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THE INFLUENCE OF ELECTROLYTE NATURE ON LEAD DIOXIDE ELECTROCRYSTALLIZATION

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During the electrodeposition of lead dioxide the simultaneous formation of two phases (α - and β -phase) may occur. Film electrodeposition begins with the formation of α -phase, and only then the formation of β -phase or two-phase deposition simultaneously begins. The nucleation of PbO_2 proceeds via the progressive mechanism both in methanesulfonate electrolytes and in nitrate ones. However, the preferred form of crystals at 2D nucleation in the case of methanesulfonate electrolyte is the cylinder, whereas in the nitrate electrolyte the crystal formation occurs in the form of cones. The rate constants of nucleation of α - and β -phases of PbO_2 in the nitrate electrolyte differ slightly, and in the case of methanesulfonate electrolyte there is a predominance of α -phase forming. An increase of methanesulfonate ions content in the deposition electrolyte changes the ratio between α - and β -phase crystallization constants. The character and kinetic parameters of 2D nucleation of lead dioxide crystals allow predicting the phase composition of coatings.

Keywords: lead dioxide, methanesulfonate/nitrate electrolyte, nucleation and growth, crystal shape, progressive growth.

Introduction

The electrodeposition of lead dioxide is recognized to be a complex multi-step process, the main features of which depend on the composition of the deposition electrolyte and hydrodynamic conditions of electrolysis [1–3]. Materials based on lead dioxide are known to be produced by electrodeposition from perchlorate, acetate, boron fluoride, plumbate, nitrate and methanesulfonate electrolytes [1,2,4–8]. Only in the latter case, it is feasible to obtain thick coatings (up to 2 mm) with low internal stresses and high stability in long electrolysis processes.

Establishing of the kinetic characteristics of the crystallization process and control of its parameters are very important, because determine basic properties of the resulting materials.

Since deposition conditions determine physicochemical properties and electrocatalytic activity of lead dioxide deposits, in the present work we tried to determine the basic parameters of the initial stages of crystallization of PbO_2 from methanesulfonate electrolytes. It should be noted that there is no such information in the literature at the moment. The comparative analysis between parameters of PbO_2 crystallization from methanesulfonate and nitrate electrolytes has been performed.

Experimental

All chemicals were reagent grade. Electrodeposition parameters of lead dioxide both in nitrate and methanesulfonate electrolytes were studied on Pt disk electrode (Pt-DE, 0.19 cm^2) by steady-state voltammetry and chronoamperometry. Before use, the Pt-DE surface was treated by the procedure described in study [9]. Such preliminary treatment permits achieving a reproducible surface. Voltammetry measurements were carried out in a standard temperature-controlled three-electrode cell. All potentials were recorded and reported vs. $\text{Ag}/\text{AgCl}/\text{KCl}_{(\text{sat.})}$ reference electrode.

Electrodeposition of lead dioxide was studied in methanesulfonate and nitrate electrolytes which contained 1 M $\text{CH}_3\text{SO}_3\text{H}$ or HNO_3 , 0.01 M $\text{Pb}(\text{CH}_3\text{SO}_3)_2$ or $\text{Pb}(\text{NO}_3)_2$ depending on the purposes of experiments.

X-ray powder diffraction data were collected on a STOE STADI P automatic diffractometer equipped with linear PSD detector (transmission mode, $2\theta/\omega$ -scan; $\text{Cu K}\alpha_1$ radiation, curved germanium (1 1 1) monochromator; 2θ -range $6.000 \leq 2\theta \leq 102.945$ $^\circ 2\theta$ with step 0.015 $^\circ 2\theta$; PSD step 0.480 $^\circ 2\theta$, scan time 50 s/step).

Qualitative and quantitative phase analysis was performed using the PowderCell program. For selected samples with relatively high degree of crystallinity the Rietveld refinement was carried out using FullProf.2k (version 5.40) program [10,11].

