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*A. Velichenko, V. Knysh, O. Shmychkova, T. Luk'yanenko***THE COMPOSITION AND PROPERTIES OF COMPOSITE PbO<sub>2</sub>-TiO<sub>2</sub> MATERIALS ELECTRODEPOSITED FROM COLLOIDAL METHANESULFONATE ELECTROLYTES****Ukrainian State University of Chemical Technology, Dnipro, Ukraine**

PbO<sub>2</sub>-TiO<sub>2</sub> nanocomposite materials are formed by electrochemical deposition of PbO<sub>2</sub> from colloidal nitrate and methanesulfonate electrolytes through the inclusion of a TiO<sub>2</sub> dispersed phase in the growing PbO<sub>2</sub> coating. These particles are delivered from the electrolyte bulk to the electrode surface by diffusion and/or migration (as a result of the appearance of partial concentration gradient in a colloidal solution due to the depletion of particles, included in the growing coating, in near-electrode zone). Composites containing from 4 to 27 wt.% TiO<sub>2</sub> can be synthesized by varying the electrolysis regimes and the composition of the electrolyte. The presence of TiO<sub>2</sub> particles in the electrolyte leads, as a rule, to the decrease of the crystal size and the growth of the content of  $\alpha$ -phase of lead dioxide in the deposit. The inclusion of particles of valve metal oxides in a PbO<sub>2</sub> matrix typically results in an increase in oxygen evolution reaction overvoltage and promotes a high activity towards the oxidative degradation of organic substances likely due to an increase in the amount of strongly bound oxygen-containing species on the electrode surface.

**Keywords:** PbO<sub>2</sub>-TiO<sub>2</sub> nanocomposites, methanesulfonate electrolyte, oxygen evolution, electrooxidation, phenolic compounds.

**Introduction**

It is recognized that electrodeposition of lead dioxide (PbO<sub>2</sub>) from different oxide particle suspensions leads to composite materials that notably differ from pure PbO<sub>2</sub> composition in terms of physico-chemical properties and electrocatalytic activity [1]. Several reviews describe the preparation of composites based on lead dioxide additionally containing oxides particles of other metals, in particular TiO<sub>2</sub>, RuO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> [2].

It appears that the deposition and formation of composite materials are also influenced by the nature of the dispersed phase, the time stability of the resulting suspension and the use of additives in the electrolytes [3,4]. Stirring of the deposition electrolyte has a significant influence as it helps to maintain the particles in suspension and favors their transportation to the electrode surface. It has been shown that increasing the stirring rate results in an increase of the dispersed phase in the coating. However, the issue of the directed synthesis of these materials is still open since some details concerning the effect of various factors on the composition and physico-chemical properties of the coatings remain to be investigated.

There are significant difficulties in preparation of the suspension electrolyte with high aggregative stability. Sedimentation of the dispersed phase highly complicates the application of suspension electrolytes, because electrolysis can be carried out only under conditions of forced mixing. Even in this case, the deposition of coatings with the stable composition is problematic due to the turbulent flows of the solution in the near-electrode zone, which creates considerable fluctuations in the content of the dispersed phase; this phenomenon becomes more and more significant as the particle size of the dispersed oxide increases. Then, an alternative experimental approach is the use of nanoparticle TiO<sub>2</sub> suspensions that are obtained, for example, by the hydrolysis of titanium alkoxy-precursors in nitric acid. In this case, the primary particle size does not exceed 15 nm [5] and, due to the high stability of suspensions towards aggregation, forced mixing in the process of coating electrodeposition is not needed. However, due to limitations on the mechanical strength, in nitrate solutions it is not possible to obtain coatings with a thickness greater than 100 microns. In this regard, we proposed to use methanesulfonate electrolytes in which PbO<sub>2</sub> composite coatings up to

2 mm thick with satisfactory mechanical properties can be prepared [4,5].

In a recent work by our group [3], we have investigated the chemical properties of these colloidal systems as well as the nucleation laws and kinetics of the electrodeposition of coatings. Herein, we report further important details on the effect of deposition conditions on the composition, physico-chemical properties and electrocatalytic activity of composite  $\text{PbO}_2\text{-TiO}_2$  materials obtained from methanesulfonate electrolytes containing nanosized  $\text{TiO}_2$  particles as a dispersed phase.

#### **Material and methods**

All chemicals were reagent grade. Lead dioxide was electrodeposited from methanesulfonate or nitrate electrolytes that contained 0.1 M  $\text{CH}_3\text{SO}_3\text{H}$  or  $\text{HNO}_3$ , and 0.1 M  $\text{Pb}(\text{CH}_3\text{SO}_3)_2$  or  $\text{Pb}(\text{NO}_3)_2$ .

