

The influence of early stages of PbO₂ nucleation on its phase composition

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Received September 14, 2016; accepted December 28, 2016; available on-line August 14, 2017

During the electrodeposition of lead(IV) oxide the simultaneous formation of two phases (α - and β -phase) may occur. Film electrodeposition begins with the formation of α -phase, and then the formation of β -phase or simultaneous two-phase deposition takes place. The nucleation of PbO₂ occurs through a progressive mechanism both in methanesulfonate and nitrate electrolytes. However, the preferred form of crystals in the case of methanesulfonate electrolyte is the cylinder, and in the nitrate electrolyte the crystal formation occurs in the form of cones. The character and kinetic parameters of 2D nucleation of lead(IV) oxide crystals allow predicting the phase composition of the coatings.

Lead(IV) oxide / Nucleation and growth / Crystal habit

1. Introduction

Electrodes based on lead(IV) oxide doped by ionic additives are known to be of great interest for investigation owing to the possibility to tailor solid-state properties and the electrocatalytic activity of PbO₂ [1-3]. Particular attention should be paid to ionic additives in the higher oxidation states +3 and +4 (compared to the Pb²⁺-ions that are known to be located at the positions of cation vacancies in lead(IV) oxide). It is generally admitted [4,5] that there are two zones on the lead(IV) oxide surface: *crystal* (PbO₂) and *hydrated* [PbO(OH)₂], which are in equilibrium and are able to exchange cations and anions with the ions present in the bulk. Replacement of lead ions both in the *hydrated* and *crystal* zones will cause not only a change of the amount of oxygen-containing particles in each zone, but their binding energies, which, in turn, will change the electrocatalytic activity of the material. The radii of the ions in the oxidation state +2 or +3 (Bi³⁺ – 1.03; Ce³⁺ – 1.02; Sn²⁺ – 1.18 Å) are close to the ionic radius of Pb²⁺ (1.19 Å), whereas those of the ions in the higher oxidation states +4 and +5 (Bi⁵⁺ – 0.76; Ce⁴⁺ – 0.87; Sn⁴⁺ – 0.69 Å) are close to the ionic radius of Pb⁴⁺ (0.78 Å). The ionic radius of F⁻ (1.33 Å) is close to the radii of OH⁻ (1.37 Å) and O²⁻ (1.40 Å) [6]. Hence, lead ion substitution is possible in both zones. This was the criterion for choosing the dopants in [7-10].

The electrodeposition of lead dioxide is known to be a complex multi-step process, the characteristics of which depend on the composition of the deposition

electrolyte and the hydrodynamic conditions of the electrolysis [1-3].

It is very important to establish the kinetic features of the crystallization process and control its parameters, because they determine the basic properties of the resulting materials.

It is also known [11,12] that additives in the deposition electrolyte can modify the shape of the crystals due to changes of the surface energy of the growing crystal faces, or be incorporated into the crystal, thereby disturbing the crystallization process.

Since the deposition conditions monitor the physico-chemical properties and electrocatalytic activity of the lead dioxide deposits, in the present work we tried to determine the basic parameters of the initial stages of PbO₂ deposition from methanesulfonate electrolytes that contained various ionic additives (Bi³⁺, Ce³⁺, Sn⁴⁺, [NiF₆]²⁻, [SnF₆]²⁻) and identify correlations between the deposition conditions and the phase composition of the coatings. Integrated data on the influence of dopants of different nature on the crystallization rate and the crystal habit are presented in this work. The difference between the parameters of crystallization of PbO₂ from methanesulfonate and nitrate electrolytes has also been analyzed. It should be pointed out that such data has up to now been absent in the literature.

2. Experimental

All the chemicals were reagent grade. The electrodeposition of doped lead(IV) oxide was studied

on a Pt disk electrode (0.19 cm²) by steady-state voltammetry and chronoamperometry. The surface of the Pt electrode was treated before use, according to the procedure described in [8]. Such a preliminary treatment makes it possible to obtain a reproducible surface. Voltammetry measurements were carried out in a standard temperature-controlled three-electrode cell. All potentials were recorded and reported vs. Ag / AgCl / KCl_(sat.).

