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Physicochemical properties of electrodeposited β-lead dioxide: effect of deposition current density

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The influence of current density on the coulometric efficiency of β-PbO_2 deposition in 0.5 M lead nitrate, the nonstoichiometry, impurity of α-PbO_2 and voltammetric double layer capacitance have been studied. While the coulometric efficiency is about 95% at current densities less than 30 mA cm^{-2}, it decreases at higher current densities. The oxygen deficiency, δ, in β-$PbO_{2-\delta}$ has been found to be invariant with the current density. X-ray diffraction studies provide a linear decrease in the weight percent of α-PbO_2 as an impurity in the β-PbO_2 with increase in current density, and the α-PbO_2 is found to be absent at 100 mA cm^{-2} or higher. The estimated double layer capacitance from the cyclic voltammograms recorded in the potential range 0.70–1.10 V, increases with deposition current density, indicating enhanced surface area.

1. Introduction

Studies on electrodeposited β-lead dioxide have been of recent interest in our laboratory [1–5] and also elsewhere [6–10]. Usually, β-PbO_2 is anodically deposited on a suitable substrate from an acidic solution containing lead(II) ions. Other compounds such as copper nitrate, sodium acetate, surfactants etc., are often added to the electrolyte to achieve desirable properties of the deposits. Teepol, for example, was used to enhance the surface area of the β-lead dioxide electrode [4]. It has been found that a variation of the electrolytic conditions causes changes in the properties of the β-lead dioxide, as a result of which it exhibits different catalytic effects on certain electrochemical reactions [11]. In order to understand this, studies on the effects of varying the deposition conditions on the physicochemical properties of β-lead dioxide have been undertaken. In the present communication, the influence of deposition current density on the crystallographic nature, the degree of nonstoichiometry, surface morphology and the cyclic voltammetric charge of the β-lead dioxide is reported.

2. Experimental details

The β-lead dioxide was deposited on a platinum or a platinized titanium substrate in an unstirred solution of 0.5 M lead nitrate having an initial pH $\sim$4 at 60° C, using a platinum cathode. The deposition was carried out at several current densities in the range 1–100 mA cm^{-2}, while maintaining the other electrolysis conditions unchanged. In each case, a monolayer (1.6 μm) of PbO_2 was deposited at 20 mA cm^{-2} for 1 min, over which the PbO_2 was grown at a required current density. As the PbO_2 became powdery at higher current densities, and uniform nucleation throughout the surface did not take place at lower current densities, the nucleation current density was chosen in the middle of the experimental range. After PbO_2 of the required thickness had been deposited, the electrolyte was allowed to cool to room temperature, the electrode taken out and washed thoroughly with distilled water. For cyclic voltammetric experiments, the PbO_2 was grown to a thickness of 50 μm on platinum (0.5 cm^2). But for the rest of the experiments, 0.5 mm thick PbO_2 was grown on platinized titanium (10 cm^2), and the deposit was mechanically detached from the substrate ensuring the absence of any trace amount of platinum in the separated PbO_2. The coulometric efficiency of PbO_2 deposition was measured from the weight gain of the platinized titanium electrode on passing 360 C of charge. The oxygen present in the lead dioxide was estimated using a powdered sample by conventional iodometric titration, but using potentiometry in place of a starch indicator. The PbO_2 was subjected to X-ray powder diffraction using CuK_α target and scanning electron microscopic studies. The PbO_2 electrode deposited on platinum was used to record cyclic voltammograms at 20° C in the potential range 0.70–1.10 V against SCE.

3. Results and discussion

3.1. *Coulometric efficiency of PbO_2 deposition*

At the potentials of oxidation of Pb^{2+} to PbO_2 (reaction 1) in an aqueous electrolyte, oxidation of water to oxygen (Reaction 2) can also take place simultaneously.

$$Pb^{2+} + 2H_2O \longrightarrow PbO_2 + 4H^+ + 2e^- \quad (1)$$

$$2H_2O \longrightarrow O_2 + 4H^+ + 4e^- \quad (2)$$

As a result, the coulometric efficiency of PbO_2 deposition is usually less than unity. Figure 1 shows the efficiency as a function of the deposition current density. The coulometric efficiency is about 95% at current densities up to about 30 mA cm^{-2}. The decrease

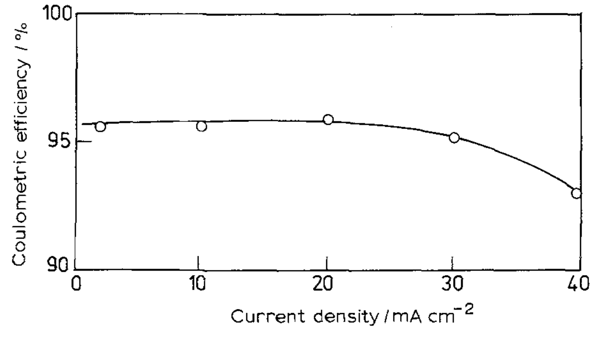

Fig. 1. Coulometric efficiency of β-PbO_2 deposition in 0.5 M lead nitrate solution at 60° C as a function of the deposition current density.

in efficiency at higher current densities is due to an increased rate of oxygen evolution (Reaction 2) or due to the loss of the PbO_2 deposit, which became powdery and settled at the bottom of the container. The powdered PbO_2, however, was not quantitatively estimated.