Platinized titanium was used as a sheet. It was treated as described in [6] before platinum layer depositing. Suspension electrolytes containing  $\text{TiO}_2$  as dispersed phase were prepared by hydrolysis of Ti(IV) isopropylate [4]. Electrolyte compositions and conditions of the deposition of composite coatings were selected hereby that in all cases the current efficiency of lead dioxide deposition was about 100%.

The results of our previous investigations [4] showed that the aggregative stable suspension electrolytes can be obtained based through the sols of titanium dioxide, which are formed by hydrolysis of titanium isopropylate. These electrolytes do not require mixing to maintain their stability. The amount of  $\text{PbO}_2$  in the samples was determined after the coating dissolution by  $\text{Pb}^{2+}$  content, which was found after amperometric titration with sodium N,N-diethylthiocarbamate [4].

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;  $\text{CuK}_{\alpha 1}$  radiation, curved germanium (1 1 1) monochromator;  $2\theta$ -range  $6.000 \leq 2\theta \leq 102.945^\circ$  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.

Oxygen evolution reaction was investigated by steady-state polarization on computer controlled EG&G Princeton Applied Research potentiostat model 273A in 1 M  $\text{HClO}_4$ . All potentials were recorded and reported vs.  $\text{Ag}/\text{AgCl}/\text{KCl}_{(\text{sat.})}$ .

The electrooxidation of organic compounds was carried out in divided cell at  $j_a = 50 \text{ mA cm}^{-2}$ . The volume of anolyte was  $130 \text{ cm}^3$ . Solution containing

phosphate buffer ( $0.25 \text{ M Na}_2\text{HPO}_4 + 0.1 \text{ M KH}_2\text{PO}_4$ ) +  $2 \times 10^{-4} \text{ M}$  organic compound (pH 6.55) was used as anolyte; phosphate buffer as catholyte. Stainless steel was used as cathode. Composite  $\text{PbO}_2\text{-TiO}_2$  electrodes were used as anodes. Electrode surface area was  $3 \text{ cm}^2$ .

The changing of the concentration of the organic substance during the electrolysis was measured by sampling (volume of  $5 \text{ cm}^3$ ) at regular intervals and measuring the absorbance of the solution in the ultraviolet and visible region (wavelength range of  $200\text{--}570 \text{ nm}$ ) using a Kontron Uvikon 940 spectrometer.

Accelerated life tests with the anode active layer of composite  $\text{PbO}_2\text{-TiO}_2$  materials were carried out in 1 M  $\text{H}_2\text{SO}_4$ .

#### **Results and Discussion**

As one can conclude from recently obtained data [4],  $\text{PbO}_2\text{-TiO}_2$  nanocomposite materials are formed by electrochemical deposition of  $\text{PbO}_2$  from colloidal nitrate and methanesulfonate electrolytes through the inclusion of a  $\text{TiO}_2$  dispersed phase in the growing  $\text{PbO}_2$  coating. In the following, we present and discuss results on important aspects concerning the characteristics of composite electrodes, including their electrochemical activity.

#### **The composition of $\text{PbO}_2\text{-TiO}_2$ composite materials**

The content of the dispersed phase in the composite depends on current density as seen in the plots of Fig. 1, where two regions can be clearly identified. In region I, the  $\text{PbO}_2$  deposition process is controlled by kinetics, which implies an increase in the deposition current of oxide with increasing potential [5–7]. This enhances the likelihood that colloidal  $\text{TiO}_2$  particles are captured, and the content of an inert oxide in the composite increases (Fig. 1, region I). In region II, when the deposition rate reaches a limiting value and the process becomes diffusion-controlled [5–7], the  $\text{TiO}_2$  content in the coating remains practically constant (Fig. 2, region II). Thus, the amount of the dispersed phase in the oxide coating is proportional to the formation rate of the oxide of the dispersion medium ( $\text{PbO}_2$ ).

The content of colloidal  $\text{TiO}_2$  in the composite can be affected by diffusion and/or migration delivery of the dispersed particles to the electrode as well as by their interaction with the surface. In the context of the latter phenomenon, it is noteworthy that the particles of the dispersed phase are included in the growing coating despite the fact that  $\text{TiO}_2$  has a positive surface charge in the base electrolyte and the charge of the electrode surface will also be positive, at the typical deposition potentials ( $>1.5 \text{ V}$ ), since the value of the zero-charge potential of  $\text{PbO}_2$

in the 0.1 M HNO<sub>3</sub> is 0.89±0.1 [8]. Interestingly, a significant increase of TiO<sub>2</sub> content occurs when deposition is carried out in methanesulfonate electrolytes (Fig. 1). The observed phenomenon is likely determined by a decrease of both the charge of discharging particles in the dispersion and that of the electrode surface due to complexation and adsorption of methanesulfonate ions, which leads to an increase in the rate of TiO<sub>2</sub> particle delivery to the electrode surface by increasing the contribution of migration component and reduce of electrostatic repulsion forces in the near-electrode area.