Electrodeposition of lead(IV) oxide was studied in methanesulfonate / nitrate electrolytes that contained 0.1 M CH₃SO₃H / HNO₃, 1 M Pb(CH₃SO₃)₂ / Pb(NO₃)₂ and 0.01 M additive (Bi(NO₃)₃, Ce(NO₃)₃, (CH₃COO)₄Sn, K₂[NiF₆], K₂[SnF₆]) depending on the purpose of the experiment.

In other experiments a platinized titanium sheet was used. The sheet was treated as described in [8] before depositing the platinum layer. Lead(IV) oxide coatings were electrodeposited at an anodic current density of 10 mA cm⁻² and a temperature of 282±2 K or 298±2 K. The coating thickness was ~50 μm.

X-ray powder diffraction data was collected on a STOE STADI P automatic diffractometer equipped with a linear PSD detector (transmission mode, 2θ/ω-scan; Cu Kα₁ radiation, curved germanium (1 1 1) monochromator; 2θ-range 6.000 ≤ 2θ ≤ 102.945 °2θ with a step of 0.015 °2θ; PSD step 0.480 °2θ, scan time 50 s/step).

Qualitative and quantitative phase analysis was performed using the PowderCell program [13]. For selected samples with a relatively high degree of crystallinity Rietveld refinements were carried out using the FullProf.2k (version 5.40) program [14,15].

3. Results and discussion

Current-time dependencies for PbO₂ deposition onto a Pt disk electrode were recorded for the investigation of the initial stages of lead(IV) oxide electrodeposition from methanesulfonate electrolytes (Fig. 1). The type of dependency is determined by the electrode potential. The largest induction period was observed at low polarizations ($E = 1550$ mV) with a stretched maximum of current. Increasing the anodic polarization leads to a substantial decrease of the induction period and an increase of the current maximum.

A linear relationship with negative slope was observed between the natural logarithm of the induction time of crystallization and the applied potential, both for the nitrate and methanesulfonate electrolytes (Fig. 2). As has been shown by Abyaneh *et al.* [16], such dependence shows that the electrocrystallization of PbO₂ begins with the formation of a monolayer on the entire surface of the electrode, and then the formation and growth of nuclei occur. Growth of lead(IV) oxide occurs through layer-by-layer crystallization, so that each new layer is formed on a renewed surface [17,18].

An increase of the current delay corresponding to the induction time can be observed if ionic dopants are present in the deposition bath. This indicates difficulties at the initial stages of the formation of lead(IV) oxide (Figs. 3 and 4).

