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# INFLUENCE OF $Bi^{3+}$ IONS ON KINETICS OF LEAD DIOXIDE ELECTRODEPOSITION FROM METHANESULFONATE ELECTROLYTES

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**Abstract.** Influence of bismuth ions on kinetics of lead dioxide electrodeposition from methanesulfonate electrolytes on Pt-electrode was studied. Experimental results are interpreted to be consistent with the mechanism proposed previously for lead dioxide electrodeposition in literature. The presence of bismuth ions in the electrodeposition solution causes decreasing rate constants of lead dioxide formation due to additive adsorption.

**Keywords:** lead dioxide, methanesulfonate electrolyte, electrodeposition, kinetics, bismuth ions.

## 1. Introduction

Lead dioxide is known to be promising as a metal oxide anodic material owing to its well-proven advantages, including low cost as compared to noble metals, ease of preparation, low electrical resistivity, good chemical stability in corrosive media, relatively large surface area and high overpotential for the oxygen evolution reaction. $PbO_2$ is widely used in oxygen and ozone evolution processes, for electrochemical combustion of organic pollutants and as positive electrode of Red-Ox flow batteries [1-4]. It was shown [5-10] that some amounts of foreign ions, surfactants, polyelectrolytes and oxides as additives to the deposition electrolyte cause changes in electrodeposition kinetics, physicochemical properties of resulting oxides and its electrocatalitical activity. Particularly, such effects were observed when small amounts of some foreign ions like sulphate-, phosphate-, fluoride-, chloride-ions as well as iron, cobalt, arsenic and indium ions were present in the solution [8-14]. Thus, $PbO_2$ modification is one of the most promising ways to change properties of lead dioxide electrodes.

Lead dioxide electrodeposition mechanism is satisfactorily described by the kinetics scheme that was fully depicted in the literature [11-14]:

$$H_2O \rightarrow OH^{\diamond}_{ads} + H^+ + e^- \qquad (1)$$

$$Pb^{2+} + OH^{\diamond}_{ads} \rightarrow Pb(OH)^{2+} \qquad (2)$$

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

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

The electrode surface state, deposition potential, lead ions concentration and hydrodynamic conditions are known to be substantially determining the nature of limiting stage of the lead dioxide electrodeposition. As a rule at the low anodic polarizations ($E < 1.6$ V) reaction will be under the kinetic control, whereas at the high polarizations a $Pb^{2+}$ ions transport to the electrode surface will be the rate-determining stage.

In the present work the kinetics of lead dioxide electrodeposition from methanesulfonate electrolytes containing bismuth ions was studied.

## 2. Experimental

Electrodeposition kinetics of the doped lead dioxide was studied on a Pt rotating disk electrode (Pt-RDE) by the cyclic and steady-state voltammetry methods. Voltammetry measurements were carried out in the standard temperature-controlled three-electrode cell with impact potentiostate PI-50-1.1, programmer PR-8 and biaxial potentiometer N-307/1. For the RDE experiments the voltammetry system SVA-1BM was used. This is a potentiostate with the gear control system of rotating electrode. The velocity of electrode rotation was measured with the electron counting cymometer C3-34.

The potential scan rate was varied within 1–100 mV/s depending on purposes of the experiments.

All potentials were recorded and reported *vs.* $Ag/AgCl/KCl_{(sat.)}$ electrode.

Since lead dioxide electrodeposition proceeds simultaneously with oxygen evolution reaction, for determination of partial $PbO_2$ electrodeposition current ($I_{PbO_2}$) and current efficiency ($CE_{PbO_2}$) of the lead dioxide total charge and charge that passed on the reduction of obtained deposit were measured [14]:

$$CE_{PbO_2} = Q_{red} / Q \qquad (5)$$

$$I_{PbO_2} = Q_{red} / t \qquad (6)$$

where $Q$ and $Q_{red}$ – charges, passed through the electrolytic cell and that passed on the reduction of $PbO_2$ deposit, accordingly; $\tau$ – electrolysis time upon state potential.