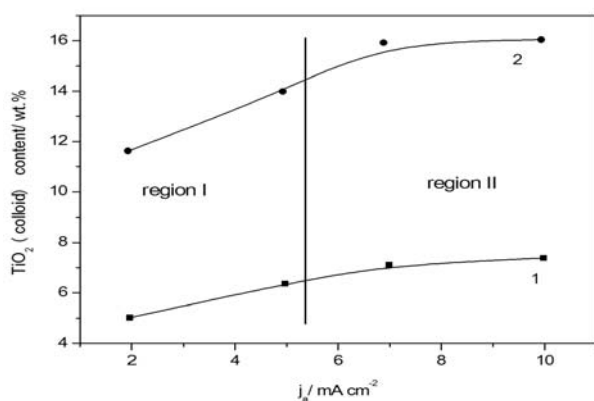


Fig. 1. The TiO<sub>2</sub> content in the composite versus anodic current density of deposition. The deposition solutions are as follows: (1) 0.1 M Pb(NO<sub>3</sub>)<sub>2</sub>+0.1 M HNO<sub>3</sub>+5.0 g dm<sup>-3</sup> TiO<sub>2</sub>(colloidal) and (2) 0.1 M Pb(CH<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>+0.1 M CH<sub>3</sub>SO<sub>3</sub>H+5.0 g dm<sup>-3</sup> TiO<sub>2</sub>(colloidal)

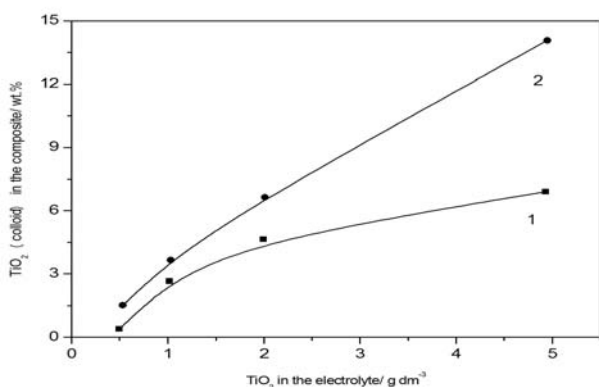


Fig. 2. The TiO<sub>2</sub> content in the composite versus TiO<sub>2</sub> content in deposition solutions: (1) 0.1 M Pb(NO<sub>3</sub>)<sub>2</sub>+0.1 M HNO<sub>3</sub>+X g dm<sup>-3</sup> TiO<sub>2</sub>(colloidal) and (2) 0.1 M Pb(CH<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>+0.1 M CH<sub>3</sub>SO<sub>3</sub>H+X g dm<sup>-3</sup> TiO<sub>2</sub>(colloidal)· j<sub>a</sub>=10 mA cm<sup>-2</sup>

One can conclude from the obtained results (Fig. 2) that an increase of the content of TiO<sub>2</sub> in the deposition electrolyte up to 5 g dm<sup>-3</sup> determines

an increase of the probability of particles capturing into the growing deposit, which leads to an increase of the TiO<sub>2</sub> content in the composite. The observed effect is probably due to an increase in the partial concentration gradient of the dispersed phase oxide with increasing its content in the electrolyte. As in the previous case, the TiO<sub>2</sub> content in the composite materials obtained from the methanesulfonate electrolytes is much higher than in analogous experiments in nitrate baths.

It is noteworthy that a significant increase in the occluded particles from the dispersed phase is observed when the deposition temperature is raised (Fig. 3). This effect is due to a decrease in the solution viscosity at higher temperatures, which, in turn, reduces diffusion limitations and accelerates the delivery of TiO<sub>2</sub> particles to the electrode surface. As mentioned earlier, the use of methanesulfonate electrolytes allows preparing composite coatings where the TiO<sub>2</sub> content is about 2-fold higher than that obtained in nitrate solutions.

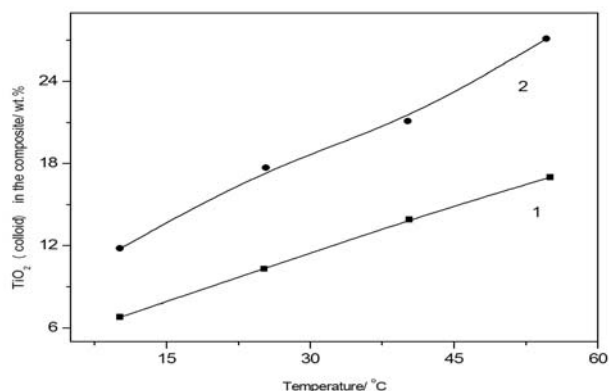


Fig. 3. The TiO<sub>2</sub> content in the composite versus temperature of deposition. The deposition solutions are as follows: (1) 0.1 M Pb(NO<sub>3</sub>)<sub>2</sub>+0.1 M HNO<sub>3</sub>+5.0 g dm<sup>-3</sup> TiO<sub>2</sub>(colloidal) and (2) 0.1 M Pb(CH<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>+0.1 M CH<sub>3</sub>SO<sub>3</sub>H+5.0 g dm<sup>-3</sup> TiO<sub>2</sub>(colloidal)· j<sub>a</sub>=10 mA cm<sup>-2</sup>

