Bismuth Doped PbO₂ Coatings: Morphology and Electrocatalytic Properties

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Abstract Modified PbO₂ 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 PbO₂-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 O₂ 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 PbO₂ 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, PbO₂ 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, PbO₂-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 Bi³⁺ 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 Bi³⁺ 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-1061 microscope and by X-ray diffraction with Advance Bruker D8 diffractometer.

XPS studies were carried out on a PHI 5000 spectrometer using monochromatic AlK α radiation for excitation. The BE value of C(1s), due to adventitious carbon and residual solvent, is 284.8 (±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. PbO₂ was deposited on Pt wire (0.13 cm²) 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 PbO_2 coating.

Figure 1. X-ray diffractograms of PbO_2 -coatings surfaces, obtained by depositing at $j_a = 10 \text{ mA cm}^{-2}$ from next solutions: 0.1 M $\text{Pb}(\text{CH}_3\text{SO}_3)_2 + 1\text{M CH}_3\text{SO}_3\text{H}$ (a); 0.1 M $\text{Pb}(\text{CH}_3\text{SO}_3)_2 + 1\text{M CH}_3\text{SO}_3\text{H} + 0.01 \text{ M Bi}(\text{NO}_3)_3$ (b).

Both reflection patterns show that the deposits consist of mixture of α - and β -phases of PbO_2 and that quite a few reflections disappeared in the spectra of the doped sample. An increase of α - PbO_2 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 PbO_2 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 PbO_2 and for bismuth-doped, respectively. It can be confirmed that

Bi-PbO_2 had smaller crystalline size in comparison with pure PbO_2 .

The SEM micrographs of undoped and doped PbO_2 reported in Fig. 2 (a,b) show, in agreement with the XRD results, that Bi-PbO_2 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 PbO_2 was grown from nitrate solutions containing surfactants and polyelectrolytes [13].

Figure 2. SEM micrographs of PbO_2 -coatings surfaces, obtained electrochemically at $j_a = 10 \text{ mA cm}^{-2}$ from next solutions: 0.1 M $\text{Pb}(\text{CH}_3\text{SO}_3)_2 + 1\text{M CH}_3\text{SO}_3\text{H}$ (a); 0.1 M $\text{Pb}(\text{CH}_3\text{SO}_3)_2 + 1\text{M CH}_3\text{SO}_3\text{H} + 0.01 \text{ M Bi}(\text{NO}_3)_3$ (b); $\times 10000$.

On the other hand, the micrographs of Bi-PbO_2 display spindle-shaped grain with uniform size and aggregates with dimensions $< 2 \mu\text{m}$. 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 PbO_2 . In particular, such morphology can be possibly explained by a two stage deposition process, where the first stage is formation of

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 PbO₂ 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. SEM micrographs of PbO₂ surfaces after use as anodes. Coatings deposited from nitrate (a) and methanesulfonate (b) solutions at $j_a = 10 \text{ mA cm}^{-2}$. $\times 20000$.

SEM/EDAX experiments were performed to evaluate the amount and distribution of bismuth in electrodeposited PbO₂. Analysis of different portion of the sample showed that bismuth is well distribute within the deposit and amounts to $\sim 2\%$ of lead. This value is confirmed by photometry measurements after chemical dissolution of the PbO₂ 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-PbO₂ 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 $\sim 5 \text{ eV}$, can be assigned to Pb(IV) [37].

Figure 4. Pb 4f and Bi 4f core level structures in PbO₂ containing 1.81 w% Bi deposit obtained at $j_a = 10 \text{ mA cm}^{-2}$.

Analysis of the Bi_{4f} region allows one to conclude that bismuth appears in the deposit in the trivalent form ($E(4f_{7/2}) = 158.0 \text{ eV}$). The data obtained are in agreement with the incorporation of Bi³⁺ as discussed [5,38]. It has been reported in earlier publications [1,15,16,23-27] that the average oxidation state of bismuth in PbO₂ is 5 which, however, would give a XPS peak at higher binding energy ($\sim 159 \text{ eV}$) 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 and 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-PbO₂ 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 PbO₂ 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 Pb⁴⁺ ion would be compensated by Pb²⁺ and OH⁻ ions, and the chemical composition is described by the

formula $\text{Pb}^{4+}_{(1-x-y)}\text{Pb}^{2+}_y\text{O}^{2-}_{(2-4x-2y)}\text{OH}^{-(4x+2y)}$. 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 $\text{BaPb}_{0.8}\text{Bi}_{0.2}\text{O}_3$ 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 $\text{Pb}^{\text{II}} + \text{Bi}^{\text{V}} = \text{Pb}^{\text{IV}} + \text{Bi}^{\text{III}}$ 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_2O_5 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.

Figure 5. Tafel plots (1 M HClO_4) for lead dioxide anodes, electrodeposited from solutions: 1 – 0.1 M $\text{Pb(CH}_3\text{SO}_3)_2$ +1 M $\text{CH}_3\text{SO}_3\text{H}$; 2 – 0.1 M $\text{Pb(CH}_3\text{SO}_3)_2$ +1 M $\text{CH}_3\text{SO}_3\text{H}$ +0.001 M Bi^{3+} ; 3 – 0.1 M $\text{Pb(CH}_3\text{SO}_3)_2$ +1 M $\text{CH}_3\text{SO}_3\text{H}$ +0.01 M Bi^{3+} at $j_a = 10 \text{ mA cm}^{-2}$.

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.

Figure 6. Nyquist impedance plots at 1.9 V for lead dioxide anodes, electrodeposited from solutions: 1 – 0.1 M $\text{Pb(CH}_3\text{SO}_3)_2$ +1 M $\text{CH}_3\text{SO}_3\text{H}$; 2 – 0.1 M $\text{Pb(CH}_3\text{SO}_3)_2$ +1 M $\text{CH}_3\text{SO}_3\text{H}$ +0.01 M Bi^{3+} at $j_a = 10 \text{ mA cm}^{-2}$.

The first features two distinct semicircles while one main circle, having a larger diameter, is observed for the latter. In line with the polarization curves, it is clear that Bi- PbO_2 has a lower electrocatalytic activity.

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 PbO₂ in 1 M HClO₄

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) – PbO₂-NT from Pb(NO₃)₂+HNO₃; (b) – PbO₂-MS from Pb(CH₃SO₃)₂+ CH₃SO₃H; (c) – Pb(CH₃SO₃)₂+ CH₃SO₃H+ Bi³⁺

Data for electrodes prepared from methanesulfonic solutions (PbO₂-MS) are also compared with analogous ones obtained with electrodes prepared from a nitric bath (PbO₂-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 intermediates 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 PbO₂-NT, indicating that one of the steps involving desorption of intermediates is slow. A conspicuous increase of R_{ct} is noted for PbO₂-MS compared to PbO₂-NT indicating that the former material is less active for water discharge. For Bi-PbO₂ 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 PbO₂, under the same electrodeposition conditions (see PbO₂-c in Table 2). It is noteworthy that this potential corresponds to the oxidation of

Bi(III) to Bi(V) (E°=2.0±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-PbO₂; 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 PbO₂ and Bi-PbO₂, 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 would lead to an increase of O₂ 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 Bi₈Pb₅O₁₇, 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 O₂ evolution process:

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 diffractograms and SEM images demonstrated that incorporation of bismuth diminishes the size of crystal particles. Micrographs of Bi-PbO₂ display spindle-shaped grain with uniform size and aggregates with dimensions < 2 µm. 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, there is then a strong segregation of bismuth on the surface. After work on PbO₂ surface, deposited from methanesulfonate bath doesn't appear an amorphous layer 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.

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