Bismuth Doped PbO$_2$ Coatings: Morphology and Electrocatalytic Properties

O. Shmychkova, T. Luk'yanenko, A. Velichenko

Physical Chemistry Department, Ukrainian State University of Chemical Technology, 49005 Dniepropetrovsk, Ukraine
*Corresponding Author: velichenko@ukr.net

Copyright © 2013 Horizon Research Publishing All rights reserved.

Abstract  Modified PbO$_2$ anodes doped with bismuth were prepared by means of electrodeposition in methanesulfonate solutions. The influence of bismuth ions on morphological and electrocatalytic properties of obtained coatings was studied. Both XRD patterns and SEM micrographs demonstrated that incorporation of bismuth diminishes the size of crystal particles. It is shown, that oxygen overpotential on micromodified electrodes is sensibly higher than on non-modified PbO$_2$-electrode. According to obtained results a hypothesis of a mechanism which include transfer of an increased number oxygen radical intermediates to Bi(III) to produce a sensible amount of Bi(IV) and Bi(V) that can participate in the O$_2$ evolution process was proposed.

Keywords  Methanesulfonate Electrolyte, Lead Dioxide, Bismuth, Morphology, Oxygen Overpotential

1. Introduction

Lead dioxide has attracted considerable attention owing to its use as a positive electrode in Red-Ox flow batteries, wastewater treatment, electrosynthesis, analytical sensors [1-8], due to a high overpotential for oxygen evolution, it is suitable for electrochemical processes at high anodic potentials such as ozone evolution [4,9-12]. The electrochemical properties of the electrodeposited PbO$_2$ are strongly affected by doping species present in the deposition bath [5,12-17], especially such effects were observed when small amounts of ions like sulphate-, phosphate-, fluoride-, chloride-ions as well as iron, cobalt, arsenic and indium ions were present in the solution [13-15,18-21]. Thus, PbO$_2$ modification is one of the most promising ways of tailoring its solid state properties as well as its electrocatalytic activity.

In the present work we examine morphological and electrocatalytic properties of lead dioxide electrodeposited from methanesulfonate electrolytes containing bismuth ions. On the one hand, PbO$_2$-materials deposited from methanesulfonate electrolytes represent a considerable interest due to its high electrochemical stability and better mechanical properties in comparison with oxides, obtained from perchlorate, nitrate, acetate and alkaline solutions [9,16,17,22]. On the other hand, despite a large number of publications [23-28], several issues on Bi effects remain to be explained to draw definitive conclusions about optimal conditions for deposition, correlation between type of deposit and its electrocatalytic reactivity.

2. Materials and Methods

All chemicals were reagent grade. Platinized titanium was used as sheet. Titanium sheet was treated as described in [29] before platinum layer depositing. Lead dioxide coatings were electrodeposited at anodic current density 10 mA cm$^{-2}$ and temperature (282±2) K. The determination of modifying additive in anodic materials was carried out photometrically with thiourea [30]. Solutions extinction was determined with blue light optical filter at 400 nm. It was established that lead dioxide modified by bismuth is formed when Bi$^{3+}$ ions are present in the deposition electrolyte. Herewith bismuth content in the oxide grows from 0.49 till 1.81 weight % during increasing of the Bi$^{3+}$ ions additive concentration in the solution from 1 till 10 mM.

Lead dioxide anodes surface morphology was studied by scanning electron microscopy (SEM) with SEM-106I microscope and by X-ray diffraction with Advance Bruker D8 diffractometer.

XPS studies were carried out on a PHI 5000 spectrometer using monochromatic AlK$_\alpha$ radiation for excitation. The BE value of C(1s), due to adventitious carbon and residual solvent, is 284.8 ($\pm 0.3$) eV.

Oxygen evolution reaction was investigated by steady-state polarization and impedance spectroscopy on computer controlled EG & G Princeton Applied Research potentiostat model 273A and lock-in Amplifier model 5210. PbO$_2$ was deposited on Pt wire (0.13 cm$^2$) at 10 mA cm$^{-2}$. All potentials were recorded and reported vs. Ag/AgCl/KCl(sat.).

3. Results and Discussion
3.1. Morphology and Structure of Coatings

A comparison of the XRD spectra reported in Fig. 1 (a,b) shows that bismuth doping causes pronounced changes in the texture of the PbO2 coating.