According to the obtained data, the use of colloidal methanesulfonate electrolytes allows varying the content of TiO<sub>2</sub> in the composite material in the range from 4 to 27 wt.% by changing the amount of TiO<sub>2</sub> particles in the solution, the temperature and the deposition current density. Thus, in contrast to the nitrate solution, the current efficiency for all proposed regimes of electrolysis and compositions of methanesulfonate solution is 100%, and the resulting coatings are characterized by a low mechanical stress and good adhesion to the substrate even for a thickness as large as 2 mm.

*The phase composition and the texture of PbO<sub>2</sub>-TiO<sub>2</sub> composite materials*

It follows from the above results that the systems based on nanoparticles dispersed in methanesulfonate electrolytes are of considerable practical interest and are worth of detailed studies. In this regard, we performed an investigation of the phase composition and texture of the obtained composites. As can be seen in Tables 1 and 2, the content of the PbO<sub>2</sub> α-phase depends on the TiO<sub>2</sub> concentration in the suspension electrolyte and has a maximum at 1.0 g dm<sup>-3</sup> TiO<sub>2</sub>.

Table 1

**The phase composition of PbO<sub>2</sub>-TiO<sub>2</sub> composites**

Deposition electrolyte	The content of PbO <sub>2</sub> phase, %	
	α	β
(M)*	17.0	83.0
(M)+1 g dm <sup>-3</sup> TiO <sub>2</sub>	32.7	67.3
(M)+2 g dm <sup>-3</sup> TiO <sub>2</sub>	23.7	76.3
(M)+5 g dm <sup>-3</sup> TiO <sub>2</sub>	15.5	84.5

Note: \* – (M) means 0.1 M Pb(CH<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>+0.1 M CH<sub>3</sub>SO<sub>3</sub>H. Coatings are deposited at  $j_a=5$  mA cm<sup>-2</sup>, T=298 K.

Table 2

**The phase composition of PbO<sub>2</sub>-TiO<sub>2</sub> composites**

Deposition electrolyte	The content of PbO <sub>2</sub> phase, %	
	α	β
(M)*	17.0	83.0
(M)+0.5g dm <sup>-3</sup> TiO <sub>2</sub>	31.9	68.1
(M)+1 g dm <sup>-3</sup> TiO <sub>2</sub>	56.1	43.9
(M)+2 g dm <sup>-3</sup> TiO <sub>2</sub>	57.3	42.7
(M)+5 g dm <sup>-3</sup> TiO <sub>2</sub>	33.8	62.2

Note: \* – (M) means 0.1 M Pb(CH<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>+0.1 M CH<sub>3</sub>SO<sub>3</sub>H. Coatings are deposited at  $j_a=10$  mA cm<sup>-2</sup>, T=298 K.

The texture differs substantially for deposits obtained from a true solution and for deposits prepared from electrolytes with a high content of disperse particles (Fig. 4). In the latter case, the degree of crystallinity of the coatings increases, as evidence by the increase of the peaks intensity and sharpness on diffractograms.

The phase composition and texture of composite coatings as well as their TiO<sub>2</sub> content are markedly affected by raising the concentration of dispersed particles and the current density because this increases the number of nucleation sites by facilitating TiO<sub>2</sub> transport to the electrode surface by diffusion or migration. The data suggest that the presence of nucleation sites on the dispersed phase particles, both on the electrode surface and in the near-electrode area, facilitates the crystallization of PbO<sub>2</sub> α-phase. It should be pointed out that a

significant increase in the number of particles leads to the surface shielding, causing polarization and accelerating of the β-phase. This explains the extreme dependence of the phase composition of lead dioxide on the content of the dispersed phase particles in the suspension electrolyte. The lack of TiO<sub>2</sub> peaks on X-ray diffraction patterns is likely due to nanoscale of dispersed phase particles in composite materials based on lead dioxide.