In order to study the polarization behaviour during PbO_2 deposition, galvanostatic polarization was carried out. The electrode potential was measured 5 min after setting the required current. During this period, the potential was constant, indicating that the reaction was under charge-transfer control, though the electrolyte was not stirred. The polarization curve, as measured, is non-linear (Fig. 2) due to the fact that the measured potentials include an ohmic potential drop (IR_Ω) because of the large area (10 cm^2) of the electrode used for this study. The solution resistance (R_Ω) was estimated from the experimental current-potential data as follows.

For an anodic charge-transfer process, the current (I) at the electrode is given by

$$I = i_0 A \exp\left[\beta n f(E - E^0 - IR_\Omega)\right] \quad (3)$$

where i_0 is the exchange current density, A the area of the electrode, E the electrode potential corresponding to I, f is F/RT and the other symbols have their usual meanings. If the above equation is written for two different currents, I_1 and I_n; and on dividing one by the other, Equation 4 is obtained.

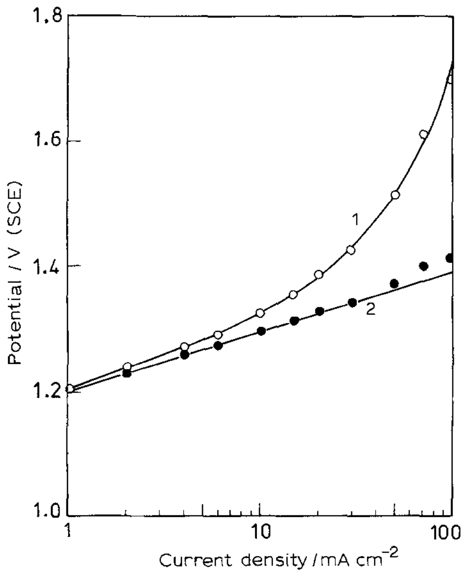

Fig. 2. Galvanostatic polarization curve during the deposition of β-PbO_2 in 0.5 M lead nitrate solution at 60° C. Curve 1 from the experimental data and curve 2 after correcting for ohmic potential drop.

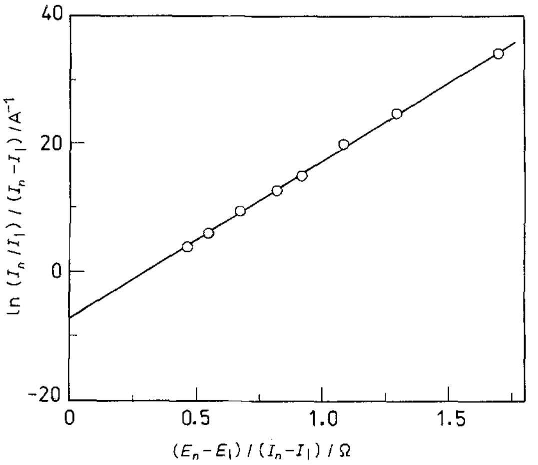

Fig. 3. The dependence of ln $(I_n/I_1)/(I_n - I_1)$ on $(E_n - E_1)/(I_n - I_1)$ from the experimental polarization data of curve 1 in Fig. 2.

$$\ln(I_n/I_1) = \beta n f\left[(E_n - E_1) - R_\Omega(I_n - I_1)\right] \quad (4)$$

which, after rearranging, becomes

$$\frac{\ln(I_n/I_1)}{(I_n - I_1)} = \beta n f\left[\frac{(E_n - E_1)}{(I_n - I_1)} - R_\Omega\right] \quad (5)$$

Keeping I_1 constant and varying I_n throughout the experimental current values, ln $(I_n/I_1)/(I_n - I_1)$ can be plotted against $(E_n - E_1)/(I_n - I_1)$. This provides a straight line with intercept $-\beta n f R_\Omega$ and slope $\beta n f$. The value of R_Ω can be calculated on dividing the intercept by the slope. The Tafel slope ($2.3\,RT/\beta nF$) and, therefore, the energy transfer coefficient (β) can also be calculated from the slope. This procedure assumes Reaction 1 alone taking place under charge transfer control throughout the experimental points, thus neglecting the minor contribution of Reaction 2.