Results and Discussion

Typical current transients for PbO_2 deposition, obtained for the initial stages of lead dioxide electrodeposition, are shown in Fig. 1. The observed j - t curves can be divided in some distinct regions [12,13] as follows: i) the current density jump in the initial period of electrode polarization; ii) induction period; iii) maximum current density, and iv) the achievement of a quasi-stationary current density. As one can see, growth of an anodic polarization leads to a substantial decreasing the induction period and to increasing current maximum. Such type of transients indicates difficulties in the initial stages of nucleation and confirms that the process is controlled by the kinetic stage [12].

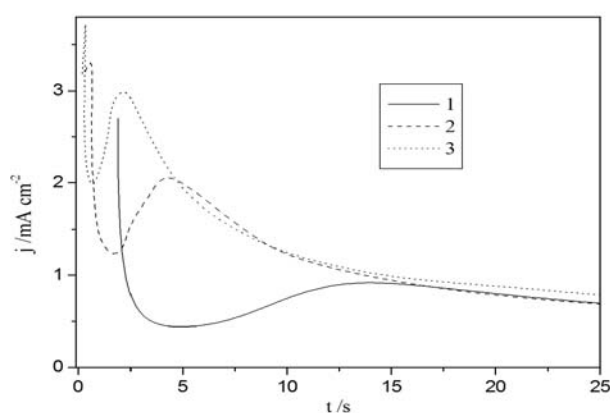


Fig. 1. Current transients for PbO_2 deposition from solution containing 0.01 M $\text{Pb}(\text{CH}_3\text{SO}_3)_2$ +1 M $\text{CH}_3\text{SO}_3\text{H}$ at different deposition potentials, mV: (1) 1550, (2) 1600, (3) 1620

During electrodeposition both the kinetic characteristics of the crystallization process and the nature of the crystal structure of formed oxide will depend on the nucleation rate, i.e. the rate of formation of crystal nuclei, linear crystallization velocity and their ratio. These parameters can be determined from the current transients of the process of lead dioxide electrodeposition [13–15].

The electrocrystallization model proposed by Abyaneh [13] was selected as an appropriate approach for the investigation of initial stages of the formation of a lead dioxide new phase, since it gives a more complete description and understanding of the growth mechanism of lead dioxide phases and allows determining the kinetic parameters of nucleation for both α - and β -phases by analysis of current-time transients. According to model suggestions of authors [13], one can establish the nature of the nucleation (instantaneous or progressive) by comparing the ratio I_{max} (current maximum) and I_{plateau} (plateau current).

Instantaneous and progressive nucleation mechanisms are limited by stages which correspond to the rapid formation of the nucleus on a small number of active sites and the slow formation of

nuclei in a large number of active sites, respectively. Both extremes are unattainable in reality. However, the existing theory allows describing the preferred mechanism of nucleation. It has been suggested that the observed delay in the nucleation step corresponds to a change of the electrode potential at non-stationary conditions during the early stages of nucleation, but the nucleation is instantaneous [13]. However, the term «instantaneous growth» actually refers to the processes that lead to the formation of nuclei of the new phase that occurs on a time scale much faster than exhaustion or prohibition of nucleation sites on the surface, through the subsequent growth of a new phase.

Also, the ratio of the maximum current to the deposition current shows a preferred geometric shape of formed nuclei. Since the difference in the currents of peak and plateaus on chronoamperograms gives an indication of the relationship between the nucleation rate constants in the directions perpendicular and parallel to the electrode surface. In the formation of oxide coatings three basic nuclei geometries, such as semi-spheroid, cone and cylinder, are considered [13]. The semi-spheroid shape of the nuclei is less energy intensive and is considered as the most simple. As a rule, the less difficulties in the crystallization, the higher the probability of the formation of semi-spheroid nuclei. The most difficult in the organization are the cylinder-shaped nuclei. The analysis of crystallization of lead dioxide from nitrate electrolytes on the glassy-carbon surface showed that conical crystals form of the deposit is preferred [14].

After investigation of initial stages of PbO₂ electrodeposition from methanesulfonate electrolyte, it was established that process proceeds by progressive mechanism of nucleation. The preferred form of crystals at 2D nucleation from methanesulfonate electrolytes is a cylinder that is in accordance with scanning electron microscopy results (Fig. 2).