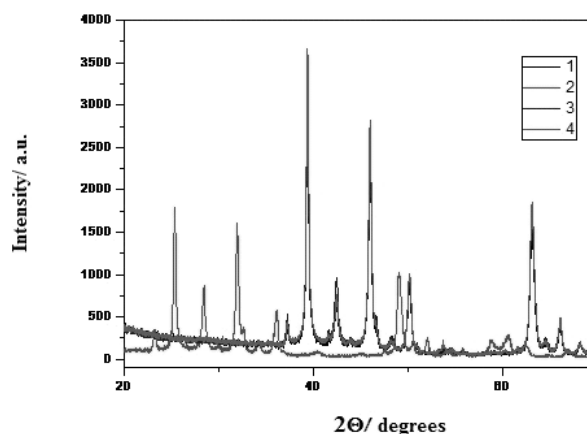
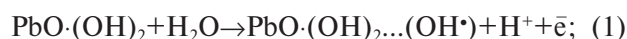


Fig. 4. X-ray diffractograms of composite materials obtained at  $j_a=5$  mA cm<sup>-2</sup> and 298 K from the following solutions: 0.1 M Pb(CH<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>+0.1 M CH<sub>3</sub>SO<sub>3</sub>H+X g dm<sup>-3</sup> TiO<sub>2</sub>(colloidal), where X is: (1) – 0; (2) – 1.0; (3) – 2.0; (4) – 5.0

*The electrocatalytic activity of PbO<sub>2</sub>-TiO<sub>2</sub> composites*

Earlier it has been reported [7] that deposition conditions of PbO<sub>2</sub>-based materials, their chemical and phase composition, as well as a number of structural factors such as the texture of the coating, are largely affected by the surface coverage by oxygen-containing radicals which also determine the electrocatalytic activity and selectivity of deposits in respect to oxygen transfer reactions.

According to the mechanism proposed by Pavlov et al. [9], oxygen evolution occurs at active sites located in a hydrous layer on PbO<sub>2</sub>. The surface consists of crystal line (PbO<sub>2</sub>) and hydrated [PbO(OH)<sub>2</sub>] zones which are in equilibrium, and the latter can exchange cations and anions due to their open structure. Oxygen evolution proceeds through the following elementary steps:



According to Trasatti and Lodi [10], if oxygen evolution reaction (OER) is limited by a second electron transfer (electrochemical desorption), an increase of bond strength of chemisorbed oxygen will lead to an increase of OER overvoltage.

According to the obtained results (Fig. 5), the OER overvoltage on  $\text{PbO}_2\text{-TiO}_2$  electrodes increases with the content of  $\text{TiO}_2$  in the composite. It should be noted that the addition of  $\text{TiO}_2$  particles to the solution increases  $\text{O}_2$  evolution on the metal substrate, similarly to data, obtained on lead dioxide doped by cobalt, nickel, and cerium ions [6,11,12]. Most likely, the observed phenomenon is due to a quite significant surface hydroxylation by oxygen-containing particles with low bond strength, which is indirectly confirmed by the phase composition and texture, significantly different from the other prepared coatings (Table 1, Fig. 4). In all other cases, the OER overvoltage on composite electrodes exceeds that which is typical of  $\text{PbO}_2$ . This is an advantage in cases where the anode works in aqueous solutions at high polarizations, and the oxygen evolution reaction is not the target process.

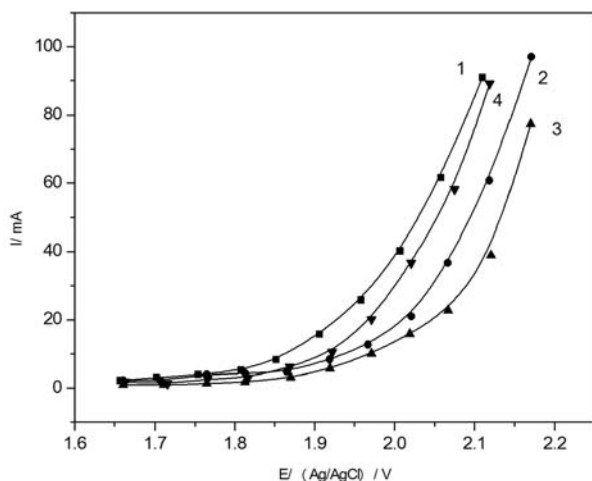


Fig. 5. Steady state polarization curves of oxygen evolution on  $\text{PbO}_2$ -based electrodes in the following solutions:

0.1 M  $\text{Pb}(\text{CH}_3\text{SO}_3)_2 + 0.1$  M  $\text{CH}_3\text{SO}_3\text{H} + X$  g  $\text{dm}^{-3}$   $\text{TiO}_2$  (colloidal),  
 where X is: (1) – 1.0; (2) – 2.0; (3) – 5.0; (4) – 0.  
 $j_a = 5$  mA  $\text{cm}^{-2}$ . Supporting electrolyte is 1 M  $\text{HClO}_4$

The current efficiency of the electrodeposition reaction on composite anodes of such type is expected to increase due to inhibition of OER. It is noteworthy that increasing of the content of  $\text{TiO}_2$  in the composite leads to the OER overvoltage growth, probably due to increasing the surface concentration

of the valve metal oxide. Evidently, sites of this type have a higher affinity for oxygen, which leads to a change in the ratio of labile and inert forms of oxygen-containing particles in favor of the latter. Since the likely rate-limiting step of OER is the electrochemical desorption (transfer of the second electron) [13], it causes a natural increase of the oxygen evolution overvoltage.

