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Electrodeposition of PbO_2 and Bi–PbO_2 on Ebonex

A. H. RAS[1] and J. F. van STADEN[2]*

[1]*Fine Chemicals Group, Research and Development Department, AECI, South Africa;* [2]*Department of Chemistry, University of Pretoria, Pretoria, 0002, South Africa*
*(*author for correspondence)*

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Electrodeposition of PbO_2 and Bi–PbO_2 on Ebonex was carried out under various conditions, and the surfaces and coating/substrate interfaces examined by SEM, XPS and SIMS. Excellent adhesion to Ebonex was obtained with both crystalline and amorphous surfaces. Low plating temperatures resulted in dark grey, bright PbO_2 and black, mirror-like Bi–PbO_2 surfaces. Extrapolation of electrode lifetime test data indicated corrosion rates of $716\,\mu m\,yr^{-1}$ for PbO_2 and $158\,\mu m\,yr^{-1}$ for Bi–PbO_2.

Keywords: *bismuth*, *benzoquinone*, *Ebonex*, *electrodeposition*, *electrocatalysis*, *lead dioxide*

1. Introduction

Lead dioxide as an anode material has found commercial application in processes such as the manufacture of sodium perchlorate and chromium regeneration [1, 2], where adsorbed hydroxyl radicals from the electrooxidation of water are believed to serve as the oxidizing agent. Although anodized lead is used in some cases, PbO_2 electroplated on a suitable substrate, such as Ti, provides greater mechanical stability. In this type of electrode configuration, adhesion of the coating to the substrate is of primary importance. This is difficult to achieve, and necessitates the introduction of an inert layer between the coating and the substrate, such as Pt or a mixture of Ti–Ta oxides [3]. The use of Ebonex [4] as a conductive ceramic substrate providing good adhesion for electrodeposited coatings has been documented [5, 6].

The electrocatalysis of anodic oxygen transfer reactions can be achieved by doping PbO_2 with Bi(iii) [7, 8]. Such modified electrode coatings enable the formation of hydroxyl radicals at lower overpotentials, and offer the possibility of enhanced current efficiencies in the anodic oxidation of organic compounds. In industrial electrosynthesis processes, the lifetime of the electrode is of primary importance to the process economics. There is a lack of information in the open literature regarding methods of preparing such coatings for industrial application as well as electrode lifetime data of such coatings in organic electrosynthesis processes.

This paper describes the electrodeposition of PbO_2 and Bi–PbO_2 on Ebonex and the surface characteristics obtained under various plating conditions. Electrode lifetimes of these coated electrodes were measured in an organic electrosynthesis system, namely the anodic oxidation of benzene to benzoquinone in an electrolyte consisting of aqueous sulphuric acid and *t*-butanol as cosolvent.

2. Experimental details

2.1. *Instrumentation*

An SPS 30V-15A direct current power supply was used for the electrodeposition and lifetime trials (available from Specitec, Randburg, South Africa). Analyses of the electrodeposits were performed on a Jeol JSM 35CF scanning electron microscope. XPS (X-ray photoelectron spectroscopy) and SIMS (secondary ion mass spectrometry) analysis were performed on a VG Scientific ESCALab MkII spectroscope.

2.2. *Chemicals*

Samples of Ebonex (porosity 15–18 vol %) were obtained from Atraverda (United Kingdom). All chemicals were supplied by Saarchem (South Africa), except for $Pb(NO_3)_2$ (obtained from N. T. Laboratories) and $Bi(NO_3)_3.5\,H_2O$ (Merck), and were used as received. Solutions were made up using deionized water (Millipore).

2.3. *Procedures*

2.3.1. Electrodeposition of PbO_2. An Ebonex rod (150 mm long, 6 mm diameter) was sandblasted with silicon carbide to provide a porous surface for the electrodeposit to adhere to, and cleaned ultrasonically in deionized water. For electrodeposition, the rod was inserted into a cylindrical titanium mesh basket 80 mm long and with a diameter of 30 mm, resulting in an interelectrode gap of 12 mm. Two titanium rods (150 mm long, 3 mm diameter) were hot welded to either side of the basket, and electrical connection to the cathodic pole of the power supply was made to these rods with crocodile clips. Teflon tape was wrapped around the Ebonex anode, leaving a cylinder of 1 cm length (1.885 cm^2) exposed for deposition. Two circles of Teflon sheet of 30 mm diameter each, and with holes of 6 mm cut out in the centre, were placed in the titanium basket and held the Ebonex rod in a central position. The electrode assembly was immersed in 200 ml of deposition solution (fresh solution was used for each trial). The required current was set on the power supply, and electrodeposition carried out for the indicated time. Stirring was effected with a 20 mm stirrer bar and a Heidolph magnetic stirrer set at 600 rpm. Afterwards, the electrode assembly was removed and washed with deionized water, air dried with compressed air, and the coated area cut and mounted for SEM analysis of the surface and the deposit/substrate interface.