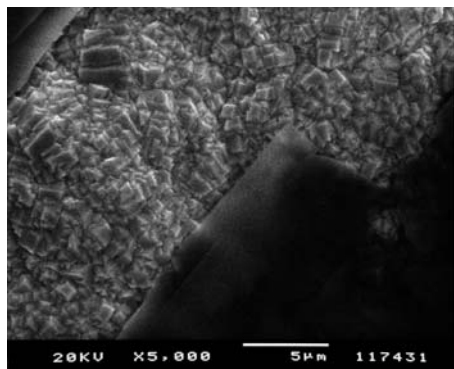


Fig. 2. SEM micrographs of PbO₂-coating surface obtained from solution containing 0.01 M Pb(CH₃SO₃)₂+1 M CH₃SO₃H

It should be noted that the ascending portion of the current transient is insensitive to the geometry

of the crystal growth, and it allows determining the kinetic parameters of 2D nucleation. The geometry of the nuclei should be taken into account at the determination of the kinetic parameters of the formation of a new phase at further formation of a crystalline deposit, when 3D nucleation is considered.

Two distinct growth mechanisms are considered [13]:

i) instantaneous growth:

$$(j-j_1)^{1/3}=(zFK_{\alpha})^{1/3}(t-t_{\alpha}); \quad (1)$$

ii) progressive growth:

$$(j-j_1)^{1/2}=(zFK_{\alpha})^{1/2}(t-t_{\alpha}), \quad (2)$$

where K_{α} (mol m⁻²s⁻¹) is the rate constant for growth of α -phase crystals in a direction which is perpendicular to the electrode surface; t_{α} (s) is the time corresponding to the beginning of α -phase formation.

During the electrodeposition of lead dioxide, the simultaneous formation of two phases (α - and β -phase) may occur. Film electrodeposition begins with the formation of α -phase, and only then the formation of β -phase or two-phase deposition simultaneously begins. It should be noted that if the deposition time of the coating is less than the induction period of the formation of α -phase ($t < t_{\alpha}$), the nucleation does not occur. And in the time region $t_{\alpha} \leq t \leq t_{\beta}$ only α -phase is formed. The formation of β -phase becomes possible while on the plot of $(j-j_1)^{1/3}$ or $(j-j_1)^{1/2}$ vs. time a slope change occurs. Then the characteristics of α -phase formation can be determined from the $j-t$ plots, corresponding to a growth model [13]:

i) instantaneous growth:

$$(j-j_1)^{1/3}=[(zFK_{\alpha})^3(t-t_{\alpha})^3+zFK_{\beta}((t-t_{\beta})^3)^{1/3}; \quad (3)$$

ii) progressive growth:

$$(j-j_1)^{1/2}=[(zFK_{\alpha})^2(t-t_{\alpha})^2+zFK_{\beta}((t-t_{\beta})^2)^{1/2}, \quad (4)$$

where K_{β} (mol m⁻²s⁻¹) is the rate constant for growth of β -phase crystals in a direction which is perpendicular to the electrode surface; t_{β} (s) is the time corresponding to the beginning of β -phase formation.

Current densities for instantaneous and progressive nucleation were calculated from the transients of lead dioxide electrocrystallization (see Fig. 1).

As has been shown in [4,14], the deviation from linearity on a current density vs. time plot is less for the progressive growth, indicating that the preferential formation of a new phase occurs through this mechanism. The main parameters of lead dioxide

crystallization from methanesulfonate electrolyte at different deposition potentials were calculated on the basis of the model proposed in [13] for progressive mechanism with simultaneous formation of α - and β -phases of PbO_2 (Table 1).

Table 1
Parameters of initial stages of lead dioxide electrocrystallization*

Deposition potential, mV	t_α	K_α	t_β	K_β
1550	3.68	3.35×10^{-7}	10.20	3.80×10^{-8}
1600	2.11	3.76×10^{-6}	2.36	1.30×10^{-5}
1620	0.55	1.87×10^{-5}	1.41	3.74×10^{-4}

Note: * – Deposition electrolyte contained 0.01M $\text{Pb}(\text{CH}_3\text{SO}_3)_2$ and 1 M $\text{CH}_3\text{SO}_3\text{H}$.

