due to the simultaneous Pb(II) oxidation and oxygen evolution reactions. There was a maximum current on the cathode branch at potentials between 1.0 and 1.1 V, due to the PbO_2 reduction reaction:[22]
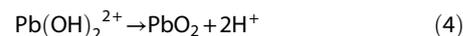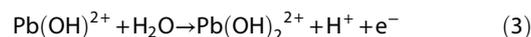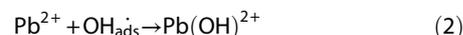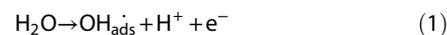
$$PbO_2 + 4H^+ \rightarrow Pb^{2+} + 2H_2O + 2e^-.$$
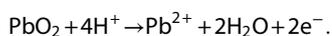
When $C_4F_9SO_3K$ was added to the electrolyte, the peak of cathodic reduction of PbO_2 decreased slightly (see Fig. 1), which indicates a slight inhibition in the rate of PbO_2 formation. Moreover, with an increase in the concentration of surfactant in the deposition electrolyte, the effect of inhibiting Pb^{2+} oxidation was not apparent. The number of electrons that take part in the kinetic stage are determined from linear potential sweep voltammetry measurements according to Delahay equation,[16] as described in the literature for analogous conditions.[23,24] The
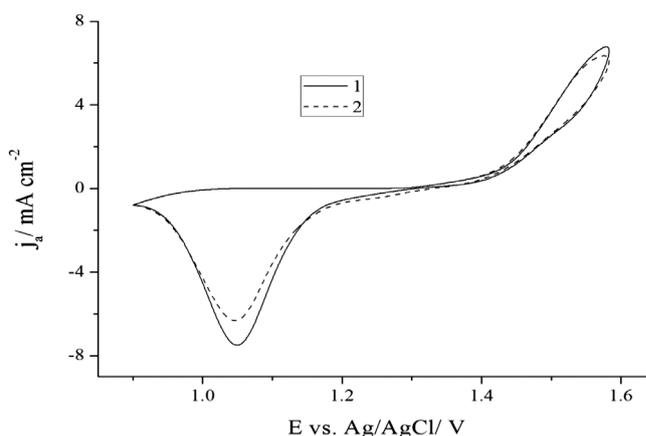
Figure 1 Cyclic voltammograms (scan range 0.9–1.6 V) on Pt in solutions containing 0.01 mol L^{-1} $Pb(NO_3)_2$ + 0.1 mol L^{-1} HNO_3 (1) + 0.003 mol L^{-1} $C_4F_9SO_3K$ (2). $v = 50$ mV s^{-1}.

transfer coefficient remained almost unchanged ($\alpha = 0.42 \pm 0.1$) when the surfactant was present in the deposition electrolyte. The calculated number of electrons in the elementary stage was 1.0 ± 0.1, confirming that PbO_2 formation is a multistep charge transfer which involves two consecutive one-electron stages, as outlined in the following kinetic scheme:

$$H_2O \rightarrow OH_{ads}^{\cdot} + H^+ + e^- \tag{1}$$

$$Pb^{2+} + OH_{ads}^{\cdot} \rightarrow Pb(OH)^{2+} \tag{2}$$

$$Pb(OH)^{2+} + H_2O \rightarrow Pb(OH)_2^{2+} + H^+ + e^- \tag{3}$$

$$Pb(OH)_2^{2+} \rightarrow PbO_2 + 2H^+ \tag{4}$$

This mechanism has been modified from the first version, proposed by Fleischmann and Liler,[25] where insoluble oxygen-containing Pb(IV) intermediates were proposed, involving the presence of several soluble intermediates such as the oxygen-containing Pb(IV) species proposed by Chang and Johnson,[26] and the oxygen-containing Pb(III) intermediate suggested by Velichenko et al.,[27] who afterwards proved the existence of both oxygen-Pb(III) and oxygen-Pb(IV) soluble intermediates.[28]

As a rule, at low anodic polarizations ($E < 1.55$ V) reactions will be under kinetic control, whereas at the high polarizations Pb^{2+} ion transport to the electrode surface will be the rate-determining stage.