Small scale electrodes of Bi–PbO$_2$ were prepared from Ebonex rods as described above, but adding a certain concentration of bismuth(III) to each deposition solution. All these electrodepositions were carried out at about 6 °C in stationary solutions. Conditions and results are given in Table 2. It was discovered during the course of these depositions that a nucleation step at a higher current density (more positive potential) was not necessary to obtain good quality Bi–PbO$_2$ coatings, and it was therefore omitted from the procedure used in the rest of the experiments.

Results of PbO$_2$ deposition are given in Table 1, and Bi–PbO$_2$ in Table 2. XPS analysis of the Bi–PbO$_2$ coatings was carried out to determine whether the surface ratio of bismuth to lead in the coating was the same as that in the deposition solution. The analyser energy was 20 eV, and the step size 0.5000 eV. Four scans of 1000 channels at 100 ms per channel were carried out. Pb and Bi peaks were detected at 138.0 and 159.0 eV, respectively. SIMS analysis was carried out to determine the homogeneity of the bismuth to lead ratio in the radial direction of the coating, with an etch time of 1500 s.

2.3.2. Electrode lifetime trials. Small scale electrode lifetime trials were carried out on PbO$_2$ and Bi–PbO$_2$ electrodeposits by immersing a coated Ebonex anode/titanium cathode electrode assembly described above in a 100 ml glass vessel with overflow set at the 78 ml mark. The ends of the coated Ebonex rod were taped off with Teflon tape, leaving a 1 cm length of coated rod exposed (surface area 1.884 cm^2), and the current was set at 0.85 A (current density 450 mA cm^{-2}). To test the electrode lifetimes in an organic system, a feed solution consisting of 1.31511 88 mass % *t*-butanol, 67 ml 98 mass % sulphuric acid, 438 ml deionized water and 203 ml benzene was pumped through the vessel using a Gilson Minipuls3 peristaltic pump (flowrate 1.3 ml min^{-1}) to waste. The temperature was controlled and the electrolyte magnetically stirred with a Heidolph heater/stirrer plate. After the lifetime test, the electrode assembly was removed and washed with deionized water. A section of the coated Ebonex rod was cut off and analysed by SEM to determine the coating thickness and the condition of the coating/Ebonex interface.

3. Results and discussion

3.1. *Electrodeposition of PbO$_2$*

Initial conditions (trial 1, Table 1) were taken from the patent by Millington [9], except that a higher current density (i.e., a more positive potential) was used. The result was a dull, highly porous lead dioxide deposit, with blocks or nodules which broke off easily. Lower current densities (i.e., less positive potentials trials 2 and 3, Table 1) gave better results. Extensive coating of the cathode with copper (in preference to lead) was observed in these trials, so that depletion of the lead content in the solution was due solely to anodic deposition. A higher current density (more positive potential) was used during the nucleation phase to facilitate the process of nucleation. Once the initial layer of lead dioxide had formed, growth was allowed to occur at a lower current density.

The effect of lower temperatures was tested in trials 4–10. The copper and nickel nitrate additives were left out in order to simplify the composition of the bath. Satisfactory electrodeposits were obtained with this solution, even at high temperatures (trial 5). Extensive deposition of lead on the cathode was observed, indicating that with time concentration of the deposition solution would become depleted of lead due both to anodic and cathodic deposition.

Stirring had a detrimental effect on the deposit (trial 6), and a higher current density (more positive potential) during the growth phase and a longer nucleation time both gave rise to block formation (trials 7–9). A longer growth phase gave a thicker, crystalline coating (trial 10, Fig. 1). Addition of a surfactant and a slight increase in temperature gave rise to a dull, crystalline surface (compare trials 4 and 11).

Decreasing the temperature 6 °C with a longer nucleation time and in the presence of a surfactant resulted in a very bright, amorphous/glassy surface with a good deposit/substrate interface (trial 13, Fig. 2). Addition of aluminium nitrate as a brightener (trials 14 and 15) did not significantly improve the coating under the conditions tested.