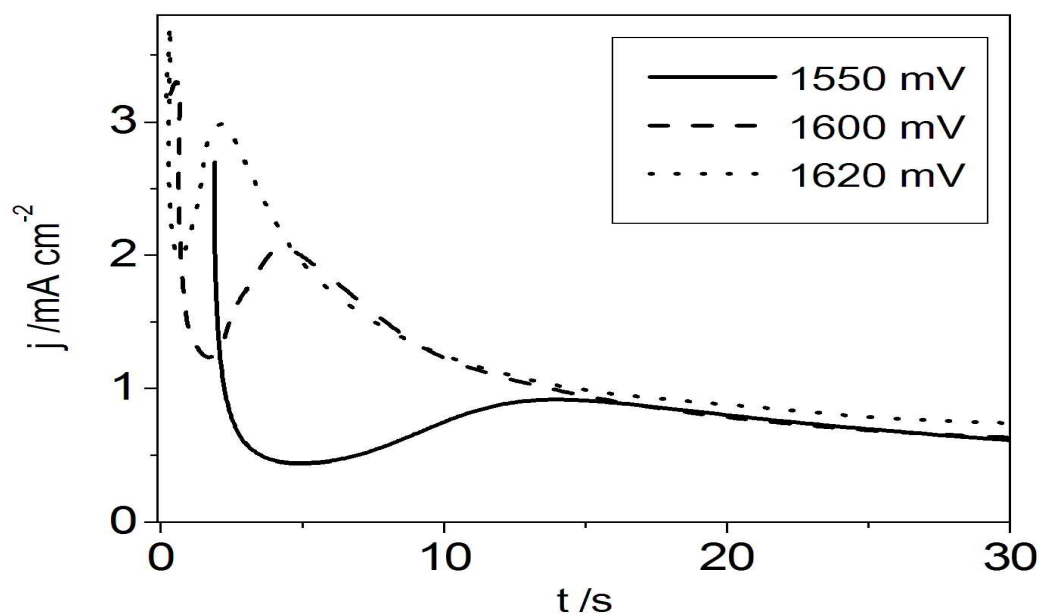


Fig. 1 Current-time dependency for PbO₂ deposition onto a Pt disk electrode from 0.01 M Pb(CH₃SO₃)₂ + 1 M CH₃SO₃H at different deposition potentials.

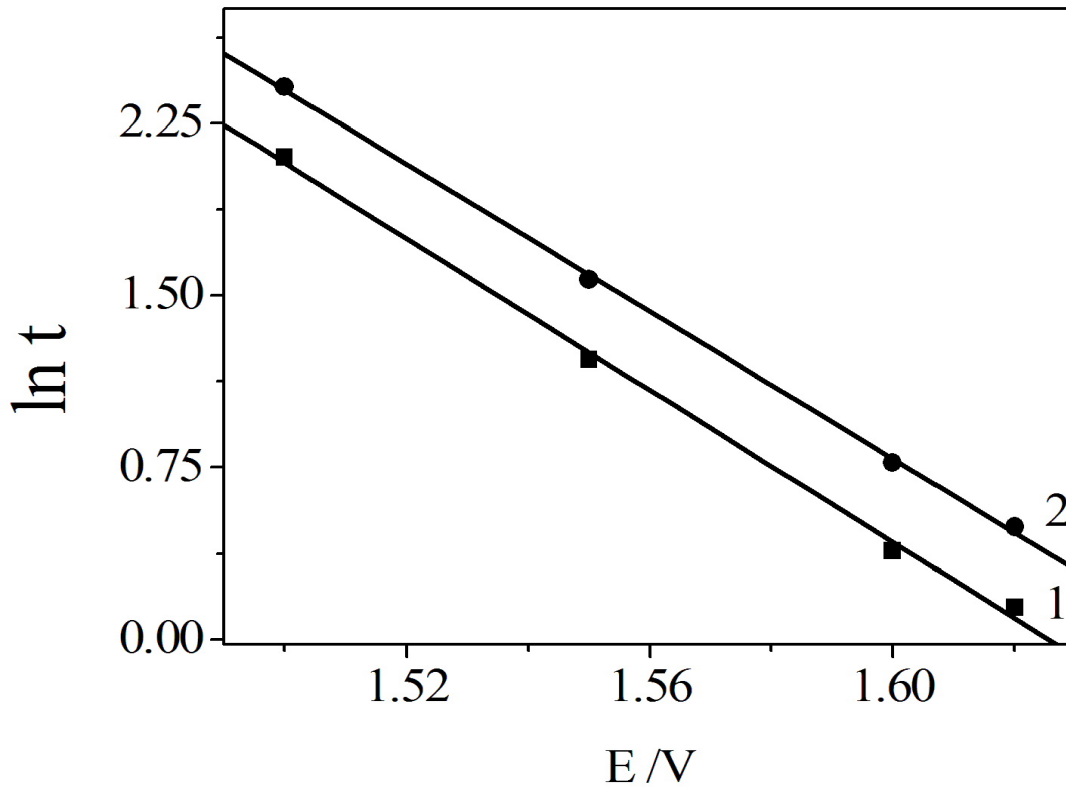


Fig. 2 Natural logarithm of the induction period of crystallization (in s) vs. potential for methanesulfonate (1) and nitrate (2) electrolytes.