Both reflection patterns show that the deposits consist of mixture of α- and β-phases of PbO2 and that quite a few reflections disappeared in the spectra of the doped sample. An increase of α-PbO2 in bismuth-doped sample is expected on the bases of previous reports [31], but the large r contribution of this phase in the case of pristine PbO2 is at variance with the common pattern observed for coatings obtained from a nitrate bath under similar conditions [32]. The peak intensities are rather low. Because the diffraction peak width is inversely proportional to crystallite size [33] the average size of particles was estimated from Scherrer’s equation. For the most intensive α (020) peak, calculations yield particle dimensions of 21.8 and 13.3 nm for pure PbO2 and for bismuth-doped, respectively. It can be confirmed that Bi-PbO2 had smaller crystalline size in comparison with pure PbO2.

The SEM micrographs of undoped and doped PbO2 reported in Fig. 2 (a,b) show, in agreement with the XRD results, that Bi-PbO2 features a conspicuously different morphology with smaller size crystals. On the one hand, lead dioxide electrodeposited from methanesulfonate electrolyte typically presents aggregates of randomly oriented submicron and nanosized crystals (Fig. 2a); such an effect was obtained when PbO2 was grown from nitrate solutions containing surfactants and polyelectrolytes [13].

Both reflection patterns show that the deposits consist of mixture of α- and β-phases of PbO2 and that quite a few reflections disappeared in the spectra of the doped sample. An increase of α-PbO2 in bismuth-doped sample is expected on the bases of previous reports [31], but the larger contribution of this phase in the case of pristine PbO2 is at variance with the common pattern observed for coatings obtained from a nitrate bath under similar conditions [32]. The peak intensities are rather low. Because the diffraction peak width is inversely proportional to crystallite size [33] the average size of particles was estimated from Scherrer’s equation. For the most intensive α (020) peak, calculations yield particle dimensions of 21.8 and 13.3 nm for pure PbO2 and for bismuth-doped, respectively. It can be confirmed that Bi-PbO2 had smaller crystalline size in comparison with pure PbO2.

The SEM micrographs of undoped and doped PbO2 reported in Fig. 2 (a,b) show, in agreement with the XRD results, that Bi-PbO2 features a conspicuously different morphology with smaller size crystals. On the one hand, lead dioxide electrodeposited from methanesulfonate electrolyte typically presents aggregates of randomly oriented submicron and nanosized crystals (Fig. 2a); such an effect was obtained when PbO2 was grown from nitrate solutions containing surfactants and polyelectrolytes [13].

On the other hand, the micrographs of Bi-PbO2 display spindle-shaped grain with uniform size and aggregates with dimensions < 2 μm. Similar morphologies have been described earlier [34,35] and appear then to be a feature of bismuth as a dopant that one connected to the methanesulfonate medium. These data support the conclusions of the previous section on changes in the nucleation and crystal growth of PbO2. In particular, such morphology can be possibly explained by a two stage deposition process, where the first stage is formation of

![Figure 1. X-ray diffractograms of PbO2-coatings surfaces, obtained by depositing at j_a= 10 mA cm^{-2} from next solutions: 0.1 M Pb(CH_3SO_3)_2+1M CH_3SO_3H (a); 0.1 M Pb(CH_3SO_3)_2+1M CH_3SO_3H +0.01 M Bi(NO_3)_3 (b).](image)

![Figure 2. SEM micrographs of PbO2-coatings surfaces, obtained electrochemically at j_a= 10 mA cm^{-2} from next solutions: 0.1 M Pb(CH_3SO_3)_2+1M CH_3SO_3H (a); 0.1 M Pb(CH_3SO_3)_2+1M CH_3SO_3H +0.01 M Bi(NO_3)_3 (b).](image)
crystallization centre of a new phase and second is crystal growth. When the electrode is fully covered by a thin layer of oxide, thickening of this layer into a macroscopic deposit occurs. It is interesting to note that after work on PbO$_2$ surface, deposited from nitric bath appears an amorphous layer superimposed on crystalline zones (Fig. 3a) whereas on one deposited from methanesulfonate bath such layer doesn’t appear (Fig. 3b), that confirms the higher stability of these electrodes.

![Figure 3](image1.png)

**Figure 3.** SEM micrographs of PbO$_2$ surfaces after use as anodes. Coatings deposited from nitrate (a) and methanesulfonate (b) solutions at $j_a=10$ mA cm$^{-2}$. ×20000.