The mechanism of electrodeposition of PbO$_2$ is likely to include the following: mass transport of lead(II) species from the bulk solution to the electrode surface, electron transfer between the electrode and the leads species ($Pb^{2+} \rightarrow Pb^{4+} + 2e^-$), and surface diffusion of lead(IV) species along with oxygen species to become incorporated into the PbO$_2$ lattice. The results of these deposition trials suggest that, in order to obtain amorphous, densely packed PbO$_2$ coatings, conditions should be chosen which enable both mass transport of lead(II) species to the electrode surface and electron transfer between the surface and the lead species in solution to occur at a slower rate than

Table 1. Electrodeposition trials of lead dioxide onto Ebonex

Trial	*Deposition solution* /%m v^{-1}	*Temp.* /°C	*Stirred*	*N(c.d.)* /mA cm^{-2}	*N(time)* /min	*G(c.d.)* /mA cm^{-2}	*G(time)* /min	*Comments*
1	20% $Pb(NO_3)_2$; 1% $Cu(NO_3)_2.3H_2O$; 1% $Ni(NO_3)_2.6H_2O$; 0.4% HNO_3	68	no	500	5	1500	30	Coating thickness not measurable due to brittle sample. Surface crystalline, extensive block formation, highly porous
2	as in 1	70	no	50	1	25	30	Surface crystalline, 38 μm thick, good interface
3	as in 1	70	no	50	1	5	150	Surface crystalline, 60 μm, good interface, smoother surface than trial 2
4	25% $Pb(NO_3)_2$; 10% HNO_3	15	no	50	1	25	30	60 μm, good interface
5	as in 4	50–62	no	50	1	25	30	35 μm, good interface
6	as in 4	15	yes	50	1	25	30	60 μm, some microcracks at interface, block formation
7	as in 4	10	no	50	1	100	10	60 μm, block formation, good interface
8	as in 4	11	no	50	5	25	30	90 μm, block formation, good interface
9	as in 4	15	no	50	15	25	30	95 μm, block formation, good interface
10	as in 4	15	no	50	15	25	123	Surface crystalline, 270 μm, good interface
11	as in 4; 0.5% Brij 35	20	no	50	1	25	30	Surface crystalline, 66 μm, good interface
12	as in 11	13	no	50	1	25	30	Surface crystalline, crystals much smaller than in 11, 56 μm, good interface
13	as in 11	6	no	50	15	25	30	Amorphous/glassy surface, 115 μm, good interface
14	as in 11; 0.1 mol dm^{-3} $Al(NO_3)_3$	12	no	50	15	25	30	Amorphous/glassy surface, 100 μm, good interface
15	as in 14	10	no	25	6	5	120	Crystalline surface, 57 μm, good interface

Table 2. Deposition of bismuth–lead dioxide onto Ebonex

Trial	*Deposition solution* /%m v^{-1}	*N*(*c.d.*) /mA cm^{-2}	*N*(*time*) /min	*G*(*c.d.*) /mA cm^{-2}	*G*(*time*) /min
1	25% $Pb(NO_3)_3$; 10% HNO_3; 0.5% Brij 35	50	15	25	103
2	as in 1; 0.12% $Bi(NO_3)_3.5H_2O$	0	0	25	110
3	as in 1; 0.23% $Bi(NO_3)_3.5H_2O$	0	0	25	110
4	as in 1; 0.46% $Bi(NO_3)_3.5H_2O$	0	0	25	108
5	as in 1; 0.73% $Bi(NO_3)_3.5H_2O$	0	0	25	60
6	as in 1; 0.92% $Bi(NO_3)_3.5H_2O$	0	0	25	120
7	as in 1; 1.10% $Bi(NO_3)_3.5H_2O$	0	0	25	60
8	as in 1; 1.28% $Bi(NO_3)_3.5H_2O$	0	0	25	60
9	as in 1; 1.83% $Bi(NO_3)_3.5H_2O$	0	0	25	120
10	as in 1; 3.67% $Bi(NO_3)_3.5H_2O$	0	0	25	91
11	as in 1; 4.58% $Bi(NO_3)_3.5H_2O$	50	15	25	110
12	as in 1; 9.15% $Bi(NO_3)_3.5H_2O$	0	0	25	125
13	as in 1; 10.99% $Bi(NO_3)_3.5H_2O$	0	0	25	154