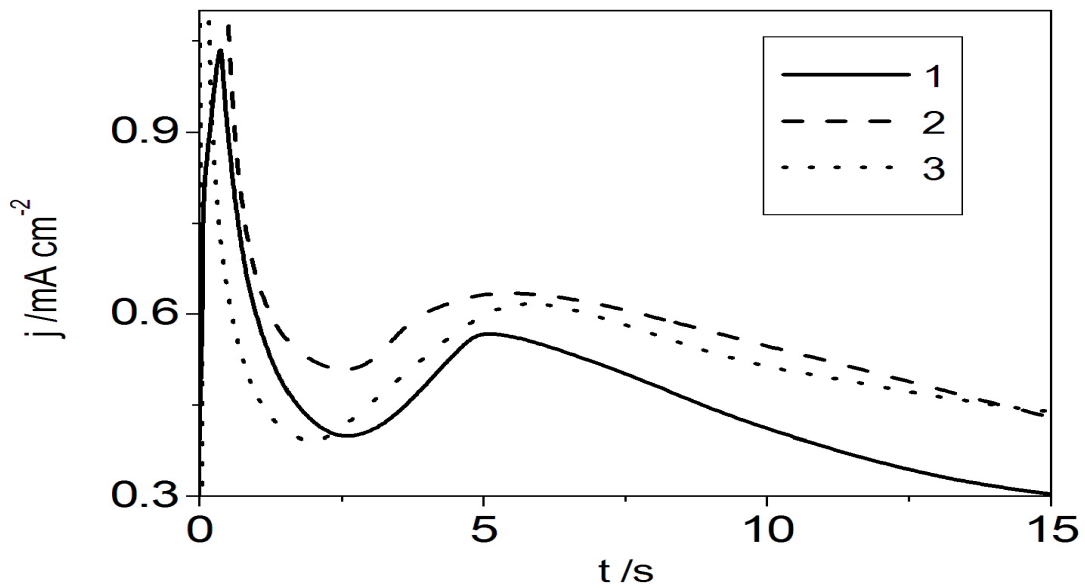


Fig. 3 Current density-time dependency for PbO₂ deposition onto a Pt disk electrode at 1620 mV from 0.01 M Pb(CH₃SO₃)₂ + 1M CH₃SO₃H + X, where X is 1 – 0.01 M Bi³⁺; 2 – 0.001 M Ce³⁺; 3 – 0.01 M Sn⁴⁺.

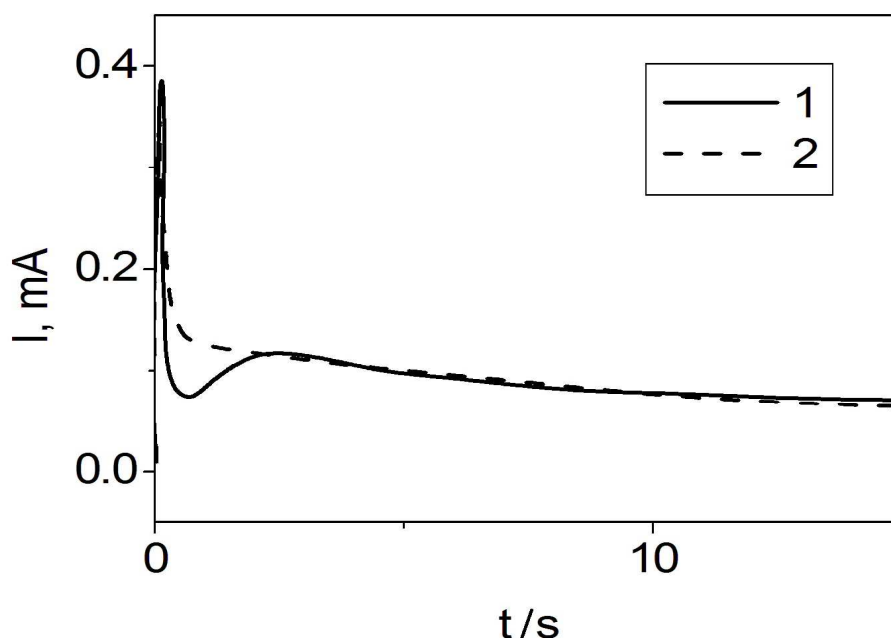


Fig. 4 Current-time dependency for PbO₂ deposition onto a Pt disk electrode at 1620 mV from 0.01 M Pb(CH₃SO₃)₂ + 1 M CH₃SO₃H + X, where X is 1 – 0.01 M [NiF₆]²⁻; 2 – 0.01 M [SnF₆]²⁻.