SEM/EDAX experiments were performed to evaluate the amount and distribution of bismuth in electrodeposited PbO$_2$. Analysis of different portion of the sample showed that bismuth is well distribute within the deposit and amounts to ~ 2% of lead. This value is confirmed by photometry measurements after chemical dissolution of the PbO$_2$ layer. At the same time, the average O/Pb ratio was 2.15 and 3.3 ± 0.01 in the absence and in the presence of Bi, respectively.

To get further insight into the effects of doping, we investigated the surface layers by X-ray photoelectron spectroscopy (Fig. 4). The XPS spectra of Bi-PbO$_2$ deposited from nitric solutions have been discussed in detail recently. [36]. The XPS spectra, in the absence and in the presence of Bi, showing the reported Pb 4f$_{7/2}$ and Pb 4f$_{5/2}$ binding energies and peak separation of ~ 5 eV, can be assigned to Pb(IV) [37].

![Figure 4](image2.png)

**Figure 4.** Pb 4f and Bi 4f core level structures in PbO$_2$ containing 1.81 w% Bi deposit obtained at $j_a=10$ mA cm$^{-2}$.

Analysis of the Bi$_4$f region allows one to the conclude that bismuth appears in the deposit in the trivalent form (E (4f$_{7/2}$)=158.0 eV). The data obtained are in agreement with the incorporation of Bi$_{3+}$ as discussed [5,38]. It has been reported in earlier publications [1,15,16,23-27] that the average oxidation state of bismuth in PbO$_2$ is 5 which, however, would give a XPS peak at higher binding energy (~ 159 eV) than observed here. On the other hand, more recent literature investigations confirm that the doping species is trivalent Bi [36].

It is interesting to point out that the, based on the at.% values, the amount of surface bismuth is 20-22% that of Pb whereas it is only about 2% in the bulk, as we mentioned above. There is then a strong segregation of bismuth on the surface, which is in accordance with the cited article by Rothenberg et al. [36]. Analysis of the O1s region reveals peaks at 529.1 and 532.4 eV corresponding to lattice oxygen ad hydroxylated species, respectively. The intensity of the latter peak is higher by a factor 1.5 but, unfortunately, we cannot rule out surface contamination by carbonate. However, the SEM/EDAX data reported above show an analogous higher bulk O/Pb ratio for the Bi-doped oxide and this is then likely related to an effect of incorporated bismuth.

The state of bismuth in Bi-PbO$_2$ has been long a matter of debate. According to Johnson [23-26] bismuth is incorporated as Bi(V) while Rothenberg et al. [36] favour Bi(III) although they do not exclude the presence of Bi(V). Our data are in better agreement with the work of the latter authors and propose a tentative model based on deviations from the ideal stoichiometry of PbO$_2$ that is imputed to the occurrence of lead cation disorder in the crystallographic structure, with cation vacancies forming interfaces (internal surfaces) between crystallographically ordered areas [39]. Each missing Pb$^{4+}$ ion would be compensated by Pb$^{2+}$ and OH$^-$ ions, and the chemical composition is described by the
formula Pb^{4+\}_{1-x-y}Pb^{2+\}_{y}O_{2-\_{2y}}(\text{OH})_{(4x+2y)}$. Especially in the case of electrochemically deposited films, the coefficients $x$ and $y$ can have high values [39].

In this framework, there are two potential ways for electro-neutrality compensation when lead ions are replaced by Bi^{3+} cations according to the ion exchange mechanism [39-42]: i) substitution of Pb^{2+} in the hydrated zone in the cation vacancy places and ii) Pb^{4+} in the lattice sites. The first case, analogous to lead dioxide modified by Fe^{3+} ions [41], is seemingly favoured by considering the comparable ionic radii of Pb(II) (119 pm) and Bi(III) (103 pm). On the other hand, replacement of Pb^{4+} (ionic radius 77.5 pm) by Bi(III) at the lattice sites would require considerable energy expenditures that is necessary for crystal lattice reorganization. Such replacement was not observed by Johnson [24]. Oxidation of Bi(III) to Bi(V) (ionic radius 76 pm) would provide a better candidate to substitute Pb(IV). In methanesulfonate solutions such transitions can be in principle observed at PbO$_2$ formation potentials [43].

If the above hypothesis is correct, one would have Bi(III) and Bi(V) simultaneously present and occupying different positions in the structure. Such a situation is encountered in BaPb$_{0.8}$Bi$_{0.2}$O$_3$ as described by Korolkov et al. [44]. These authors also state that if both Bi and Pb atoms exist simultaneously in different valent states, the redox reaction Pb$^{II} +$ Bi$^{V} =$ Pb$^{IV} +$ Bi$^{III}$ can take place, and, in this connection, we think that due to the high number of defects, in our Bi-enriched electrode surface the dopant is initially present mainly in the trivalent form. This conclusion seemingly agrees with the limited stability of Bi$_2$O$_3$ mentioned by Rothenberg et al. [36] and, in any case, we have no evidence that Bi(V) is formed during deposition.