As been suggested in [12], either the predominance of one phase over another or ingesting the growing centers of one phase by another may occur, depending on the composition of electrolyte. The formation of one phase is noticeably lagged behind the other. The type of lagging phase depends on the deposition conditions: there is a slight predominance of the growth of α -phase of PbO_2 at low polarizations; α -phase becomes stunted at high polarization, and there is overlap and ingesting formed α -phase growth centers by β -phase crystals on the surface of the electrode.

An effect of differences in deposition currents at the same concentration of lead ions in nitrate and methanesulfonate electrolytes, which was ascertained in [12], can probably be explained by a change in the nature of discharging particles, in particular the formation of complex lead compounds with methanesulfonic acid [12], which should facilitate lead dioxide crystallization on the positively charged electrode surface.

In all cases, the type of nucleation is progressive. However, the preferred form of crystals at 2D nucleation in the case of methanesulfonate electrolyte is the cylinder, and in the nitrate electrolyte the crystal formation occurs in the form of cones. The rate constants of nucleation of α - and β -phases of PbO_2 in the nitrate electrolyte differ slightly, and

there is a predominance of α -phase forming in case of methanesulfonate electrolyte (Table 2).

The geometric shape of crystals depends on the ratio between the lead dioxide nucleation constants which describes the crystal growth in parallel and perpendicular directions to the surface. When oxides are crystallized, the preferred geometric shapes are the cylinder and the cone. Such a geometrical shape as a cube during the nucleation of oxides is not possible; the hemispheroid form of crystals is realized only in some cases, when there are no difficulties in the crystallization.

The electrocrystallization of PbO_2 begins with the formation of a monolayer over the entire surface of the electrode, and only then there is the formation and growth of 3D nuclei. The growth of lead dioxide occurs through crystallization layer by the next layer, so each consequent layer is formed on the renewed surface [12].

Since particles like $\text{Pb}(\text{CH}_3\text{SO}_3)_2$, $\text{Pb}(\text{CH}_3\text{SO}_3)^+$ or $\text{Pb}(\text{CH}_3\text{SO}_3)^{3-}$ can be adsorbed from the solution bulk on the surface of the growing oxide, the influence of methanesulfonate ion concentration in the electrolyte on parameters of lead dioxide crystallization has been estimated. According to the obtained results, an increase in CH_3SO_3^- ions concentration in the deposition electrolyte leads to a significant reduction in the induction period, that indicates the facilitation of the initial stages of phase formation of lead dioxide and also causes a noticeably increase in the deposition current.

At 0.1 mol dm^{-3} acid concentration in the deposition electrolyte and electrode polarization of 1500 mV, the mechanism of nucleation is progressive both for nitrate and methanesulfonate electrolytes. A preferred form of crystals at 2D nucleation is a cylinder and for the nitrate electrolyte crystal formation occurs in the form of cones.

According to the obtained data (see Table 2), an increase in methanesulfonate ions concentration in the deposition electrolyte changes the ratio between α - and β -phases crystallization constants. Thus, in case of nitrate electrolyte the growth of β -phase is predominant. When nitric acid is replaced by methanesulfonic, i.e. the ratio between Pb^{2+} and

Table 2
Influence of deposition electrolyte on initial parameters of lead dioxide electrocrystallization