According to the obtained data one can conclude that the nature of the depositing electrolyte considerably influences the phase composition of the lead(IV) oxide coatings and the crystallographic orientation of certain faces. The coatings obtained from the methanesulfonate bath at 298 K were almost entirely composed of α -phase. It was found that addition of dopants in the deposition electrolyte increases the content of β -phase in the deposit (Table 1).

Table 1 The phase composition of lead(IV) oxide coatings depending on deposition conditions (methanesulfonate bath).

Deposit	T (K)	Content (wt.%) of α -PbO ₂ / β -PbO ₂
PbO ₂	282	59/41
PbO ₂	298	90/10
PbO ₂ – Bi	282	5/95
PbO ₂ – Ce	298	83/17
PbO ₂ – Sn	298	44/56
PbO ₂ – [NiF ₆]	298	0/100
PbO ₂ – [SnF ₆]	298	38/62

The existence of two linear parts in the plot of $(j-j_1)^{1/3}$ vs. t (Fig. 5), according to [16], indicates the simultaneous deposition of two phases of PbO₂, where

the formation of one phase noticeably lags behind the formation of the other. The nature of the lagging phase depends on the electrolyte: for the nitrate bath it is β , for methanesulfonate it is α . Moreover, as has been shown by investigations using inversion voltamperometry, reduction of deposits obtained from methanesulfonate baths (α -phase) occurs at a lower potential than for coatings deposited from nitrate baths (β -phase) [17,18].

The X-ray powder diffraction patterns confirmed that all the investigated samples contained two phases: α -PbO₂ (structure type Fe₂N_{0.94}, space group *Pbcn*) and β -PbO₂ (TiO₂ rutile structure type, space group *P4₂/mnm*). Differences were observed only in the ratio of these two phases and the degree of crystallinity of the samples (see Table 1).

The analysis of the obtained curves (Figs. 3,4) revealed that in the case of the methanesulfonate electrolytes the crystallization proceeds according to a progressive mechanism. For the nitrate electrolytes there is a change in the mechanism from progressive to instantaneous for high concentrations of surfactants. The preferred form of crystals at 2D nucleation in the presence of additives in nitrate electrolytes is semi-spheroid, but in the case of methanesulfonate electrolytes, the cylinder becomes the preferred form. The main parameters of crystallization of lead(IV) oxide in the presence of dopants are presented in Table 2.

The structure of the surface and physico-chemical properties of the deposits are discussed in detail in our previous publications cited above [7-10,17,18].