3.2. Electrocatalytic Properties

Electrocatalytic properties of obtained materials were studied in respect to oxygen evolution reaction. The rate of oxygen evolution process can change in relation to nature and amount of foreign additive. The change of composite materials properties in relation to oxygen evolution reaction mainly depends on changes in chemical properties of oxide surface that, in turn, leads to bond strength change of oxygen-containing particles chemisorbed on the electrode surface.

According to obtained results (Fig. 5), oxygen overpotential on micromodified electrodes is sensibly higher than on non-modified PbO$_2$-electrode which depends on bismuth content in deposit. In addition, the Tafel slope increased from 149 to 176 mV/dec for nonmodified and for 1.81 weight % Bi-doped PbO$_2$, respectively.

On the one hand, adsorption of electrolyte ions can probably increase the Tafel slope [45,46] and it has been reported, in this respect, that bismuth seems to favour incorporation of electrolyte anions into PbO$_2$ [47]. On the other hand, segregation of bismuth induces surface heterogeneity due to sites with different electroactivity for water oxidation.

Tafel plots alone provide limited information about of electrode reactions mechanisms and, to obtain more insights, the process of oxygen evolution was also investigated by impedance spectroscopy. As an illustrative example, Fig. 6 shows a comparison of Nyquist plots relative to PbO$_2$ and Bi-PbO$_2$ electrodes.

In the Table are reported results obtained by fitting the equivalent circuit with pseudo-capacity, as described in [45]. Using both the Boucamp’s equivalent circuit simulation and ZsimpWin 3.21 programmes, in the potential interval of Tafel linearity.
Table. Impedance spectroscopy data for PbO$_2$ in 1 M HClO$_4$

| E, V  | $R_s$, ohm | $R_{ct}$, ohm | $R_p$, ohm | $10^3 C_{dl}$, F | n   | $10^3 C_p$, F | n   |
|-------|------------|---------------|------------|-----------------|-----|--------------|-----|
| PbO$_2$ (a) |
| 1.70  | 2.19       | 0.22          | 323.80     | 1.50            | 0.78| 1.35         | 0.92|
| 1.80  | 2.22       | 0.17          | 77.17      | 0.59            | 0.98| 1.78         | 0.92|
| 1.90  | 2.21       | 0.26          | 15.00      | 2.00            | 0.80| 0.71         | 1.00|
| PbO$_2$ (b) |
| 1.70  | 1.58       | 5.11          | 104.90     | 5.50            | 0.82| 4.93         | 0.95|
| 1.80  | 1.58       | 4.81          | 11.13      | 0.52            | 0.83| 4.97         | 0.95|
| 1.85  | 1.55       | 4.20          | 4.45       | 0.4             | 0.83| 6.30         | 0.95|
| 1.90  | 1.60       | 3.57          | 1.78       | 0.49            | 0.85| 8.38         | 0.98|
| PbO$_2$-Bi (c) |
| 1.70  | 1.94       | 19.68         | 168.4      | 0.66            | 0.78| 1.30         | 0.82|
| 1.80  | 1.98       | 11.46         | 29.6       | 0.44            | 0.84| 1.08         | 0.76|
| 1.85  | 1.92       | 5.74          | 15         | 0.54            | 0.85| 1.01         | 0.88|
| 1.90  | 1.86       | 0.52          | 8.86       | 0.76            | 0.64| 0.97         | 1.00|

Lead dioxide electrodeposited from next solutions: (a) – PbO$_2$-NT from Pb(NO$_3$)$_2$+HNO$_3$; (b) – PbO$_2$-MS from Pb(CH$_3$SO$_3$)$_2$+ CH$_3$SO$_3$H; (c) – Pb(CH$_3$SO$_3$)$_2$+ CH$_3$SO$_3$H+ Bi$^3+$. Data for electrodes prepared from methanesulfonic solutions (PbO$_2$-MS) are also compared with analogous ones obtained with electrodes prepared from a nitric bath (PbO$_2$-NT). In this table, the entries have the usual meaning [48]: $R_s$ is the solution resistance; $C_{dl}$ is the double layer capacity; $R_{ct}$ is the faradaic charge transfer leading to formation of adsorbed intermediated from water oxidation; $C_p$ is a capacitive component that is related to the adsorption pseudocapacity and provides important information on the behaviour of intermediates; $R_p$ is related to desorption of intermediates; a high value of $R_p$ indicates a low reactivity of intermediates in reactions (desorption) following water discharge. The n value is the exponent in the so-called constant phase element and the case n = 1 describes an ideal capacitor.