Deposition electrolyte	t_α	K_α	t_β	K_β
0.01 M $\text{Pb}(\text{CH}_3\text{SO}_3)_2 + 1$ M $\text{CH}_3\text{SO}_3\text{H}$	4.56	2.76×10^{-7}	7.29	4.80×10^{-8}
0.1 M $\text{Pb}(\text{NO}_3)_2 + 0.1$ M HNO_3	1.11	4.23×10^{-6}	2.56	1.45×10^{-5}
0.1 M $\text{Pb}(\text{NO}_3)_2 + 0.1$ M $\text{CH}_3\text{SO}_3\text{H}$	1.54	1.08×10^{-5}	2.49	3.30×10^{-5}
0.1 M $\text{Pb}(\text{CH}_3\text{SO}_3)_2 + 0.1$ M $\text{CH}_3\text{SO}_3\text{H}$	1.20	3.38×10^{-5}	2.78	1.04×10^{-6}
0.1 M $\text{Pb}(\text{NO}_3)_2 + 1$ M HNO_3	0.84	4.34×10^{-5}	1.95	3.85×10^{-4}
0.1 M $\text{Pb}(\text{CH}_3\text{SO}_3)_2 + 1$ M $\text{CH}_3\text{SO}_3\text{H}$	0.88	1.23×10^{-5}	1.07	7.44×10^{-7}
0.1 M $\text{Pb}(\text{NO}_3)_2 + 1$ M $\text{HNO}_3 + 1.2$ M $\text{CH}_3\text{SO}_3\text{Na}$	1.14	4.51×10^{-6}	1.96	2.27×10^{-5}
0.01 M $\text{Pb}(\text{NO}_3)_2 + 1$ M HNO_3	4.75	5.48×10^{-8}	12.34	7.10×10^{-8}

CH_3SO_3^- ions becomes 2, β -phase growth also prevails, but the ratio between K_α and K_β constants decreases.

When the ratio between Pb^{2+} and CH_3SO_3^- ions concentrations in the deposition electrolyte is 10 and 12, respectively, a decrease in the induction period has been also observed.

It should be noted that I_{max} for the electrolyte containing only methanesulfonate ions is much higher than for electrolytes based on nitric acid. In this case the ratio between Pb^{2+} and CH_3SO_3^- ions in the deposition electrolyte does not influence on the I_{max} value. When $1.2 \text{ mol dm}^{-3} \text{ CH}_3\text{SO}_3\text{Na}$ was added to the nitrate electrolyte, the value of I_{max} increases but does not coincide with that of the methanesulfonate electrolyte. It has been found that the crystallization of lead dioxide takes place in all cases via the progressive mechanism. The preferred geometric shape of crystals formed during 2D nucleation is a cylinder. It should be observed that for nitrate electrolytes the cone is a preferred form of crystals with nitric acid concentration of 0.1 mol dm^{-3} , and it changes to a cylinder if nitric acid concentration is 1 mol dm^{-3} . With changing in the nature of the acid in the deposition electrolyte, the kinetic parameters of the initial crystallization steps also change (see Table 2). In particular, the nucleation reduces. The nature of acid affects the ratio between α - and β -phases crystallization constants in different amount. Thus, in the presence of nitric acid, the growth of β -phase is noticeably predominant. In case of methanesulfonate ion, there is predominance in α -phase growth. It should also be noted that the α -phase growth prevails in 20 times when the electrolyte contains only ions Pb^{2+} and CH_3SO_3^- ions in the ratio equal to 10.

This effect of changing the kinetic parameters of 2D nucleation of lead dioxide probably will affect the 3D crystallization of the coating and, as a consequence, the phase composition of the coating (Table 3).

Thus, the content of β -phase is much higher in a deposit obtained from the nitrate electrolyte than in case of a coating obtained from an electrolyte based on methanesulfonic acid. The features and kinetic parameters of 2D nucleation of lead dioxide crystals allow prognosticating the phase composition of the coatings.

Both a decrease in the induction period and the reduction of stationary current value (I_s) are observed in chronoamperometric curves obtained at $E=1400 \text{ mV}$ on the rotating electrode (Fig. 3, curves 1, 2). The reduction of I_s current with increasing of angular velocity is negligible and can be explained in terms of aspiration of the soluble intermediate Pb(III) product from the reaction zone.