All chemicals were reagent and analytical reagent grade. Doubly distilled water derived by tap water dual distillation with glass redistiller of RG type was used for solutions preparing. Electrolytes temperature was maintained at 293±2 K.

Gravity measurements were performed on the electron analytical laboratory balances of ESJ-200-4 model.

Electrodeposition of lead dioxide was studied in the methanesulfonate electrolytes that contained 1 M $CH_3SO_3H$, 0.01 M $Pb(CH_3SO_3)_2$ and 0.001–0.01 M $Bi(NO_3)_3$ depending on purposes of the experiments.

The Pt-RDE surface was treated before using by the procedure described in [14]. Such preliminary treating permits to stabilize electrode area state.

## 3. Results and Discussion

On the cyclic voltammograms (potential scan range 0.8–1.8 V) some typical regions can be picked out (Fig. 1). The anodic branch of the curve at potentials higher than 1.55 V features an exponential current growth corresponding to the simultaneous reactions of lead (II) oxidation and oxygen evolution. In the cathodic branch of the curve a current peak due to lead dioxide reduction can be observed at 1.2–1.3 V potentials. The reaction proceeds following the scheme:

$$PbO_2 + 4H^+ \rightarrow Pb^{2+} + 2H_2O + 2e^- \qquad (7)$$

It was confirmed [11] that both cathodic peak square and value which characterize the lead dioxide quantity can be used for $PbO_2$ elecrodeposition rate evaluation. When bismuth ions are added to the deposition solution, lead dioxide electrodeposition process inhibition takes place. In this case cathodic reduction peak decreasing can be observed (Fig. 1).

It was shown that in the presence of various bismuth ions amount in deposition electrolyte reduction potential of deposited oxide changes. Reduction peak of lead dioxide shifts to the smaller potentials when content of the additive in the solution increases (Fig. 2). Such an effect is explained by probable change in phase composition of oxide deposits [8].

Lead dioxide formation rate decreasing in the presence of added bismuth ions can also be observed on steady state polarization curves (Fig. 3) obtained both for total (oxygen evolution and lead ions oxidation) and partial Pb(II) electrooxidation processes.

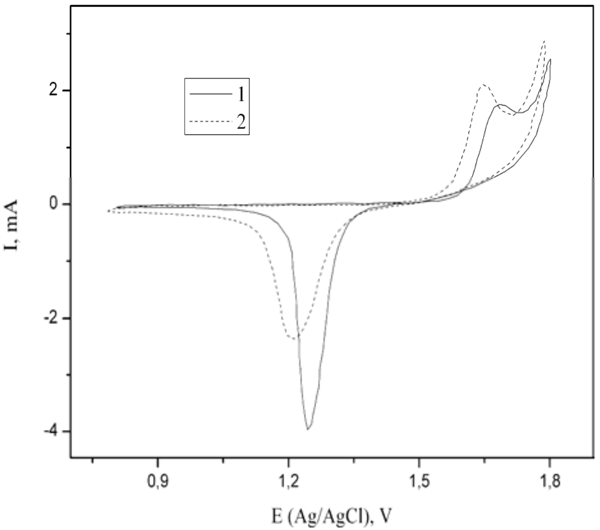

**Fig. 1.** Cyclic voltammograms on Pt-RDE in solutions containing 0.01 M $Pb(CH_3SO_3)_2$+1 M $CH_3SO_3H$ (1) and 0.01 M $Pb(CH_3SO_3)_2$+1 M $CH_3SO_3H$+0.001 M $Bi^{3+}$ (2); $v$ =100 mV/s; scan potentials from 0.8 to 1.8 V

