



Electrocrystallization of lead dioxide: Influence of early stages of nucleation on phase composition



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ABSTRACT

It has been revealed that coatings obtained from methanesulfonate bath at investigated conditions (10 mA cm⁻²; pH = 1.0) are almost entirely composed of α -phase. It was found that the gradual transition from α - to β -phase in the coating occurs in the presence of additives in deposition electrolytes. It was proposed to use charge coming on the formation of nuclei as the correlation parameter to predict the phase composition of obtained lead dioxide deposits. Electrocrystallization of PbO₂ begins with the formation of a monolayer on the electrode surface, then the formation and growth of three-dimensional nuclei takes place. The simultaneous formation of α and β phases results in the presence of two linear areas on the plot of $(j - j_1)^{1/3}$ vs. time for the progressive growth of crystals. The formation of one phase is noticeably lagged behind the other. At layer-by-layer crystallization and significant lagging of one of phases may occur ingesting of growing centers of one phase by another. The type of lagging phase depends on the nature of electrolyte: for nitrate bath it is β , for methanesulfonate – α .

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1. Introduction

Electrodes based on lead dioxide doped by ionic additives are known to be of great interest for investigation owing to tailoring solid state properties as well as electrocatalytic activity of PbO₂ [1–7]. Particular attention should be paid to ionic additives in high oxidation states +3, and +4 (compared to places of cation vacancies of lead dioxide, in which Pb²⁺-ions are known to be localized). It is recognized [8–11], that there are two zones on the lead dioxide surface: crystal (PbO₂) and hydrated [Pb(OH)₂], that are in equilibrium and are capable to exchange cations and anions with the ions present in the bulk. Lead ions replacement both in hydrated and crystal zone would cause not only the change of amount of oxygen-containing particles in each zone, but their binding energies, that in turn will change the electrocatalytic activity of materials. The radii of the ions [12] in the oxidation state +2, +3 (Bi³⁺ – 1.03; Ce³⁺ – 1.02; Sn²⁺ – 1.18 Å) are close to ionic radius of Pb²⁺ (1.19 Å), ions in a higher oxidation state +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 radii of OH⁻ (1.37 Å) or O²⁻ (1.40 Å). Hence, lead ion substitution on them is possible in both zones. This was the criterion for choosing of dopants.

In the present work we examine early stages of electrocrystallization of PbO₂ from methanesulfonate electrolytes that contain various ionic additives (Bi³⁺, Ce³⁺, Sn⁴⁺, [NiF₆]²⁻, [SnF₆]²⁻) and identify correlations between the deposition conditions and phase composition of coatings. It should be pointed out that such data is currently absent in the literature.

2. Experimental

All chemicals were reagent grade. Electrodeposition regularities of doped lead dioxide were studied on a Pt disk electrode (Pt-DE, 0.19 cm²) by steady-state voltammetry, chronoamperometry. The Pt-DE surface was treated, before use, by the procedure described in [13]. Such preliminary treatment permits to achieve 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.).

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The inversion voltamperometry was used for estimation of the deposition regularities of lead dioxide both in nitrate and methanesulfonate electrolytes. The method consisted in the accumulation of pre-analyzed oxide on the working electrode by the electrolysis at a controlled potential and its subsequent electrochemical dissolving under the linearly changing potential.

Electrodeposition of lead dioxide was studied in the methanesulfonate/nitrate electrolytes that contained 1 M $\text{CH}_3\text{SO}_3\text{H}/\text{HNO}_3$, 0.01 M $\text{Pb}(\text{CH}_3\text{SO}_3)_2/\text{Pb}(\text{NO}_3)_2$ and 0.01 M additive ($\text{Bi}(\text{NO}_3)_3$, $\text{Ce}(\text{NO}_3)_3$, $(\text{CH}_3\text{COO})_4\text{Sn}$, $\text{K}_2[\text{NiF}_6]$, $\text{K}_2[\text{SnF}_6]$) depending on purposes of the experiments.

In other section of experiments platinumized titanium was used as substrate. Titanium sheet was treated as described in [13] before platinum layer depositing. Lead dioxide coatings were electrodeposited at anodic current density 10 mA cm^{-2} and temperature $(282 \pm 2) \text{ K}$ or $(298 \pm 2) \text{ K}$. The coating thickness was $\sim 50 \mu\text{m}$.

X-ray powder diffraction data were collected on a STOE STADI P automatic diffractometer [14] equipped with linear PSD detector (transmission mode, $2\theta/\omega$ -scan; $\text{Cu } K\alpha_1$ radiation, curved germanium (111) monochromator; 2θ -range $6000 \leq 2\theta \leq 102,945^\circ$ 2θ with step 0.015° 2θ ; PSD step 0.480° 2θ , scan time 50 s/step).

Qualitative and quantitative phase analysis was performed using the PowderCell program [15]. For selected samples with relatively high degree of crystallinity the Rietveld refinement was carried out using FullProf.2k (version 5.40) program [16,17].