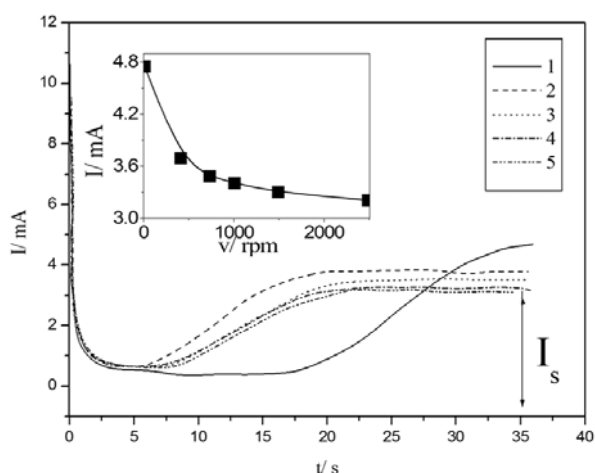


Fig. 3. Chronoamperometric curves obtained at 1400 mV on Pt-RDE in $0.1 \text{ M Pb}(\text{CH}_3\text{SO}_3)_2 + 0.1 \text{ M CH}_3\text{SO}_3\text{H}$ at different angular velocities of the electrode, rpm: (1) 0; (2) 400; (3) 750; (4) 1500; (5) 2500. Inset: stationary current value vs. angular velocity of the electrode at 1400 mV

With the angular velocity growth, the induction period significantly changes (see Fig. 3, curves 1, 2), and after 1000 rpm remains virtually constant. The induction period is determined by the time required to the nucleation of phases, i.e. to create a certain concentration of ad-atoms of PbO_2 or Pb(IV) particles like Pb(OH)_2^{2+} on the surface layer that decompose with PbO_2 formation [6,9]. Increasing the angular velocity should promote the growth rate of accumulation of PbO_2 in the surface layer and thereby lead to a reduction of time required for the nucleation. When a film of lead dioxide has been formed on the platinum electrode surface, a change of rate-determining step (to the second electron transfer step) takes place. Therefore, the reduction of the induction period is due to an increase in the

Table 3

Influence of the deposition electrolyte on the phase composition of lead dioxide

Deposition electrolyte	The content of PbO_2 phase, %	
	α	β
$0.1 \text{ M Pb}(\text{NO}_3)_2 + 1 \text{ M HNO}_3$	15.5	84.5
$0.1 \text{ M Pb}(\text{CH}_3\text{SO}_3)_2 + 1 \text{ M CH}_3\text{SO}_3\text{H}$	90.0	10.0
$0.1 \text{ M Pb}(\text{NO}_3)_2 + 1 \text{ M HNO}_3 + 1.2 \text{ M NaCH}_3\text{SO}_3$	43.8	56.2

Note: coatings are deposited at $j_e = 5 \text{ mA cm}^{-2}$, $T = 298 \text{ K}$.

rate of OH-radicals formation and an increase in the rate of a second electron transfer step. The analysis of current transients revealed that the nucleation is instantaneous. The preferred form of crystals at 2D nucleation is a semi-spheroid.

It should be noted that the effect of current reduction with increasing the angular velocity of the electrode is less pronounced at low potential in methanesulfonate deposition electrolyte compared with perchlorate and nitrate electrolytes [3,9,12]. This is probably due to a more significant interaction of Pb(III) intermediate product with the electrode surface.

For more detailed analysis of methanesulfonate ion influence on the initial stages of the nucleation, the current-time transients were obtained from the electrolytes with different content of methanesulfonate ions.

According to the obtained data, an increase in the content of CH_3SO_3^- ions concentration in the deposition electrolyte leads to the extreme dependence of the current maximum. With increasing methanesulfonate ions concentration, the current peak increases; and when ion concentration is higher than 0.4 mol dm^{-3} , the current peak decreases reaching a minimum value at a concentration of $1.2 \text{ mol dm}^{-3} \text{ CH}_3\text{SO}_3\text{Na}$.

This indicates the facilitation of the initial stages of the lead dioxide nucleation. In this case, the observed effect of acceleration in the formation of two-dimensional nuclei is probably associated with changes in the ratio of different complex particles in the deposition electrolyte.

The main parameters of crystallization of lead dioxide at different concentration of methanesulfonate ion in solution are collected in the Table 4.

Under these deposition conditions the mechanism of nucleation is progressive. The preferred form of crystals at 2D nucleation is cylinder. Only at a concentration of methanesulfonate ion equal to 1.2 mol dm^{-3} , cone-shaped crystals are probably formed.