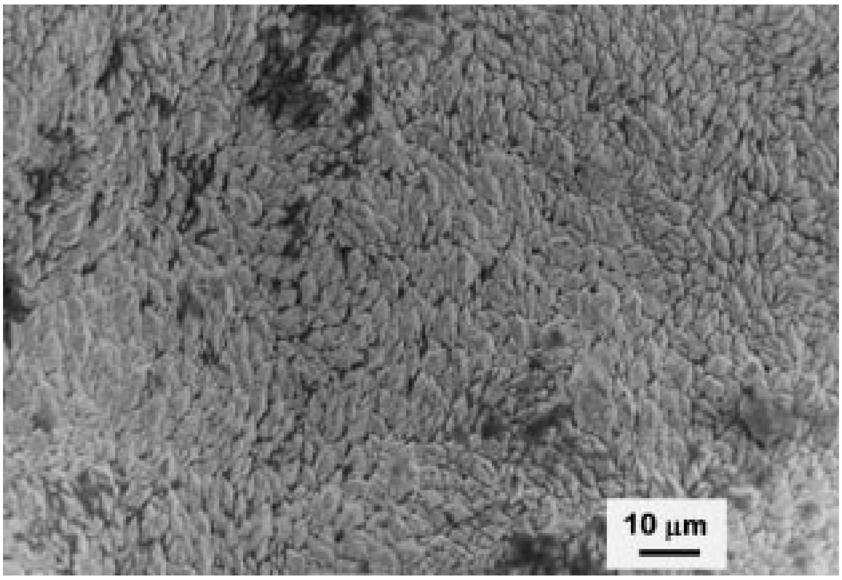

Fig. 1. SEM micrograph 7677 of trial 10, Table 1.

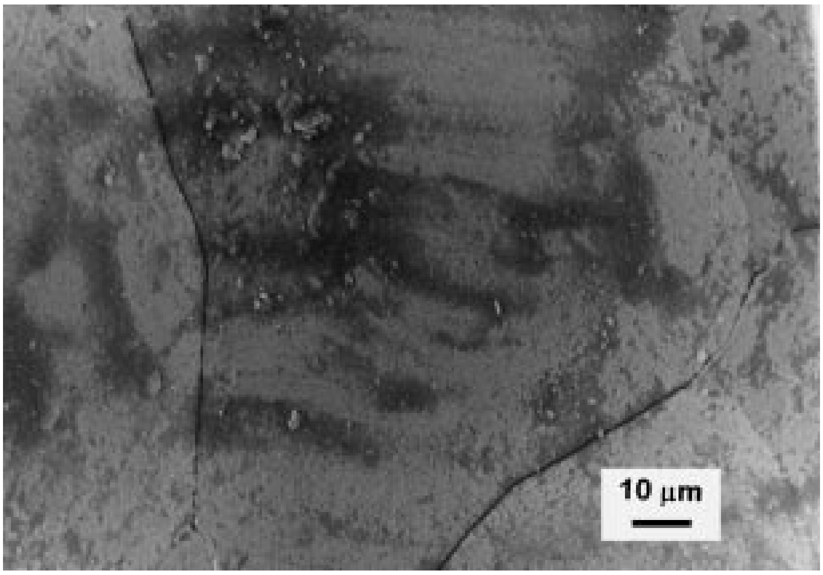

Fig. 2. SEM micrograph 7741 of trial 13, Table 1.

surface diffusion of deposited species. Thus, stationary solutions (slow mass transport) and low current densities (slow electron transfer) were advantageous. At the same time, it appears that a high anodic potential is required to provide sufficient energy for nucleation and/or growth. This combination of low current density and high anodic potential is accomplished by maintaining a low temperature.

An amorphous, dark grey coating of bright appearance with no pitting was concluded to be the most desirable coating, as this should indicate a densely packed structure with a smooth surface and low porosity, which should provide for high mechanical strength and minimal surface fouling during the electrooxidation of organic compounds. The conditions used in trial 13 were therefore used to coat an Ebonex rod with lead dioxide for use in a lifetime test. The only change in the deposition procedure was to allow a growth time of 103 min instead of 30 min, in order to obtain a coating thickness comparable to that of commercially available lead dioxide electrodes (typically 200–1000 μm). The coating produced was darkgrey and bright, with no sign of pitting. A section of the coated Ebonex at the end of the rod was cut off and SEM analysis showed a lead dioxide coating thickness of 290–310 μm (see micrograph 7757 in Fig. 3) and a fairly smooth, amorphous surface. The interface between the coating and the Ebonex substrate appeared to be excellent, with no sign of rifts or cracking.