3. Results and discussions

3.1. Early stages of nucleation and growth of lead dioxide

Current transients for PbO_2 deposition on Pt disk electrode were obtained for investigation of initial stages lead dioxide electrodeposition from methanesulfonate electrolytes. A typical j - t curve of PbO_2 deposition is shown on Fig. 1. Observed transient can be divided on several characteristic regions [18]: the current density step in the initial period of electrode polarization corresponding to charging of the double electrical layer; induction period corresponding to the time required for beginning of the phase formation; maximum current density due to a decrease in the concentration of electroactive species in the near electrode space and the achievement of a quasi-stationary current density. The type of transient is determined by the electrode potential. At low polarizations ($E = 1.55 \text{ V}$) the biggest induction period with a further stretched maximum of current is observed. Increasing of an anodic polarization leads to a substantial decreasing of the induction period and to increasing of current maximum.

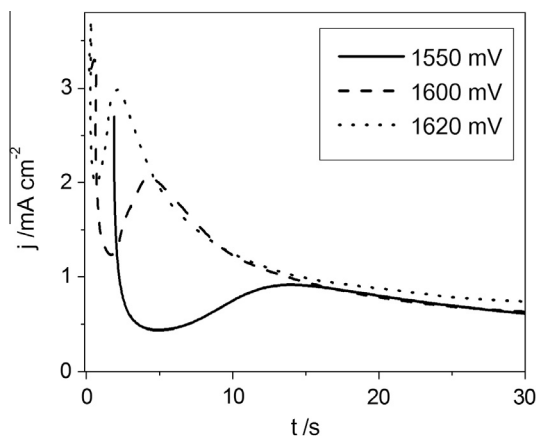


Fig. 1. Current transients for PbO_2 deposition on Pt disk electrode from 0.01 M $\text{Pb}(\text{CH}_3\text{SO}_3)_2 + 1 \text{ M } \text{CH}_3\text{SO}_3\text{H}$ at different deposition potentials.

A linear relationship between the natural logarithm of the induction time of crystallization and the applied potential with negative slope is observed both for nitrate and methanesulfonate electrolytes (Fig. 2). Such dependence shows that the electrocrystallization of PbO_2 begins with the formation of a monolayer on the entire surface of the electrode, and then the formation and growth of nuclei occurs. Growth of lead dioxide occurs through layer-by-layer crystallization, so each following layer is formed on the renewed surface.

According to transients obtained from nitrate and methanesulfonate electrolytes (Fig. 3), one can conclude that despite the same concentration of lead ions in solution, there are significant differences in currents of the deposition that is an unusual effect caused, probably, by adsorption of negatively charged lead methanesulfonate complexes on positively charged electrode [19].

Lead dioxide formation takes place at constantly renewed surface. 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 on the growing oxide surface from the bulk. According to [19] data, three lead(II)-methanesulfonate complexes are characterized as being the predominant species, thus particles like $\text{Pb}(\text{CH}_3\text{SO}_3)_2$ and $\text{Pb}(\text{CH}_3\text{SO}_3)_3^-$ can be in the surface layer. With the potential growth the electrode surface will become redundant positively charged, that would promote the binding of particles with the opposite sign on the surface. Complex compounds with a neutral or negative charge, adsorbed on the surface, would

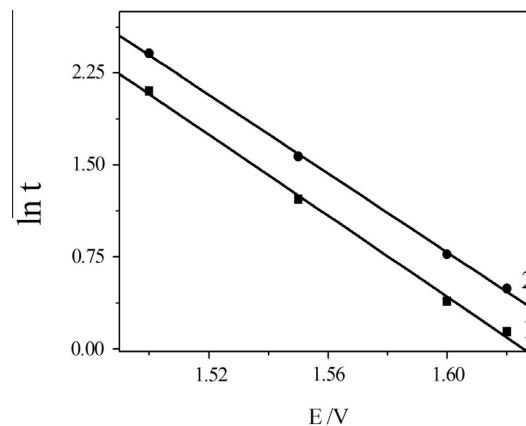


Fig. 2. Plot of the natural logarithm of the induction period of crystallization vs. potential for methanesulfonate (1) and nitrate (2) electrolytes.

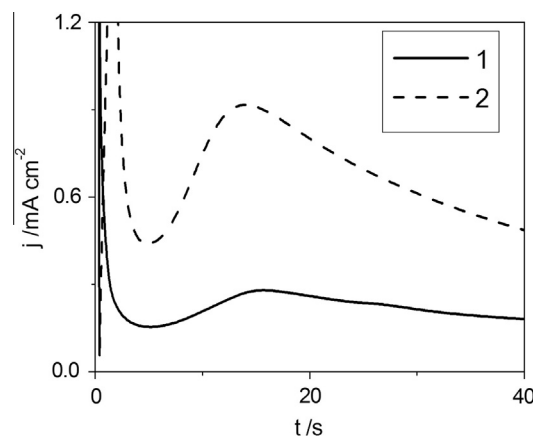


Fig. 3. Current transients for PbO_2 deposition at 1.55 V on Pt disk electrode from different electrolytes: (1) 0.01 M $\text{Pb}(\text{NO}_3)_2 + 1 \text{ M } \text{HNO}_3$; (2) 0.01 M $\text{Pb}(\text{CH}_3\text{SO}_3)_2 + 1 \text{ M } \text{CH}_3\text{SO}_3\text{H}$.

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