With growth of the solution acidity, an increase in the induction period of lead dioxide deposition as well as an increase of the deposition current is observed. In this case, the crystallization occurs also through the progressive mechanism. The preferred

form of crystals at 2D nucleation is cylinder.

It should be noted that a substrate, on which oxide is deposited, and its surface pretreatment prior the plating play a significant role in the nucleation of crystals. The parameters of the initial stages of Pb^{2+} electrocrystallization on the platinum electrode and on the surface of lead dioxide were compared. Platinum was selected due to the low rate of oxidation and destruction at high anodic potentials. Depending on the substrate material, the characteristics of initial stages of deposition may differ significantly. The influence of the substrate on the initial stages of PbO_2 crystallization was investigated at electrode potential of 1500 mV. Chronoamperometric curves of crystallization on Pt electrode and on lead dioxide deposited on Pt electrode are shown in Fig. 4.

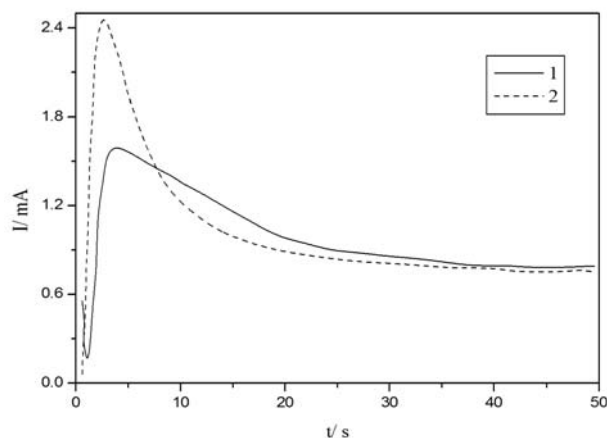


Fig. 4. Chronoamperometric curves of PbO_2 electrodeposition obtained at $E=1500 \text{ mV}$ and $T=298 \text{ K}$ from electrolytes containing: (1) $0.1 \text{ M Pb}(\text{NO}_3)_2+0.1 \text{ M HNO}_3+0.3 \text{ M NaCH}_3\text{SO}_3$ on Pt disk electrode; (2) $0.1 \text{ M Pb}(\text{NO}_3)_2+0.1 \text{ M HNO}_3+0.3 \text{ M NaCH}_3\text{SO}_3$ on PbO_2/Pt disk electrode

When lead dioxide has been deposited on a substrate of lead dioxide, an increase in deposition current and a very short induction period of PbO_2 crystallization was observed. Approximately after 40 seconds of deposition, a quasi-stationary current is observed, which coincides in both cases: at deposition on Pt disk electrode and on PbO_2/Pt disk electrode.

For all the above mentioned cases, the crystallization takes place via the progressive

Table 4

Influence of methanesulfonate ion on parameters of initial stages of PbO_2 nucleation

Deposition electrolyte	t_α	K_α	t_β	K_β
$0.1 \text{ M Pb}(\text{NO}_3)_2+1.0 \text{ M HNO}_3+0.1 \text{ M NaCH}_3\text{SO}_3$	0.55	1.91×10^{-6}	2.09	2.47×10^{-6}
$0.1 \text{ M Pb}(\text{NO}_3)_2+1.0 \text{ M HNO}_3+0.3 \text{ M NaCH}_3\text{SO}_3$	0.87	5.73×10^{-6}	1.82	9.38×10^{-6}
$0.1 \text{ M Pb}(\text{NO}_3)_2+1.0 \text{ M HNO}_3+0.4 \text{ M NaCH}_3\text{SO}_3$	0.47	10.20×10^{-6}	1.70	1.96×10^{-5}
$0.1 \text{ M Pb}(\text{NO}_3)_2+1.0 \text{ M HNO}_3+0.5 \text{ M NaCH}_3\text{SO}_3$	0.51	9.34×10^{-6}	1.91	1.64×10^{-5}
$0.1 \text{ M Pb}(\text{NO}_3)_2+1.0 \text{ M HNO}_3+0.6 \text{ M NaCH}_3\text{SO}_3$	0.58	5.57×10^{-6}	1.54	1.94×10^{-5}
$0.1 \text{ M Pb}(\text{NO}_3)_2+1.0 \text{ M HNO}_3+0.8 \text{ M NaCH}_3\text{SO}_3$	0.80	5.15×10^{-6}	1.50	2.17×10^{-5}
$0.1 \text{ M Pb}(\text{NO}_3)_2+1.0 \text{ M HNO}_3+1.2 \text{ M NaCH}_3\text{SO}_3$	1.14	4.51×10^{-6}	1.96	2.27×10^{-5}