We chose the degradation of an aromatic compound, namely 4-nitroaniline, for elucidating the electrocatalytic activity of  $\text{PbO}_2\text{-TiO}_2$  anode materials. This compound was chosen as a model since it is an important pollutant and, additionally, the kinetics of its degradative oxidation can be easily studied by UV-vis spectroscopy.

As shown by Borrás et al. [14], the overall mechanism for the electrochemical oxidation of aromatic organic compounds involves three following consecutive irreversible steps: (i) oxidation to a quinoid compound; (ii) ring opening reaction with formation of aliphatic acids; and (iii) mineralization to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . According to literature data [15], a relatively large number of intermediates is formed during the anodic oxidation of p-nitroaniline. Main intermediates are benzoquinone and maleic acid. Only aliphatic acids are detected in the solution after prolonged electrolysis.

We followed the disappearance of intermediate aromatic products as a function of electrolysis time for different concentrations of the initial compound. The mechanism of electrochemical oxidation of the target compound is qualitatively the same for unmodified and modified  $\text{PbO}_2$  electrodes; this allows a comparison of electrocatalytic activities in terms process rates which, instead depend appreciably on the electrode material.

Interesting data have been obtained for composite electrodes based on  $\text{PbO}_2$  deposited from suspension methanesulfonate electrolytes containing nanosized  $\text{TiO}_2$  particles as the dispersed phase. As shown in Table 3, the degradation rate of p-nitroaniline is higher  $\text{PbO}_2\text{-TiO}_2$  than for pure  $\text{PbO}_2$  electrodes and is enhanced by an increase in  $\text{TiO}_2$  content in the composite. It is also seen in Table 3 that stirring of the suspension causes a further increase in the rate constants of p-nitroaniline degradation.

Increasing of the oxidation rate of p-nitroaniline on composite  $\text{PbO}_2\text{-TiO}_2$  anodes is presumably due to the increasing of number of oxygen-containing species with high bond strength.

Table 3

**Kinetic parameters of the electrochemical oxidation of p-nitroaniline ( $2 \times 10^{-4}$  M) on modified PbO<sub>2</sub>-anodes**

Deposition electrolyte	Apparent heterogeneous rate constant, $k \cdot 10^2, \text{min}^{-1}$
(M)*	1.68
(M)+1 g dm <sup>-3</sup> TiO <sub>2</sub>	2.33
(M)+2 g dm <sup>-3</sup> TiO <sub>2</sub>	2.76
(M)+5 g dm <sup>-3</sup> TiO <sub>2</sub>	3.02

Note: \* – (M) means 0.1 M Pb(CH<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>+0.1 M CH<sub>3</sub>SO<sub>3</sub>H. Coatings are deposited for 30 min at  $j_a=10 \text{ mA cm}^{-2}$ , T=298 K. Electrode area is 3 cm<sup>2</sup>.

**Conclusions**

Composites containing TiO<sub>2</sub> nanoparticle in PbO<sub>2</sub> matrices can be obtained by electrodeposition technique. These particles are delivered from the electrolyte bulk to the electrode surface by diffusion and/or migration (as a result of the appearance of partial concentration gradient in a colloidal solution due to the depletion of particles, included in the growing coating, in near-electrode zone). The content of the composite material depends on: (i) the electrolysis conditions; (ii) the surface charge of the dispersed phase particles and of the electrode; (iii) the PbO<sub>2</sub> deposition rate; and (iv) the concentration of components in the solution. By varying the electrolysis regimes and the composition of the electrolyte, composites containing of 4 to 27 wt.% TiO<sub>2</sub> can be synthesized. The phase composition and texture of the resulting composites depend on the electrolysis conditions and the composition of the electrolyte. Thus, the presence of TiO<sub>2</sub> particles in the electrolyte leads, as a rule, to a decrease of the crystal size and growth of the content of  $\alpha$ -phase of lead dioxide in the deposit.

The inclusion of particles of valve metal oxides into a PbO<sub>2</sub> matrix typically leads to an increase of OER overvoltage likely due to an increase of the amount of strongly bound oxygen-containing species on the electrode surface. Composite materials based on lead dioxide containing occluded TiO<sub>2</sub> nanoparticles exhibit a high activity towards the oxidative degradation of organic substances due to increasing of the number of oxygen-containing particles strongly bounded to the electrode surface.