Steady-state polarization curves are shown in Fig. 2. These curves take into account the partial Pb(II) electro-oxidation process, in the absence and in the presence of surfactant.[16,23,24] In the lower potential range, plots of E versus log j are linear ($r = 0.99$) indicating that the PbO_2 electrodeposition process is controlled kinetically. The limiting diffusion current of the partial oxidation of Pb^{2+} ions is reached at deposition potentials above 1.8 V. One can observe some decrease in the rate of PbO_2 formation in the presence of added surfactant from these curves.

Apparent heterogeneous rate constants were calculated according to the Koutecky–Levich equation[17,29] from intercepts of $1/I$ versus $1/\omega^{1/2}$ plots. Results show that the presence of $C_4F_9SO_3K$ in the deposition solution caused the apparent heterogeneous rate constant to decrease slightly from $(4.06 \pm 0.1) \times 10^{-4}$ to $(3.28 \pm 0.1) \times 10^{-4}$ ms^{-1} as the concentration of dopant increases from 0 to 0.003 mol L^{-1}. These results
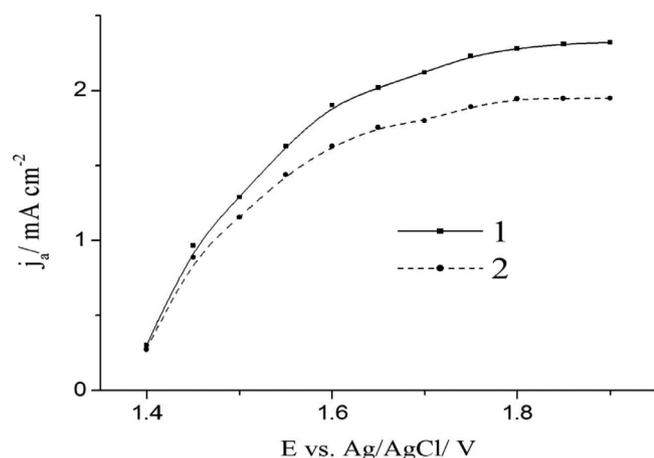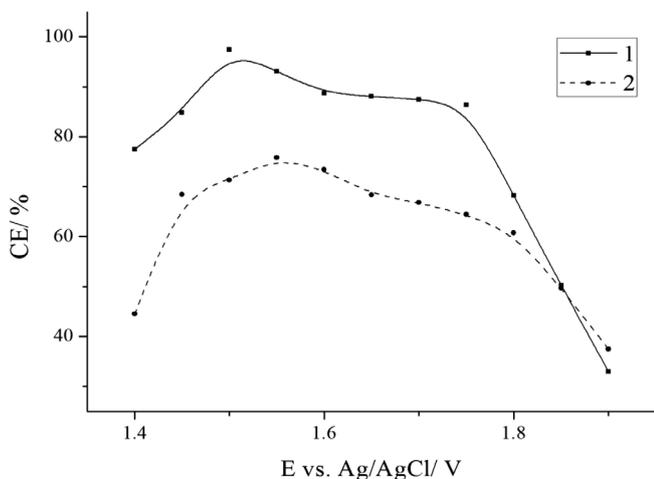
Figure 2 Steady-state polarization curves for partial PbO₂ electrodeposition current on Pt disk electrode in solutions containing 0.01 mol L^{-1} Pb(NO₃)₂ + 0.1 mol L^{-1} HNO₃ (1) + 0.003 mol L^{-1} C₄F₉SO₃K (2).

Figure 4 The Frumkin isotherm of C₄F₉SO₃K adsorption on PbO₂. θ and C, surface coverage and equilibrium concentration, respectively.