mechanism; the main kinetic parameters are presented in the Table 5. A preferred form of crystals at 2D nucleation on the lead dioxide surface is the cylinder; and in case of platinum, crystallization nuclei are cones.

Table 5
Parameters of initial stages of lead dioxide crystallization depending on the acidity of the deposition solution and a type of the substrate

Acid concentration	t_{α}	K_{α}	t_{β}	K_{β}
0.1 M HNO ₃	0.43	5.41×10^{-6}	1.12	6.1×10^{-6}
1 M HNO ₃	0.87	5.73×10^{-6}	1.82	9.38×10^{-6}
Pt disk electrode	0.43	5.41×10^{-6}	1.12	6.10×10^{-6}
PbO ₂ /Pt disk electrode	0.24	3.32×10^{-5}	1.28	7.28×10^{-5}

The differences in characteristics of the nucleation of lead dioxide from nitrate and methanesulfonate electrolytes are obviously associated with the specific effect of methanesulfonate ions on the water structure in the near-electrode layer. As it was shown in the work [15], in electrolytes containing methanesulfonate ions the amount of oxygen-bound particles adsorbed on the surface is increased on the surface, they being involved in the formation of lead dioxide. This contributes to an increase in the rate of nucleation of lead dioxide [15].

Conclusions

It was found that the nucleation of lead dioxide occurs via the progressive mechanism. The preferred form of crystals at 2D nucleation is the cylinder in case of methanesulfonate electrolyte, whereas the crystal formation occurs in the form of cones in nitrate electrolyte. The rate constants of nucleation of α - and β -phases of PbO₂ in the nitrate electrolyte differ slightly, and in case of methanesulfonate electrolyte there is a predominance of α -phase formation. An increase in methanesulfonate ions content in the deposition electrolyte changes the ratio between α - and β -phase crystallization constants. Thus, in case of nitrate electrolyte the growth of β -phase is predominant. When nitric acid is replaced by methanesulfonic, i.e. the ratio between Pb²⁺ and CH₃SO₃⁻ ions becomes 2, β -phase growth also prevails, but the ratio between K_{α} and K_{β} constants decreases. When the electrolyte contains only ions Pb²⁺ and CH₃SO₃⁻ ions in the ratio equal to 10, the α -phase growth prevails in 20 times. The character and kinetic parameters of 2D nucleation of lead dioxide crystals allow prognosticating the phase composition of coatings.

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THE INFLUENCE OF ELECTROLYTE NATURE ON LEAD DIOXIDE ELECTROCRYSTALLIZATION

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During the electrodeposition of lead dioxide the simultaneous formation of two phases (α - and β -phase) may occur. Film electrodeposition begins with the formation of α -phase, and only then the formation of β -phase or two-phase deposition simultaneously begins. The nucleation of PbO_2 proceeds via the progressive mechanism both in methanesulfonate electrolytes and in nitrate ones. However, the preferred form of crystals at 2D nucleation in the case of methanesulfonate electrolyte is the cylinder, whereas in the nitrate electrolyte the crystal formation occurs in the form of cones. The rate constants of nucleation of α - and β -phases of PbO_2 in the nitrate electrolyte differ slightly, and in the case of methanesulfonate electrolyte there is a predominance of α -phase forming. An increase of methanesulfonate ions content in the deposition electrolyte changes the ratio between α - and β -phase crystallization constants. The character and kinetic parameters of 2D nucleation of lead dioxide crystals allow predicting the phase composition of coatings.

Keywords: lead dioxide; methanesulfonate/nitrate electrolyte; nucleation and growth; crystal shape; progressive growth.

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