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**REFERENCES**

1. *Electrochemical oxygen transfer reactions: electrode materials, surface processes, kinetic models, linear free energy correlations, and perspectives. A review* / R. Vargas, C. Borrás, D. Mendez et al. // *J. Solid State Electrochem.* – 2016. – Vol.20. – P.875-893.
2. *Cattrin S., Musiani M.* Electrosynthesis of nanocomposite materials for electrocatalysis / S. Cattarin // *Electrochim. Acta.* – 2007. – Vol.52. – P.2796-2805.
3. *Electrodeposition of composite PbO<sub>2</sub>-TiO<sub>2</sub> materials from colloidal methanesulfonate electrolytes* / V. Knysh, T. Luk'yanenko, O. Shmychkova et al. // *J. Solid State Electrochem.* – 2017. – Vol.21. – P.537-544.
4. *Electrodeposition of PbO<sub>2</sub>-TiO<sub>2</sub> nanocomposite materials from suspension electrolytes* / A.B. Velichenko, V.A. Knysh, T.V. Luk'yanenko et al. // *Theor. Exp. Chem.* – 2016. – Vol.52. – P.127-131.
5. *Electrodeposition PbO<sub>2</sub>-TiO<sub>2</sub> and PbO<sub>2</sub>-ZrO<sub>2</sub> and its physicochemical properties* / A.B. Velichenko, V.A. Knysh, T.V. Luk'yanenko et al. // *Mater. Chem. Phys.* – 2012. – Vol.131. – P.686-693.
6. *Electrodeposition of Ni<sup>2+</sup>-doped PbO<sub>2</sub> and physicochemical properties of the coating* / O. Shmychkova, T. Luk'yanenko, R. Amadelli et al. // *J. Electroanal. Chem.* – 2016. – Vol.774. – P.88-94.
7. *Bi-doped PbO<sub>2</sub> anodes: electrodeposition and physicochemical properties* / O. Shmychkova, T. Luk'yanenko, A. Velichenko et al. // *Electrochim. Acta.* – 2013. – Vol.111. – P.332-338.
8. *Campbell M.A., Peter L.M.* Detection of soluble intermediates during deposition and reduction of lead dioxide // *J. Electroanal. Chem.* – 1996. – Vol.306. – P.185-194.
9. *Pavlov D., Monahov B.* Mechanism of the elementary electrochemical processes taking place during oxygen evolution on the lead dioxide electrode // *J. Electrochem. Soc.* – 1996. – Vol.143. – P.3616-3629.
10. *Trasatti S., Lodi G.* Electrodes of conductive metallic oxides. Part B. – Elsevier: Amsterdam, 1981. – 521 p.
11. *Electrodeposition of Co-doped lead dioxide and its physicochemical properties* / A. B. Velichenko, R. Amadelli, E. A. Baranova et al. // *J. Electroanal. Chem.* – 2002. – Vol.527. – P.56-64.
12. *Electrodeposition of Ce-doped PbO<sub>2</sub>* / O. Shmychkova, T. Luk'yanenko, A. Velichenko et al. // *J. Electroanal. Chem.* – 2013. – Vol.706. – P.86-92.
13. *Influence of the electrode history and effects of the electrolyte composition and temperature on O<sub>2</sub> evolution at  $\beta$ -PbO<sub>2</sub> anodes in acid media* / R. Amadelli, A. Maldotti, A. Molinari et al. // *J. Electroanal. Chem.* – 2002. – Vol.534. – P.1-12.
14. *Study of the oxidation of solutions of p-chlorophenol and p-nitrophenol on Bi-doped PbO<sub>2</sub> electrodes by UV-Vis and FTIR in situ spectroscopy* / C. Borrás, T. Laredo, J. Mostany et al. // *Electrochim. Acta.* – 2004. – Vol.49. – P.641-648.

15. Jimenez Jado N.E., Fernandez Sanchez C., Ochoa Gomez J.R. Electrochemical degradation of nitroaromatic wastes in sulfuric acid solutions: Part I // *J. Appl. Electrochem.* – 2004. – Vol.34. – P.551-556.

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**THE COMPOSITION AND PROPERTIES OF COMPOSITE PbO<sub>2</sub>-TiO<sub>2</sub> MATERIALS ELECTRODEPOSITED FROM COLLOIDAL METHANESULFONATE ELECTROLYTES**

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*PbO<sub>2</sub>-TiO<sub>2</sub> nanocomposite materials are formed by electrochemical deposition of PbO<sub>2</sub> from colloidal nitrate and methanesulfonate electrolytes through the inclusion of a TiO<sub>2</sub> dispersed phase in the growing PbO<sub>2</sub> coating. These particles are delivered from the electrolyte bulk to the electrode surface by diffusion and/or migration (as a result of the appearance of partial concentration gradient in a colloidal solution due to the depletion of particles, included in the growing coating, in near-electrode zone). Composites containing from 4 to 27 wt.% TiO<sub>2</sub> can be synthesized by varying the electrolysis regimes and the composition of the electrolyte. The presence of TiO<sub>2</sub> particles in the electrolyte leads, as a rule, to the decrease of the crystal size and the growth of the content of  $\alpha$ -phase of lead dioxide in the deposit. The inclusion of particles of valve metal oxides in a PbO<sub>2</sub> matrix typically results in an increase in oxygen evolution reaction overvoltage and promotes a high activity towards the oxidative degradation of organic substances likely due to an increase in the amount of strongly bound oxygen-containing species on the electrode surface.*

**Keywords:** PbO<sub>2</sub>-TiO<sub>2</sub> nanocomposites; methanesulfonate electrolyte; oxygen evolution; electrooxidation; phenolic compounds.