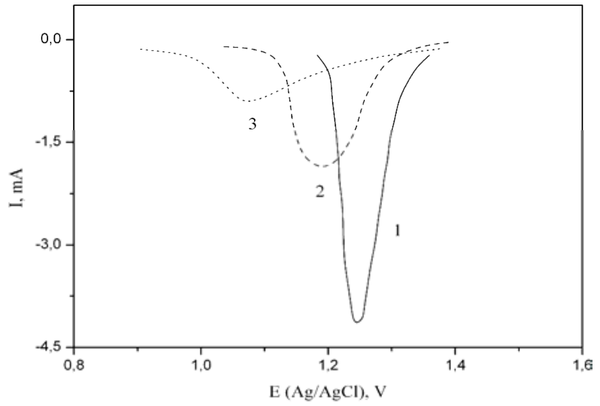

**Fig. 2.** Cyclic voltammograms cathodic branches (scan range 0–1.8 V) on Pt-RDE in solutions containing 0.01 M $Pb(CH_3SO_3)_2$+1 M $CH_3SO_3H$ (1); 0.01 M $Pb(CH_3SO_3)_2$+1 M $CH_3SO_3H$+0.001 M $Bi^{3+}$ (2) and 0.01 M $Pb(CH_3SO_3)_2$+1 M $CH_3SO_3H$+0.01 M $Bi^{3+}$ (3)

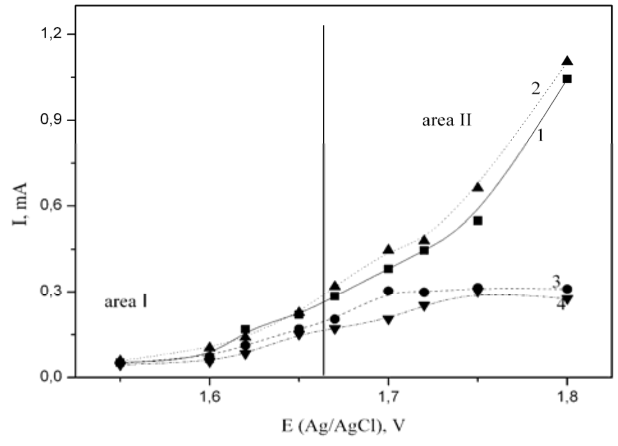

**Fig. 3.** Steady state polarization curves for total (1, 2) and partial (3, 4) $PbO_2$ electrodeposition current on Pt-RDE in solutions 0,01 M $Pb(CH_3SO_3)_2$+1 M $CH_3SO_3H$ (1, 3) and 0,01 M $Pb(CH_3SO_3)_2$+1 M $CH_3SO_3H$+0,001 M $Bi^{3+}$ (2, 4)

Tafel plots ($E$–log$i$) for $I$–$E$ curves at low polarization regions (area I) are linear ($r$ = 0.99), that indicates kinetic control of lead dioxide electrodeposition process. At the same time it should be noted that in low anodic potential regions with the rotating velocity increases anodic current drop can be observed due to the soluble intermediate product Pb(III) asportation from reaction zone. The observed effect indicates second electron transfer as rate-determining stage in this case [11].

Voltammetry method with linear potential sweep was applied both to the determination of electrons number that take part in the kinetic stage and charge transfer coefficient for the $Pb^{2+}$ electrooxidation reaction. Anodic peak value on the $I$–$E$ curve (Fig. 4) is a characteristic value in this method and it depends on potential sweep rate both in reversible and irreversible processes. When the potential sweep rate increases anodic peak shifts towards $E$ growth, which indicates irreversible electron transfer. In this case the obtained dependence should be described by Delakhey equation [15].

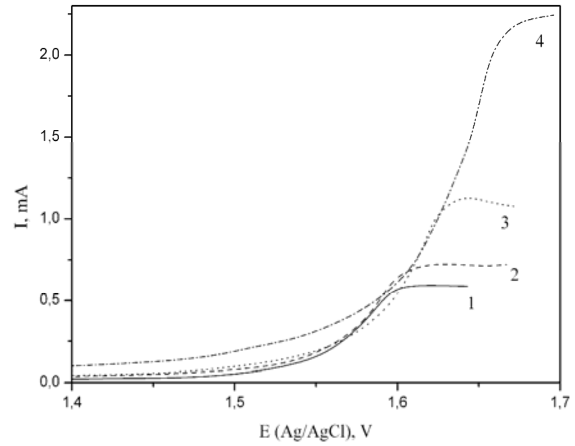

**Fig. 4.** Anodic voltammograms on Pt-RDE in 0.01 M $Pb(CH_3SO_3)_2$+1 M $CH_3SO_3H$ at various scan velocities, mV/s: 5 (1); 10 (2); 20 (3) and 50 (4)