We think it is particularly interesting to note the relative value of $R_{ct}$ and $R_p$ as well as their potential dependence. It is seen that $R_p$ is larger than $R_{ct}$, particularly for PbO$_2$-NT, indicating that one of the steps involving desorption of intermediates is slow. A conspicuous increase of $R_{ct}$ is noted for PbO$_2$-MS compared to PbO$_2$-NT indicating that the former material is less active for water discharge. For Bi-PbO$_2$ a further loss of electrocatalytic activity occurs in the interval 1.7 + 1.85 V. As the potential is increased further, $R_{ct}$ decreases by about an order of magnitude, and at 1.9 V it becomes lower than for unmodified PbO$_2$, under the same electrodeposition conditions (see PbO$_2$-c in Table 2). It is noteworthy that this potential corresponds to the oxidation of Bi(III) to Bi(V) ($E^{\circ}=2.0 \pm 0.2$ V) [49] whose build-up can lead to increased water oxidation.

In the examined potential range, $R_{ct}$ is clearly potential dependent only in the case of Bi-PbO$_2$; however, plots of E vs. log(1/ $R_{ct}$), analogous to Tafel plots [45], are not linear. Conversely, analogous E vs. log(1/ $R_p$) are linear with slopes of 116 and 155 mV/dec for PbO$_2$ and Bi-PbO$_2$, respectively. These results are in good agreement with those obtained from quasi steady-state polarization measurements (Fig. 5) and suggest a mechanism whereby a step involving desorption of oxygen radical intermediates controls the kinetics [45]. At least in the lower potential range of Tafel linearity, we do not envisage the participation of Bi(V) in water oxidation since an appreciable surface concentration of this oxidizing agent would lead to an increase of O$_2$ evolution [24]. Our results are consistent with the presence of Bi(III) domains that do not sustain water oxidation which then takes place at a reduced number of sites. Bismuth oxides, among which is Bi$_3$PbO$_{17}$, are good oxygen conductive materials [50] and, at relatively high potential, an hypothesis for a mechanism may include transfer of an increased number oxygen radical intermediates to Bi(III) to produce a sensible amount of Bi(IV) and Bi(V) that can participate in the O$_2$ evolution process:

$$S_{Pb(IV)} H_2O \rightarrow S_{Pb(IV)} OH + H^+ + e^-$$
$$S_{Bi(III)} O^2- \rightarrow S_{Bi(IV)} O^2- H^+$$
$$S_{Bi(V)} O^2- \rightarrow S_{Bi(V)}(O)_{2}^2+ H^+$$
According to literature [51], Bi(IV) is thermodynamically stable in acid with respect to formation of Bi(III) and Bi(V) by disproportionation.

4. Conclusion

Both X-ray diffractions and SEM images demonstrated that incorporation of bismuth diminishes the size of crystal particles. Micrographs of Bi-PbO₂ display demonstrated that incorporation of bismuth diminishes the oxygen radical intermediates to Bi(III) to produce a sensible mechanism which include transfer of an increased number electroactivity for water oxidation. A hypothesis of a surface heterogeneity due to sites with different content in deposit and segregation of bismuth that induces [7] non-modified PbO₂-electrode which depends on bismuth micromodified electrodes is sensibly higher than on stability of these electrodes. Superimposed on crystalline zones that confirms the higher stability of these electrodes.

According to obtained results, oxygen overpotential on micromodified electrodes is sensibly higher than on non-modified PbO₂-electrode which depends on bismuth content in deposit and segregation of bismuth that induces surface heterogeneity due to sites with different electroactivity for water oxidation. A hypothesis of a mechanism which include transfer of an increased number oxygen radical intermediates to Bi(III) to produce a sensible amount of Bi(IV) and Bi(V) that can participate in the O₂ evolution process was proposed.