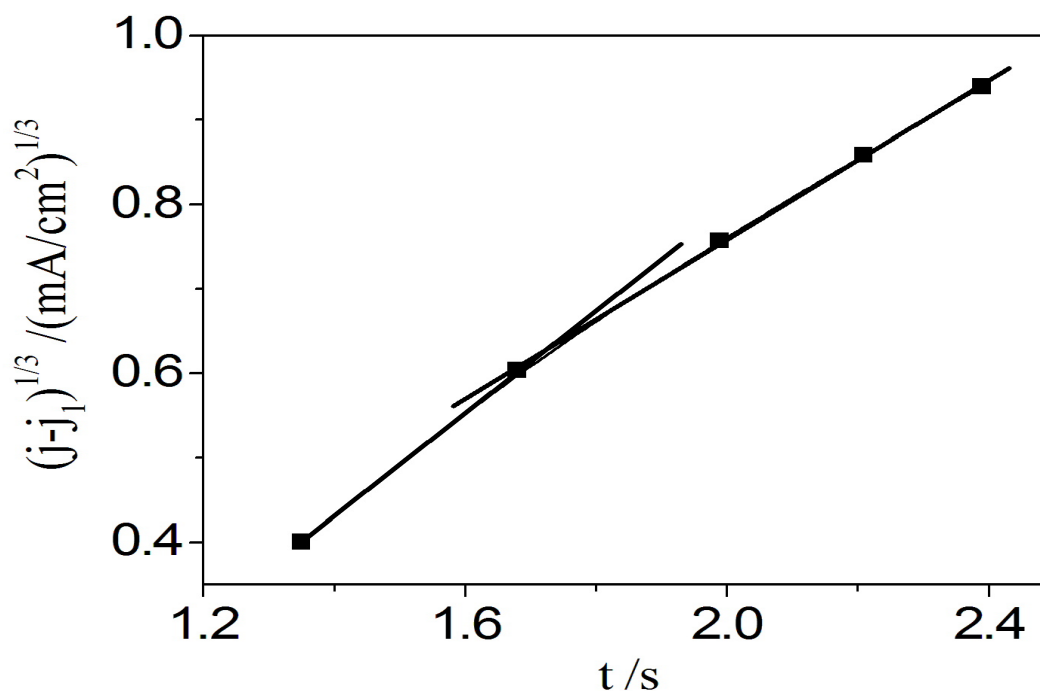


Fig. 5 Plot of $(j-j_1)^{1/3}$ vs. time of recorded during the electrocrystallization of PbO₂ from 0.01 M Pb(CH₃SO₃)₂ + 1 M CH₃SO₃H at 1620 mV.

Table 2 Parameters^a of the initial stages of lead(IV) oxide electrocrystallization.

Deposition electrolyte	t_α	K_α	t_β	K_β
0.01 M Pb(CH ₃ SO ₃) ₂ + 1 M CH ₃ SO ₃ H + 0.01 M Bi ³⁺	2.17	9.20×10^{-6}	4.71	4.1×10^{-6}
0.01 M Pb(CH ₃ SO ₃) ₂ + 1 M CH ₃ SO ₃ H + 0.001 M Ce ³⁺	2.40	2.12×10^{-6}	4.40	8.95×10^{-8}
0.01 M Pb(CH ₃ SO ₃) ₂ + 1 M CH ₃ SO ₃ H + 0.01 M Sn ⁴⁺	1.56	2.06×10^{-5}	4.41	6.28×10^{-7}
0.01 M Pb(CH ₃ SO ₃) ₂ + 1 M CH ₃ SO ₃ H + 0.01 M [NiF ₆] ²⁻	0.02	4.61×10^{-5}	0.05	9.78×10^{-7}
0.01 M Pb(CH ₃ SO ₃) ₂ + 1 M CH ₃ SO ₃ H + 0.01 M [SnF ₆] ²⁻	0.64	3.92×10^{-6}	1.99	5.32×10^{-5}

^a t_α (s) – time corresponding to the beginning of α -phase formation; K_α (mol m⁻² s⁻¹) – rate constant for growth of α -phase crystals in the direction perpendicular to the electrode surface; t_β (s) – time corresponding to the beginning of β -phase formation; K_β (mol m⁻² s⁻¹) – rate constant for growth of β -phase crystals in the direction perpendicular to the electrode surface.

Conclusions

It was found that the nucleation of lead(IV) oxide occurs through a progressive mechanism. The preferred crystal habit in the case of methanesulfonate electrolyte is the cylinder, whereas in the nitrate electrolyte the crystals occur in the form of cones. The preferred crystal habit in the presence of additives in nitrate electrolytes is semi-spheroid, and in the case of methanesulfonate the cylinder remains the preferred shape. The rate constants of nucleation of the α - and β -phases of PbO₂ in the nitrate electrolyte differ only slightly, but in the case of

methanesulfonate electrolyte the formation of α -phase predominates. An increase of the concentration of methanesulfonate ions in the deposition electrolyte changes the ratio between the α - and β -phase crystallization constants. In the case of the nitrate electrolyte the growth of the β -phase is predominant and in the deposit obtained from the nitrate electrolyte the content of β -phase is much higher than in the coatings obtained from the electrolyte based on methanesulfonic acid. The character and kinetic parameters of 2D nucleation of lead(IV) oxide crystals allow predicting the phase composition of the coatings.

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