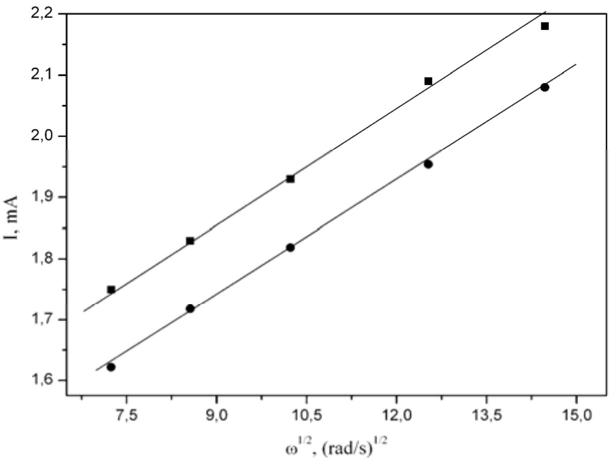

**Fig. 5.** Anodic current dependence ($E$ = 1.8 V) on the square root of angular velocity at Pt-RDE rotation in solutions containing 0.01 M $Pb(CH_3SO_3)_2$+1 M $CH_3SO_3H$ (1) and 0.01 M $Pb(CH_3SO_3)_2$+1 M $CH_3SO_3H$+0.001 M $Bi^{3+}$ (2)

In all cases the calculated elementary stage electron number was equal to one, which confirms staging of the charge transfer, i.e. the existence of two one-electron stages for the $PbO_2$ formation reaction, and satisfies the kinetic scheme presented above for the explanation of lead dioxide electrodeposition regularities in the presence of $Bi^{3+}$ ions in deposition electrolyte. Charge transfer coefficient ($\alpha n_\alpha$) determined from $E_p$–ln$\upsilon$ dependence [16] was 0.4. The presence of bismuth ions in deposition electrolyte causes its decreasing, that can be explained by the increase of influence of chemical stages on the regularities of process passing.

When anodic polarization grows (area II, Fig. 3) limiting current of lead dioxide deposition can be observed. In analyzed potential range measured lead dioxide electrodeposition partial current values depend on the angular velocity of electrode rotation and subordinates Levich equation (Fig. 5, correlation factor $r$ = 0.99). Such results indicate diffusion control of the process at high anodic polarizations [11].

When the electrode rotation velocity increases both the lead dioxide cathodic reduction peak and anodic current drops can be observed. According to the kinetic mechanism mentioned above, the observed effect indicates the formation of soluble intermediate product that is able to further electrochemical transformations with the second electron transfer and lead dioxide formation. The second electron transfer stage is slow at low anodic polarizations, which leads to anodic current drop when electroactive intermediate product is removed from reaction zone in the solution bulk during the electrode rotation velocity increasing.

For finding out the $Bi^{3+}$ concentration 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 (9):

$$\frac{1}{I}=\frac{1}{nkFSc_0}+\frac{1}{0.62nFSD^{2/3}\nu^{-1/6}c_0}\cdot\frac{1}{v^{1/2}} \qquad (9)$$

where $n$ is the number of electrons transferred in the half reaction; $S$ – electrode area, $cm^2$; $\omega$ – angular velocity of electrode rotation, rad/s; $\nu$ – solution kinematic viscosity, Pa·s and other terms have their conventional electrochemical significance [17].

As was showed in the calculations, the presence of additives in the deposition solution causes the apparent heterogeneous rate constant value decreasing (Table 1).