3.2. *Electrodeposition of Bi–PbO_2*

Coatings obtained were mostly bright and black, with little or no pitting. SEM analysis of trial 11 (Table 2) showed the surface to be very smooth, with some particulate matter adhering to it. The interface showed no signs of rifts or cracking (micrograph no. 7762 in Fig. 5).

3.3. *Characterization of Bi–PbO_2 deposits*

XPS analyses of some of these electrodeposits revealed that there is a poor correlation between the ratio of bismuth to lead in the coating with that in the deposition solution (see Table 3). To test reproducibility, a duplicate of trial 6 (Table 2) was carried out, and the deposits obtained from these two trials were analysed by XPS and SIMS. The deposit from trial 6 gave a bismuth to lead ratio of 0.01 (as opposed to the ratio of 0.025 in the deposition solution), while the duplicate gave a ratio of 0.15. SIMS analysis showed the first deposit to have a constant ratio over the outer few microns of the coating, while its duplicate showed enrichment of bismuth at the surface. It was concluded that future investigation would be required in order to define a procedure for obtaining uniform electrodeposits of the required bismuth content with good repeatability.

3.4. *Electrode lifetime trials*

3.4.1. PbO_2. The coating thickness after 954 h ranged from 232 to 268 μm, measured at various points on various SEM micrographs, which translates into a coating loss of 716 μm yr^{-1} in the worst case. Although high, this is feasible at the commercial scale; if a lead dioxide electrode of 2 mm thick coating were used in the large scale process, an electrode lifetime of more than 2.5 yr could be achieved.

SEM analysis (Fig. 4) showed the surface to be rougher than before the test, believed to be due to the dissolution and redeposition of PbO_2 in a less compact form.

3.4.2. Bi–PbO_2. An electrode for a lifetime trial was prepared using the conditions for trial 6 (Table 2). The coating was bright and black, and SEM analysis

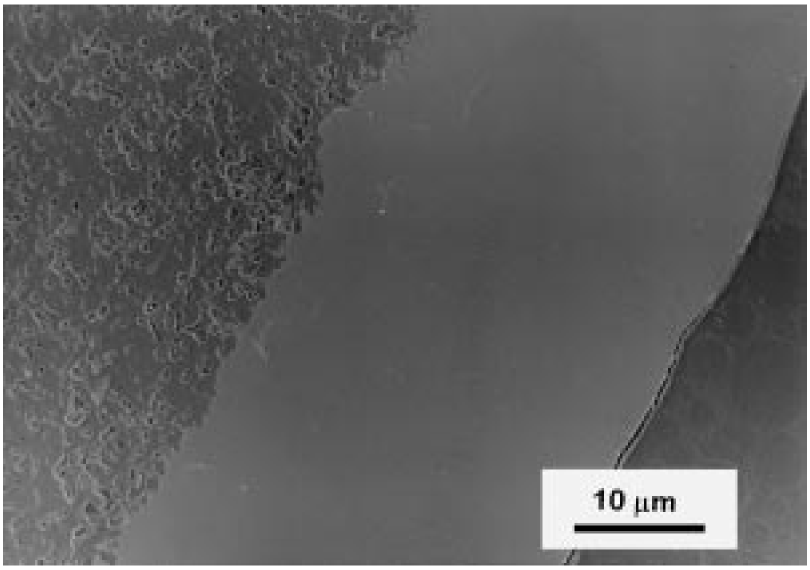

Fig. 3. Cross section of lead dioxide/Ebonex deposited according to trial 13, Table 1 (micrograph 7757).