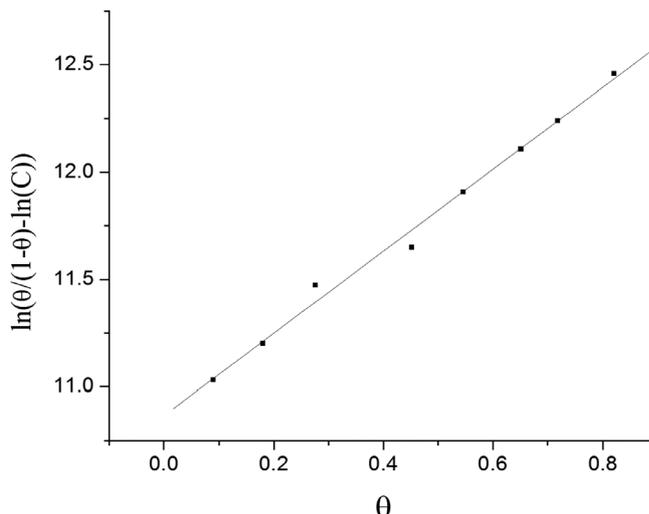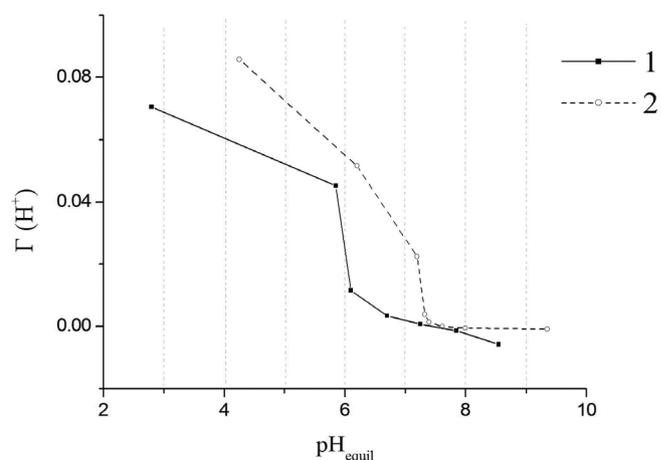are in agreement with the voltammetry data (see Fig. 1) discussed above in this section.

Figure 3 shows the dependences of the current efficiency (CE) of PbO₂ formation obtained from stationary polarization curves. The CE of PbO₂ decreased when surfactants were added to the solution, whereas the inhibition effect was insignificant with an increase in the concentration of surfactant. The observed effect is probably due to a decrease in the number of active centres on the electrode surface.

Adsorption measurements were performed on a PbO2 powder at zero charge potential.[30] As one can see from the experimental data, the adsorption of surfactant is satisfactorily described by the Frumkin isotherm (Fig. 4, correlation factor 0.996). The value of interaction parameter calculated from the Frumkin equation is 1.00 ± 0.05 that suggests the slight interaction between adsorbed molecules. The value of the energy of adsorption interaction ($-\Delta G$) for potassium perfluorobutanesulfonate is 33.20 ± 0.01 kJ mol^{-1}, which indicates the specific character of adsorption.

As a result of potentiometric measurements (Fig. 5), it was established that the adsorption of C₄F₉SO₃K on PbO₂ was accompanied by a shift of the pH₀ (zero charge pH) of the oxide to a region of higher value. This suggests that adsorption proceeds without the participation of functional groups of both a surfactant and the oxide surface. This hypothesis is well-supported by the data on the adsorption material balance.[11] The obtained data indicate the weak chemical adsorption of surfactant on lead dioxide,[31] that is confirmed by a slight displacement of the pH₀ of the oxide.[32]

The critical micelle concentration (CMC) of C₄F₉SO₃K was determined in order to establish whether micellization is present in the solution. Its value in 0.1 mol L^{-1} Pb(NO₃)₂ + 0.1 mol L^{-1} HNO₃ solution was rather large and amounted to 0.020 ± 0.001 mol L^{-1}. This also confirmed that all the working electrolytes were true solutions.