REFERENCES

[1] X. Li, D. Fletcher, F.C. Walsh, Electrodeposited lead dioxide coatings, Chem. Soc. Rev., Vol. 40, No. 7, 3879-3894, 2011.
[2] H. Li, Y. Chen, Y. Zhang, W. Han, X. Sun, J. Li, L. Wang, Preparation of Ti/PbO₂-Sn anodes for electrochemical degradation of phenol, J. Electroanal.Chem. Vol. 689, 193-200, 2013.
[3] A. Oury, A. Kirchev, Y. Bultel, Potential response of lead dioxide/lead(II) galvanostatic cycling in methanesulfonic acid: a morphologico-kinetics interpretation, J. Electrochem. Soc. Vol. 160, A148-A154, 2013.
[4] M.A. Quiroz, S. Reyna, C.A. Martinez-Huitle, S. Ferro, A. De Battisti, Electrocatalytic oxidation of p-nitrophenol from aqueous solutions at Pb/PbO₂ anodes, Appl. Catalysis B: Environmental, Vol. 59, 259-266, 2005.
[5] Y. Liu, H. Liu, J. Ma, Comparison of degradation mechanism of electrochemical oxidation of di- and tri-nitrophenols on Bi-doped lead dioxide electrode: Effect of the molecular structure, Appl. Catalysis B: Environmental, Vol. 91, 284-299, 2009.
[6] C. Borras, P. Rodrigues, T. Laredo, J. Mostany, B. R. Scharifker, Electrooxidation of aqueous p-methoxyphenol on lead oxide electrodes, J. Electrochem. Soc., Vol. 34, 583-589, 2004.
[7] J. Iniesta, J. Gonzalez-Garcia, E. Exposito, V. Montiel, A. Aldaz, Influence of chloride ion on electrochemical degradation of phenol in alkaline medium using bismuth doped and pure PbO₂ anodes, Water Research, Vol. 35, No. 14, 3291-3300, 2001.
[8] S. Stucky, R. Kotz, B. Carcer, W. Suter, Electrochemical waste water treatment using high overvoltage anode. Part II: Anode performance and applications, J. Appl. Electrochem., Vol. 21, No. 2, 99-104, 1991.
[9] R. Amadelli, L. Samiolo, A. De Battisti, A. B. Velichenko, Electro-oxidation of some phenolic compounds by electrogenerated O₃ and by direct electrolysis at PbO₂ anodes, J. Electrochem. Soc., Vol. 158, P87-P92, 2011.
[10] A. B. Velichenko, R. Amadelli, E. V. Grudev, T. V. Luk'yenko, F. I. Danilov, Electrodeposition of lead dioxide from methansulfonate solutions, J. Power Sources, Vol. 191, 103-110, 2009.
[11] A. Velichenko, V. Knysh, T. Luk'yenko, L. Dmitrikova, Y. Velichenko, D. Devilliers, PbO₂ based composite materials deposited from suspension electrolytes: electrosynthesis, physico-chemical and electrochemical properties, Chem. and Chem. Technology, Vol. 6, No. 2, 123-133, 2012.
[12] A. B. Velichenko, D. Devilliers, Electrodeposition of fluorine-doped PbO₂, J. Fluorine Chem., Vol. 128, 269-276, 2007.
[13] A. B. Velichenko, V. A. Knysh, T. V. Luk’yenko, Y. A. Velichenko, D. Devilliers, Electrodeposition PbO₂-TiO₂ and PbO₂-ZrO₂ and its physicochemical properties, Materials Chem. and Physics, Vol. 131, No. 3, 686-693, 2012.
[14] R. Amadelli, L. Samiolo A. B. Velichenko, V. A. Knysh, T. V. Luk’yenko, F. I. Danilov, Composite PbO₂-TiO₂ materials deposited from colloidal electrolyte: electrosynthesis and physicochemical properties, Electrochim. Acta, Vol. 54, No. 22, 5239-5245, 2009.
[15] I. H. Yeo, Y. S. Lee, D. C. Johnson, Growth of lead dioxide on a gold electrode in the presence of foreign ions, Electrochim. Acta, Vol. 37, 1811-1815, 1992.
[16] S. E. Treimer, J. Feng, D. C. Johnson, Photoassisted electrochemical incineration of selected organic compounds, J. Electrochem. Soc., Vol. 148, E321-E325, 2001.
[17] E. Brillas, R. Bastida, E. Llosa, J. Casado, Electrochemical destruction of aniline and 4-chloroaniline for wastewater treatment using a carbon-PTFE O₂-fed cathode, J. Electrochem. Soc., Vol. 142, 1733-1741, 1995.
[18] A. B. Velichenko, R. Amadelli, V. A. Knysh, T. V. Luk’yenko, F. I. Danilov, Mechanism of electrooxidation of carbon-PTFE O₂-fed cathode, J. Electrochem. Soc., Vol. 148, 1733-1741, 1995.
[19] A. B. Velichenko, E. A. Baranova, D. V. Girenko, R. Amadelli, F. I. Danilov, Mechanism of electrodeposition of lead dioxide from nitrate solutions containing colloidal TiO₂, J. Electroanal. Chem., Vol. 632, No. 1, 192-196, 2009.
[20] A. B. Velichenko, A. B. Velichenko, E. A. Baranova, D. V. Girenko, R. Amadelli, F. I. Danilov, Mechanism of electrodeposition of lead dioxide from nitrate solutions, Russ. J. Electrochem., Vol. 39, No. 6, 615-621, 2003.
[21] A.B. Velichenko, D.V. Girenko, S.V. Kovalyov, A.N. Gnatenko, R. Amadelli, F.I. Danilov, Lead dioxide electrodeposition and its application: influence of fluoride and iron ions, J. Electroanal. Chem., Vol. 454, 203-208, 1998.