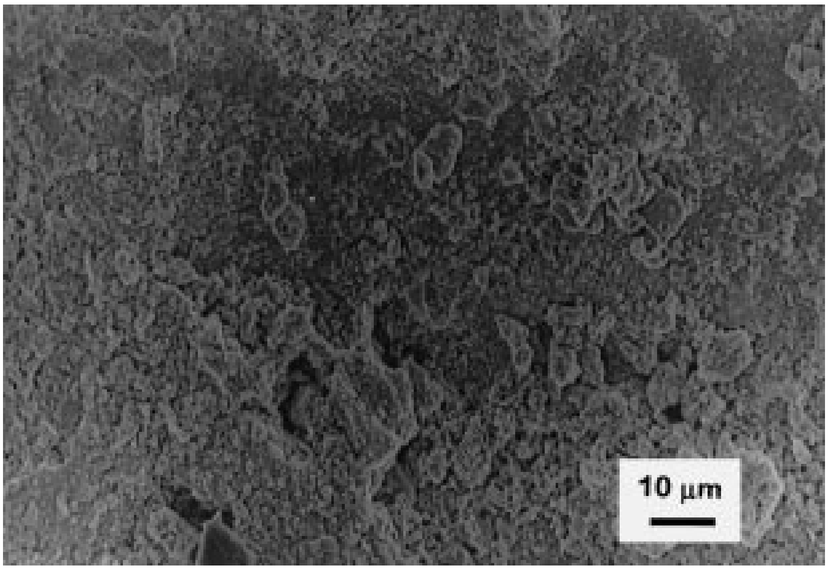

Fig. 4. Surface of lead dioxide/Ebonex electrode tested for 954 h (micrograph 7969).

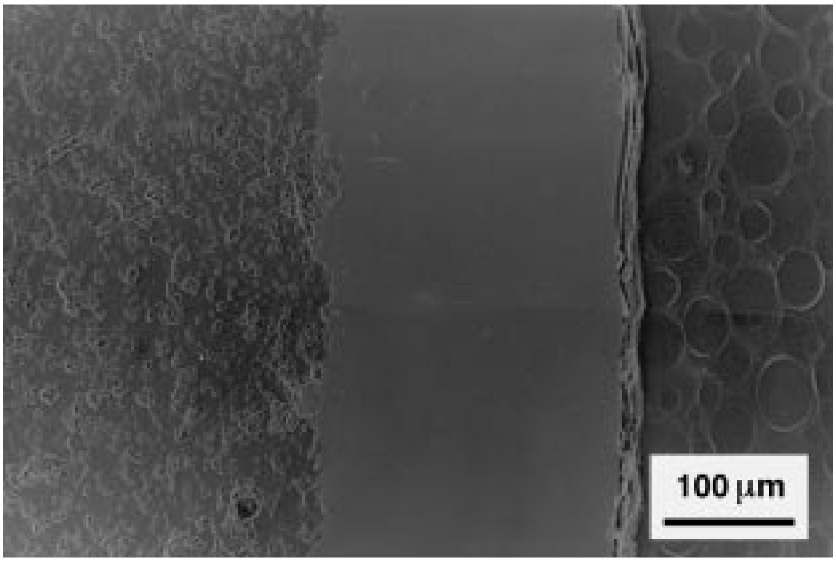

Fig. 5. SEM micrograph 7762 of Bi–PbO_2/Ebonex interface (trial 11, Table 2).

of a cross section showed the coating thickness to be 214–222 μm thick. After the test, SEM analysis showed the coating loss to be 142–158 μm loss per annum, which is significantly better than undoped lead dioxide.

Table 3. Comparison of Bi:Pb ratio in deposition solution and coating

Deposition solution consisted of 25% $Pb(NO_3)_3$; 10% HNO_3; 0.5% Brij 35. In each case, $Bi(NO_3)_3.5H_2O$ was added to give the concentration indicated

$Bi(NO_3)_3.5H_2O$ /%m v^{-1}	*Bi:Pb ratio in deposition solution*	*Bi:Pb ratio in coating (XPS)*
1.10	0.030	0.06
1.83	0.050	0.03
4.58	0.125	0.01/0.15
9.15	0.250	0.67

4. Conclusion

Good quality (smooth and compact) PbO_2 electrodeposits can be obtained in a plating bath of relatively simple composition, with low temperature being the key factor. Adhesion of the deposit to the substrate is vital, and this can be achieved by using a substrate of similar physical properties to lead dioxide, such as Ebonex.

It appears that the presence of bismuth during deposition gives a better quality of coating structure, perhaps due to more compact, dense packing of the atoms. The bismuth-lead dioxide coatings are black and very bright (mirror-like), indicating that bismuth acts as a brightener and leveller during deposition. Considerable benefit is derived from the presence of bismuth in the lead dioxide coating in terms of coating life time, and this can have a significant impact on the economic feasibility of industrial electrosynthesis processes which depend on PbO_2 as an anode material.

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