It was found that during electrodeposition of PbO₂ in the presence of C₄F₉SO₃K in the electrolyte, the additive was included in the growing deposit with the formation of a composite oxide-surfactant coating. Thus, it was found that an increase in the concentration of surfactant does not affect its content in the coating. The latter was *c.* 2.00 ± 0.05 wt% when the concentration of

Figure 3 Current efficiency of lead dioxide *versus* potential of deposition in solutions containing 0.01 mol L^{-1} Pb(NO₃)₂ + 0.1 mol L^{-1} HNO₃ (1) + 0.003 mol L^{-1} C₄F₉SO₃K (2).

Figure 5 PbO₂ (0.5 g) potentiometric titration results; concentration of potassium perfluorobutanesulfonate 0 (1) and 0.003 mol L^{-1} (2).

$C_4F_9SO_3K$ in the deposition electrolyte changed from 0.0015 until 0.005 mol L^{-1}. A surfactant concentration of 0.003 mol L^{-1} was chosen as working solution. At this concentration, according to the adsorption isotherm (see Fig. 4), we are in the region of hundred-degree surface filling, which means that one molecule of a surfactant corresponds to each adsorption center on the surface; and the electrolyte will remain the true solution, when the surfactant is added.

The data obtained can be adequately explained on the basis of a number of hypotheses. On the one hand, using a classical electrodeposition scheme, when surfactant adsorption occurs on the surface of growing PbO$_2$, the phenomenon of changing the additive content in the coating can be caused by two factors: (i) heterogeneous (concentration on a growing surface due to adsorption) and (ii) migratory (flow from the solution bulk to the surface under the influence of an electric field). On the other, we cannot exclude that not only crystallization but also colloidal particle formation occurs in the supersaturated layer of the solution, and that some particles adhere to the surface of the growing crystals, as observed in the case of synthesis of PbO$_2$-TiO$_2$ composites.[29] It should be noted that it is possible that all of the described effects occur simultaneously with different contributions. None of these hypotheses contradict the obtained experimental data.

An increase in the anode current density allowed us to obtain composites containing ≤17.00 ± 0.05 wt% of organic substance (Table 1). The observed effect is probably due to an increase in the positive charge of the electrode, which contributes to an increase in the adsorption of anionic surfactants on the surface of the growing oxide. An increase of the deposition temperature to 60 °C facilitated coatings with surfactant contents ≤10.00 ± 0.05 wt%.

The inclusion of surfactants in a growing coating leads to a change in the texture and structure of the resulting film. It is widely recognized[8] that the surface of nonmodified PbO$_2$-sample is homogeneous and large-crystalline. With an increase of surfactants in the coating, a decrease in the size and shape of crystalline blocks of PbO$_2$ was observed. As can be seen from SEM images, the presence of surfactants in the coating prevented the formation of large crystalline blocks, and when the organic content was 14.00 ± 0.05 wt%, significant internal stresses were observed in the coating [Fig. 6(a) and (b)]. The crystals exhibit sharp angles on both images. SEM/EDAX experiments [Fig. 6(c)] were performed to evaluate the amount and distribution of elements in electrodeposited composite. Low peaks corresponding to O and F indicate a satisfactory distribution of modifying elements in the entire sample bulk, not only on the coating surface. In addition, it was not possible to detect the S peak because it is too near of the very intense Pb peak.

Because a change in the physicochemical properties of oxides should lead to a change in the degree of filling of oxygen-containing particles of various types,[27] it possible to assume that the electrocatalytic activity of the obtained electrode materials also should change.

The electrocatalytic activity of PbO$_2$ deposited from a solution containing a surfactant was studied both in the respect to the O$_2$ evolution reaction and the oxidation of 4-chlorophenol. As follows from the steady-state polarization curves shown in Fig. 7, the O$_2$ evolution reaction decelerated on a PbO$_2$-C$_4$F$_9$SO$_3$K composite.