[22] N.B. Tahar, A. Savall, Electrochemical degradation of phenol in aqueous solution on bismuth doped lead dioxide: a comparison of the activities of various electrode formulations, J. Appl. Electrochem., Vol. 29, 277-283, 1999.

[23] H. Yeo, D.C. Johnson, Electrocatalysis of anodic oxygen-transfer reactions. Effect of groups IIIA and VA metal oxides in electrodeposited β-lead dioxide electrodes on bismuth doped lead dioxide: a comparison of the activities of various electrode formulations, J. Electrochemical Soc., Vol. 134, 1973-1977, 1987.

[24] W.R. LaCourse, Y.-L. Hsiao D.C. Johnson, W.H. Weber, Electrocataytic oxidations at electrodeposited bismuth (III)-doped beta-lead dioxide film electrodes, J. Electrochem. Soc., Vol. 136, 3714-3719, 1989.

[25] I.H. Yeo, D.C. Johnson, Electrocatalysis of anodic oxygen transfer reactions: comparison of structural data with electrocatalytic phenomena for bismuth-doped lead dioxide, J. Electrochem. Soc., Vol. 137, 1395-1401, 1990.

[26] H. Chang, D.C. Johnson, Electrochemical analysis of anodic oxygen-transfer reactions. Activation of PbO₂-film electrodes in 1.0M HClO₄ by addition of bismuth(III) and arsenic(III, V), J. Electrochem. Soc., Vol. 137, 2452-2457, 1990.

[27] L.A. Larew, J.S. Gordon, Y.-L. Hsiao, D.C. Johnson, D.A. Buttry, Electrocataytic analysis of anodic oxygen-transfer reactions: application of an electrochemical quartz crystal microbalance to a study of pure and bismuth-doped beta-lead dioxide film electrodes, J. Electrochem. Soc., Vol. 137, 3071-3078, 1990.

[28] L. Lubenov, M. Bojinov, T. Tzetkoff, Electrochemical oxidation of toluene derivatives on Bi-doped PbO₂ in sulphuric acid solution, J. Solid State Electrochem., Vol. 11, 1613-1620, 2007.

[29] A.B. Velichenko, V.A. Knyshev, T.V. Luk’yanenko, D. Devilliers, F.I. Danilov, Electrodeposition of PbO₂-ZrO₂ composite materials., Russ. J. Electrochem., Vol. 44, 1251-1256, 2003.

[30] Z.S. Mukhina, E.I. Nikitina, L.M. Budanova, R.S. Volodarskaya, L.Y. Polyak, A.A. Tikhonova, Methods of analysis of metals and alloys (in russian), Moscow, 1959.

[31] H.Y. Chen, L. Wu, C. Ren, Q.Z. Luo, Z.H. Xie, X. Jiang, S.P. Zhu, Y.K. Xia, Y.R. Luo, The effect and mechanism of bismuth doped lead oxide on the performance of lead-acid batteries, J. Power Sources, Vol. 95, 108-118, 2001.

[32] A.B. Velichenko, R. Amadelli, A. Benedetti, D.V. Girenko, S.V. Kovalyov, F.I. Danilov, Electrosynthesis and physicochemical properties of PbO₂, J. Electrochem. Soc., Vol. 149, C445-C449, 2002.

[33] Niemantsverdriet, J.W. Spectroscopy in catalysis: an introduction, VCH, Weinheim; New York; Basel; Cambridge; Tokyo, 1995.