Since lead dioxide formation process proceeds simultaneously with oxygen evolution reaction, so for the $Bi^{3+}$ concentration influence estimation on oxygen evolution process $PbO_2$ current efficiency dependence on the electrodeposition potential was investigated (Fig. 6). At low anodic polarizations region (area I) $PbO_2$ deposition occurs practically with 100 % current efficiency. In this area deposition process is under kinetic stages control. With potential growth (area II) lead dioxide

*Table 1*

**Effects of Bi(III) on the electrodeposition of $PbO_2$ on a Pt–RDE ($E$ = 1.7 V)**

| Electrodeposition solution | Charge transfer coefficient, $\alpha n_\alpha$ | Apparent heterogeneous rate constant, $10^4$ $k$, $m \cdot s^{-1}$ |
|---|---|---|
| 0.01 M $Pb(CH_3SO_3)_2$+1 M $CH_3SO_3H$ | 0.400 | 14.9 |
| 0.01 M $Pb(CH_3SO_3)_2$+1 M $CH_3SO_3H$+0.001 M $Bi^{3+}$ | 0.398 | 11.4 |
| 0.01 M $Pb(CH_3SO_3)_2$+1 M $CH_3SO_3H$+0.008 M $Bi^{3+}$ | 0.393 | 10.2 |
| 0.01 M $Pb(CH_3SO_3)_2$+1 M $CH_3SO_3H$+0.01 M $Bi^{3+}$ | 0.324 | 8.6 |

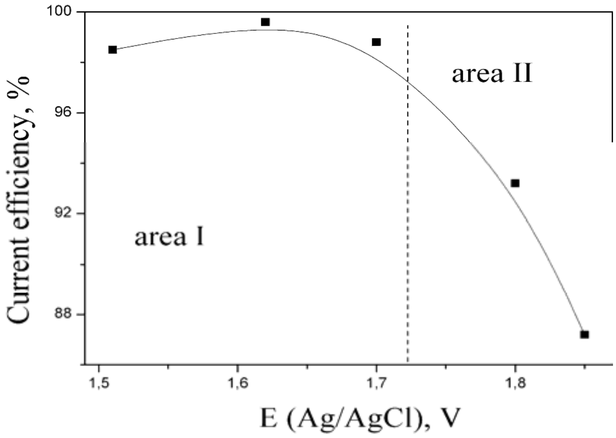

**Fig. 6**. Current efficiency dependence on deposit potential of the lead dioxide deposited from methanesulfonate electrolyte containing 0.0005 M $Bi(NO_3)_3$

current efficiency decreases due to increasing oxygen evolution rate during oxide electrodeposition limiting current is attained (diffusion control).

## 4. Conclusions

According to the experimental data discussed in this work, one can conclude that the presence of bismuth ions in the deposition electrolyte influences kinetics of lead dioxide electrodeposition without changing the process mechanism. In this way, at low anodic polarizations second electron transfer stage is rate determining, whereas at high anodic polarizations such stage is diffusion transport of the lead ions to the electrode surface. The presence of additives in the deposition solution leads to the inhibition of $PbO_2$ electrodeposition process due to $Bi^{3+}$ ions adsorption on the electrode surface. When concentration of the bismuth ions in the electrolyte increases, the apparent heterogeneous rate constant for anodic Pb(II) oxidation decreases.

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## ВПЛИВ ЙОНІВ $Bi^{3+}$ НА КІНЕТИКУ ЕЛЕКТРООСАДЖЕННЯ ДІОКСИДУ СВИНЦЮ З МЕТАНСУЛЬФОНАТНИХ ЕЛЕКТРОЛІТІВ

***Анотація.*** *Вивчено кінетику електроосадження діоксиду свинцю з метансульфонатних електролітів на Pt у присутності та без йонів бісмуту. Електроосадження перебігає за механізмом, запропонованим в літературі для діоксиду свинцю. У разі введення до електроліту осадження йонів бісмуту константа швидкості гетерогенної реакції утворення діоксиду свинцю знижується через адсорбцію модифікуючої домішки.*

***Ключові слова:*** *діоксид свинцю, метансульфонатний електроліт, електроосадження, кінетика, йони бісмуту.*