As has been found in many papers[13,16,21] the rate of the O$_2$ evolution process can change due to the nature and amount of additive. Such a change depends mainly on changes in chemical properties of the oxide surface that, in turn, change the bond strength of oxygen-containing particles chemisorbed on the electrode surface.
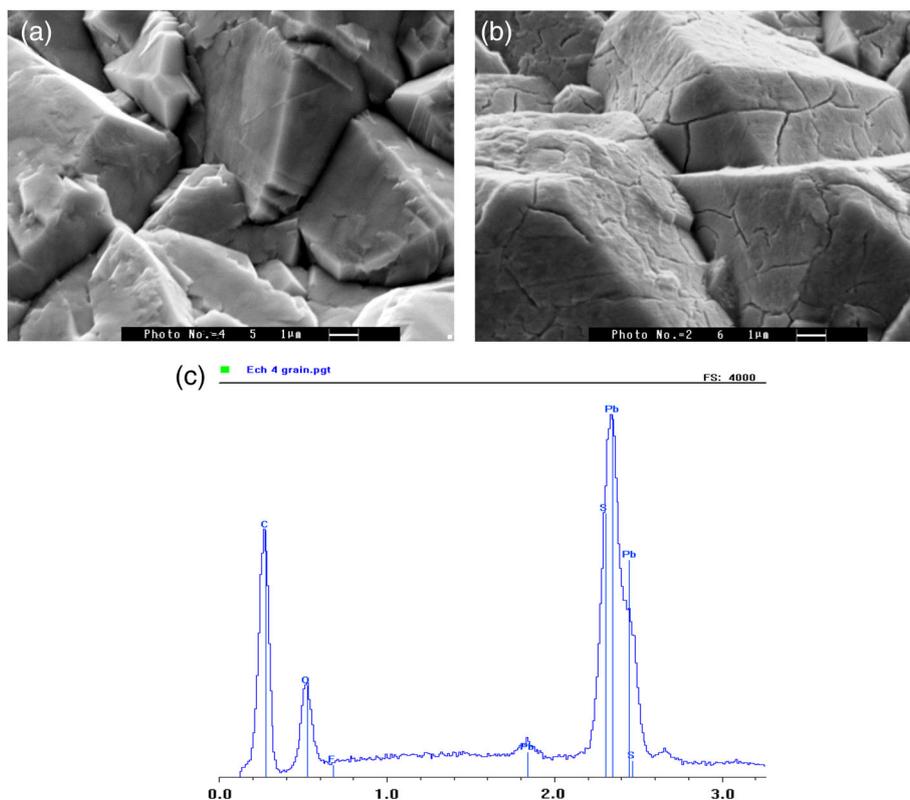
According to the mechanism proposed by Pavlov et al.,[33] O$_2$ evolution proceeds at active sites localized in the hydrated PbO$_2$ layer. The surface of lead dioxide has crystalline (PbO$_2$) and hydrated [PbO(OH)$_2$] zones, which are in equilibrium and, in the latter case, are capable of exchanging cations and anions. The process of O$_2$ evolution can be described by the following scheme:

$$PbO\cdot(OH)_2 + H_2O \rightarrow PbO\cdot(OH)_2\ldots(OH^\bullet) + H^+ + e^- \quad (5)$$

$$PbO\cdot(OH)_2\ldots(OH^\bullet) \rightarrow PbO\cdot(OH)_2 + O + H^+ + e^- \quad (6)$$

$$2\,O \rightarrow O_2 \quad (7)$$
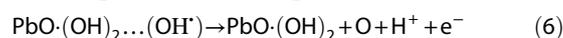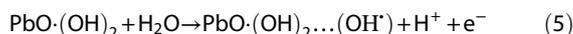
Trassatti[34] has shown that if the oxygen evolution reaction is limited by the stage of transfer of the second electron (electrochemical desorption), an increase in the bond strength of chemisorbed oxygen will lead to an increase in the overvoltage of O$_2$ evolution. Under conditions when the transfer of the first electron (electrochemical adsorption) will be the limiting stage, the overvoltage of the O$_2$ evolution reaction will decrease. As is known, the process of O$_2$ evolution on PbO$_2$ is controlled by the stage of transfer of the second electron;[35] therefore, the growth in overvoltage in our case indicates an increase in the bond strength of oxygen-containing radicals with the electrode surface.