[34] P.K. Shen, X.L. Wei, Morphologic study of electrochemically formed lead dioxide, Electrochim. Acta, Vol. 48, 1743-1747, 2003.

[35] Y. Liu, H. Liu, Comparative studies on the electrocatalytic properties of modified PbO₂ anodes, Electrochim. Acta, Vol. 53, 5077-5083, 2008.

[36] S. Rothenberg, D.J. Payne, A. Bourlanges, R.G. Egdell, A study of the metal to nonmetal transition in Bi-doped β-PbO₂ by high resolution X-ray photoemission, J. Appl. Phys., Vol. 102, 113717-1137234, 2007.

[37] G. Li, H.Y. Yip, K.H. Wong, C. Hu, J. Qu, P.K. Wong, Photoelectrochemical degradation of methylene blue with beta-PbO₂ electrodes driven by visible light irradiation, J. Environ. Sci., Vol. 23, 998-1003, 2011.

[38] W.-H. Yang, W.-T. Yang, X.-Y. Lin, Preparation and characterization of a novel Bi-doped PbO₂ electrode, Acta Phys.-Chim. Sin., Vol. 28, 831-836, 2012.

[39] P. Ruetschi, R. Giovanoli, On the presence of OH⁻ ions, Pb²⁺ ions and cation vacancies in PbO₂, Power Sources, Vol. 13, 81-97, 1991.

[40] P. Ruetschi, Influence of crystal structure and interparticle contact on the capacity of PbO₂ electrodes, J. Electrochem. Soc., Vol. 139, 1347-1351, 1992.

[41] A.B. Velichenko, R. Amadelli, G.L. Zacchetti, D.V. Girenko, F.I. Danilov, Electrodeposition of Fe-doped lead dioxide electrocatalysts, Electrochim. Acta, Vol. 45, 4341-4350, 2000.

[42] A.B. Velichenko, R. Amadelli, E.A. Baranova, D.V. Girenko, F.I. Danilov, Electrodeposition of Co-doped lead dioxide and its physicochemical properties, J. Electroanal. Chem., Vol. 527, 56-64, 2002.

[43] P.K. Leung, C. Ponce de Leon, C.T.J. Low, F.C. Walsh, Ce(III)/Ce(IV) in methanesulfonic acid as the positive half cell of a redox flow battery, Electrochim. Acta, Vol. 56, 2145-2153, 2011.

[44] D.V. Korolkov, G.P. Kostikova, Y.P. Kostikov, X-ray photoelectron spectra and atom valency distribution in oxide BaPb₁₋ₓBixO₃ superconductor, Physica C, Vol. 383, 117-121, 2002.

[45] R. Amadelli, A. Maldotti, A. Molinari, F.I. Danilov, A.B. Velichenko, Influence of the electrode history and effects of the electrolyte composition and temperature on O₂ evolution at beta-PbO₂ anodes in acid, J. Electroanal. Chem., Vol. 534, 1-12, 2002.

[46] A. Lasia, Influence of adsorption of organic compounds and surface heterogeneity on the hydrogen evolution reaction, Can. J. Chem., Vol. 75, 1615-1623, 1997.

[47] B.S. Nielsen, J.L. Davis, P.A. Thiel, Surface properties of PbO₂ and Bi-modified PbO₂ electrodes, J. Electrochem. Soc., Vol. 137, 1017-1022, 1990.

[48] B.E. Conway, G. Ping, Evaluation of Cl⁻ adsorption in anodic Cl₂ evolution at Pt by means of impedance and potential-relaxation experiments. Influence of the state of surface oxidation of the Pt, J. Chem. Soc. Faraday Trans., Vol. 87, 2705-2714, 1991.

[49] J. Lee, Y. Einaga, A. Fujishima, S.-M. Park, Electrochemical oxidation of Mn²⁺ on boron-doped diamond electrodes with Bi³⁺ used as an electron transfer mediator, J. Electrochem. Soc., Vol. 151, E265-E270, 2004.

[50] F. Honnart, J.C. Boivin, D. Thomas, K.J. de Vries,
Bismuth-lead oxide, a new highly conductive oxygen materials, Solid State Ionics, Vol. 9–10, 921-924, 1983.

[51] M. H. Ford-Smith, J. J. Habeeb, The kinetics of the oxidation of halide ions by bismuth(IV) in aqueous solution: evidence for Bi^{IV} as a reactive intermediate, J. Chem. Soc. Chem. Commun., 1445, 1969.