**REFERENCES**

1. Vargas R., Borrás C., Méndez D., Mostany J., Scharifker B.R. Electrochemical oxygen transfer reactions: electrode materials, surface processes, kinetic models, linear free energy correlations, and perspectives. A review. *Journal of Solid State Electrochemistry*, 2016, vol. 20, pp. 875-893.

2. Cattarin S., Musiani M. Electrosynthesis of nanocomposite materials for electrocatalysis. *Electrochimica Acta*, 2007, vol. 52, pp. 2796-2805.

3. Knysh V., Luk'yanenko T., Shmychkova O., Amadelli R., Velichenko A. Electrodeposition of composite PbO<sub>2</sub>-TiO<sub>2</sub> materials from colloidal methanesulfonate electrolytes. *Journal of Solid State Electrochemistry*, 2017, vol. 21, pp. 537-544.

4. Velichenko A.B., Knysh V.A., Luk'yanenko T.V., Nikolenko N.V. Electrodeposition of PbO<sub>2</sub>-TiO<sub>2</sub> nanocomposite materials from suspension electrolytes. *Theoretical and Experimental Chemistry*, 2016, vol. 52, pp. 127-131.

5. Velichenko A.B., Knysh V.A., Luk'yanenko T.V., Velichenko Yu.A., Devilliers D. Electrodeposition PbO<sub>2</sub>-TiO<sub>2</sub> and PbO<sub>2</sub>-ZrO<sub>2</sub> and its physicochemical properties. *Materials Chemistry and Physics*, 2012, vol. 131, pp. 686-693.

6. Shmychkova O., Luk'yanenko T., Amadelli R., Velichenko A. Electrodeposition of Ni<sup>2+</sup>-doped PbO<sub>2</sub> and physicochemical properties of the coating. *Journal of Electroanalytical Chemistry*, 2016, vol. 774, pp. 88-94.

7. Shmychkova O., Luk'yanenko T., Velichenko A., Meda L., Amadelli R. Bi-doped PbO<sub>2</sub> anodes: electrodeposition and physico-chemical properties. *Electrochimica Acta*, 2013, vol. 111, pp. 332-338.

8. Campbell S.A., Peter L.M. Detection of soluble intermediates during deposition and reduction of lead dioxide. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry*, 1991, vol. 306, pp. 185-194.

9. Pavlov D., Monahov B. Mechanism of the elementary electrochemical processes taking place during oxygen evolution on the lead dioxide electrode. *Journal of the Electrochemistry Society*, 1996, vol. 143, pp. 3616-3629.

10. Trasatti S., Lodi G., *Electrodes of conductive metallic oxides. Part B.* Elsevier, Amsterdam, 1981. 521 p.

11. Velichenko A.B., Amadelli R., Baranova E.A., Girenko D.V., Danilov F.I. Electrodeposition of Co-doped lead dioxide and its physicochemical properties. *Journal of Electroanalytical Chemistry*, 2002, vol. 527, pp. 56-64.

12. Shmychkova O., Luk'yanenko T., Amadelli R., Velichenko A. Electrodeposition of Ce-doped PbO<sub>2</sub>. *Journal of Electroanalytical Chemistry*, 2013, vol. 706, pp. 86-92.

13. Amadelli R., Maldotti A., Molinari A., Danilov F.I., Velichenko A.B. Influence of the electrode history and effects of the electrolyte composition and temperature on O<sub>2</sub> evolution at  $\beta$ -PbO<sub>2</sub> anodes in acid media. *Journal of Electroanalytical Chemistry*, 2002, vol. 534, pp. 1-12.

14. Borrás C., Laredo T., Mostany J., Sharifker B.R. Study of the oxidation of solutions of *p*-chlorophenol and *p*-nitrophenol on Bi-doped PbO<sub>2</sub> electrodes by UV-Vis and FTIR in situ spectroscopy. *Electrochimica Acta*, 2004, vol. 49, pp. 641-648.

15. Jiménez Jado N.E., Fernández Sánchez C., Ochoa Gómez J.R. Electrochemical degradation of nitroaromatic wastes in sulfuric acid solutions: Part I. *Journal of Applied Electrochemistry*, 2004, vol. 34, pp. 551-556.