According to the obtained results, oxygen overpotential on modified electrodes is significantly higher than on the nonmodified PbO$_2$-electrode and depends on the surfactant content in deposit, as was observed in the case of bismuth.[16] The obtained values of the Tafel slopes are significantly higher than theoretical. The data obtained show that oxygen overpotential for undoped PbO$_2$ is 1.676 V; for 3×10^{-5} mol L^{-1} C$_4$F$_9$SO$_3$K in the deposition electrolyte it is 1.727; for 3×10^{-4} mol L^{-1} it is 1.768; and for 3×10^{-3} mol L^{-1} it is 1.679 V, which indicates 100% filling of the surface of PbO$_2$ with a surfactant at such a concentration.

According to the literature,[36,37] at high anodic potentials, the electro-oxidation of most organic substances also proceeds with the participation of oxygen-containing particles chemisorbed on the electrode. 4-Chlorophenol was chosen as model compound in order to study the effect of C$_4$F$_9$SO$_3$K on the catalytic activity of PbO$_2$-based composite electrodes with respect to organic substances. This is due to the fact that the process of electro-oxidation of phenolic compounds on unmodified PbO$_2$-electrodes is well studied and described in the literature.[38–41] Benzoquinone and maleic acid are recognized as the main

j_a (mA cm^{-2})	$\omega \pm 0.05$ (wt%)
4	1.92
6	5.72
8	14.14
20	16.63

Table 1 The content of surfactant in PbO$_2$-C$_4$F$_9$SO$_3$K composites depending on the anode current density[a]

[a]Composites deposited from 0.1 mol L^{-1} HNO$_3$+ 0.1 mol L^{-1} Pb(NO$_3$)$_2$+ 0.003 mol L^{-1} C$_4$F$_9$O$_3$SK.
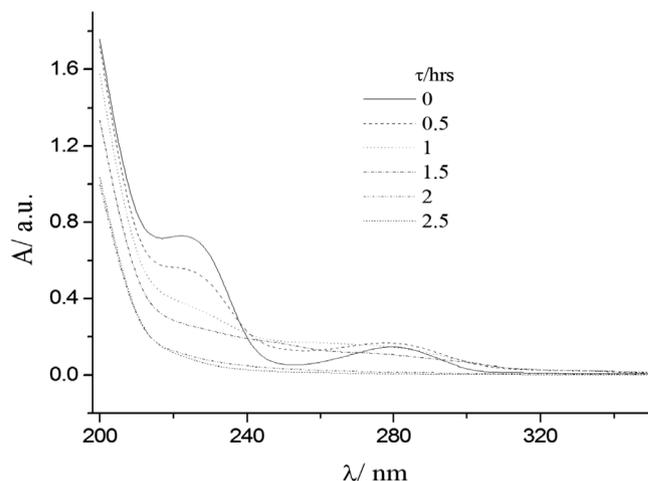
Figure 6 SEM micrographs of (a) PbO$_2$-1.92 wt% and (b) PbO$_2$-14.1 wt% C$_4$F$_9$SO$_3$K; (c) EDX spectrum of sample in (a).
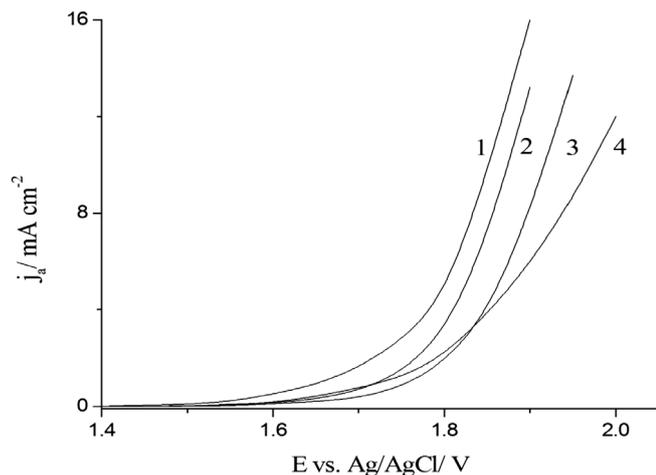
Figure 7 Steady-state polarization curves of oxygen evolution in 1 mol L^{-1} H$_2$SO$_4$ (Scan rate 1 mV s^{-1}, $t = 25$ °C) on PbO$_2$-electrodes, deposited from next solutions: 0.1 mol L^{-1} Pb(NO$_3$)$_2$ + 0.1 mol L^{-1} HNO$_3$ + X mol L^{-1} C$_4$F$_9$SO$_3$K, where X is 0 (1), 3×10^{-5} (2), 3×10^{-4} (3) and 3×10^{-3} (4). Coating electrodeposited on Ti/Pt sheet.

Figure 8 Electronic absorption spectra of solutions with 0.1 mmol L^{-1} initial concentration of 4-chlorophenol during electrolysis on PbO$_2$-1.92 wt% C$_4$F$_9$SO$_3$K anode.

intermediate products in the anodic oxidation of 4-chlorophenol. In this regard, a convenient way to evaluate the conversion rate of 4-chlorophenol is the disappearance time of aromatic intermediates, which can be determined from the UV spectra of solutions at different electrolysis times.

The UV spectrum of the 4-chlorophenol initial solution is characterized by two peaks at wavelengths of 230 and 280 nm.[38] At the first time of electrolysis, there is a decrease in the peak at 230 nm, as well as a slight increase in the peak at 280 nm and the appearance of the plateau at 250–270 nm, which is due to a decrease in the concentration of 4-chlorophenol and the accumulation of benzoquinone in the solution. A further increase in electrolysis time leads to the disappearance of peaks at 230 and 280 nm, as well as a decrease of plateau at 250–270 nm due to a decrease in the concentrations of both 4-chlorophenol and benzoquinone (Fig. 8). HPLC data indicated that the aromatic compounds were completely destroyed with the formation of only aliphatic electrolysis products (in particular, maleic acid) after 4 h of electrolysis

Table 2 The rate of 4-chlorophenol oxidation on the composites involved

Anode	Heterogeneous rate constant (±0.01 h^{-1})
PbO_2	0.28
PbO_2-1.92 wt% $C_4F_9SO_3K$	0.82
PbO_2-14.1% wt$C_4F_9SO_3K$	0.83

on an unmodified PbO_2-anode. As follows from Table 2, the conversion rate of 4-chlorophenol increasef with increasing of surfactant content in the composite. The observed effect is due both to an increase in the direct electrochemical oxidation rate of 4-chlorophenol and inhibition of the oxygen evolution reaction on PbO_2–fluoropolymer composite. The simultaneous action of these two factors will increase the conversion rate of 4-chlorophenol.

CONCLUSION

The addition of $C_4F_9SO_3K$ into the PbO_2 deposition electrolyte has practically no effect on the kinetics of Pb^{2+} electro-oxidation; the mechanism of the process as a whole also does not change. In the region of low polarizations, the limiting stage is the second electron transfer, apparent from the slight decreased in heterogeneous rate constant with increasing surfactant concentration in the deposition electrolyte. It was shown that the observed effect is due to the adsorption of fluoropolymer and, as a consequence, the blocking of active centres on the surface of the growing oxide.

It was found that during electrodeposition of PbO_2 in the presence of $C_4F_9SO_3K$ in the electrolyte, the additive is included in the growing oxide with the formation of a composite oxide-surfactant coating. Depending on the composition of the deposition electrolyte and the electrolysis conditions, the surfactant content in the composite coating ranges from 2.00 ± 0.05 to 17.00 ± 0.05 wt%. The inclusion of surfactants in the growing coating with almost unchanged kinetic regularities of electrodeposition leads to a change in the texture and structure of the resulting films.

It was found that, the obtained PbO_2–fluoropolymer composite materials differ from unmodified PbO_2 in terms of their electrocatalytic activity. When using the composites involved as anodes, the inhibition of O_2 evolution and an almost three-fold increase in the rate of electrochemical conversion of 4-chlorophenol to aliphatic compounds were observed.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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