The plot of ln $(I_n/I_1)/(I_n - I_1)$ against $(E_n - E_1)/(I_n - I_1)$ for the polarization curve (Fig. 2) is shown in Fig. 3. The value of R_ω calculated is 0.29 Ω. The polarization data was corrected for the ohmic potential drop (IR_Ω) and the corrected polarization curve is shown in Fig. 2. It can be seen that the plot is linear with a Tafel slope of 95 mV. This value is close to the Tafel slope (92 mV) calculated from Fig. 3. The value of the energy transfer coefficient thus becomes 0.32, assuming $n = 2$. The Tafel slope and energy transfer coefficient obtained here for Reaction 1 are comparable to the values (98 mV and 0.30, respectively) reported previously in lead acetate and acetic acid mixed electrolytes [12].

3.2. *Oxygen deficiency*

Lead dioxide is nonstoichiometric with a deficiency in oxygen ($PbO_{2-\delta}$). The preparation involves the anodic oxidation of both Pb^{2+} and H_2O (Reaction 1), thus implying that the degree of nonstoichiometry depends on the rate of oxidation or the deposition current

Table 1. The δ value in $PbO_{2-\delta}$ prepared at different current densities

Current density/ mA cm^{-2}	O/Pb ratio	δ
2	1.95	0.05
10	1.96	0.04
25	1.94	0.06
50	1.96	0.04
100	1.94	0.06

Table 2. The powder XRD data of β-PbO_2 deposited at different current densities

Current density/ mA cm^{-2}	2θ/ radians	Relative intensity/%	h k l index	
			α-PbO_2	β-PbO_2
2	23.6	15	1 1 0	–
	25.4	98	–	1 1 0
	28.5	37	1 1 1	–
	32.0	100	–	1 0 1
	36.2	29	–	2 0 0
	49.1	59	–	2 1 1
5	23.6	11	1 1 0	–
	25.4	97	–	1 1 0
	28.5	29	1 1 1	–
	32.0	100	–	1 0 1
	36.2	27	–	2 0 0
	49.1	58	–	2 1 1
10	23.6	9	1 1 0	–
	25.4	95	–	1 1 0
	28.5	21	1 1 1	–
	32.0	100	–	1 0 1
	36.2	26	–	2 0 0
	49.1	58	–	2 1 1
25	25.4	81	–	1 1 0
	28.5	11	1 1 1	–
	32.0	100	–	1 0 1
	36.2	24	–	2 0 0
	49.1	58	–	2 1 1
50	25.4	81	–	1 1 0
	28.5	7	1 1 1	–
	32.0	100	–	1 0 1
	36.2	24	–	2 0 0
	49.1	62	–	2 1 1
100	25.4	88	–	1 1 0
	32.0	100	–	1 0 1
	36.2	38	–	2 0 0
	49.1	91	–	2 1 1
Pure α-PbO_2	23.6	38	1 1 0	–
	28.5	100	1 1 1	–
	36.0	38	2 0 0	–
	49.4	52	2 0 2	–
	50.5	47	2 1 1	–

density. The value of δ (Table 1), however, is in the range 0.04–0.06 irrespective of the current density.

3.3. *X-ray diffraction studies*

Lead dioxide electrodeposited from acidic solutions is usually reported to be in the tetragonal β-form, though a small amount of the orthorhombic α-form is also codeposited [13]. The effect of various organic additives to acidic lead nitrate solutions resulted in varying proportions of the α- and β-forms [6]. The electrolytic conditions such as stirring of the electrolyte also influence the crystallographic nature. Literature on the influence of current density on the α-PbO_2 impurity in the β-PbO_2 deposited from acidic electrolytes is at variance. The presence of α-PbO_2 was detected at very high current densities [14]. Pure β-PbO_2 was deposited [15] from lead perchlorate solution at 1 mA cm^{-2}. It was also reported [13] that pure β-PbO_2 was deposited at 0.1 mA cm^{-2} from very dilute acidic perchlorate solution. In contrast to these results, however, it was reported [16, 17] that α- and β-modifications were codeposited at 1–10 mA cm^{-2}, only trace amounts of α-PbO_2 were detected at 25–40 mA cm^{-2} and pure β-PbO_2 was formed at 100 mA cm^{-2} in electrolytes of 80–340 g dm^{-3} of lead nitrate containing nitric acid.

The XRD results obtained for the β-PbO_2 prepared at various current densities in unstirred lead nitrate solution are given in Table 2. The data for pure α-PbO_2 prepared from alkaline lead acetate solution [18] are also given for comparison. It can be seen that the XRD pattern of α-PbO_2 prepared from alkaline solution does not indicate the presence of β-modification. Similarly, the β-PbO_2 prepared at 100 mA cm^{-2} does not contain the α-modification. However, the XRD pattern of the β-PbO_2 prepared at lower current densities indicates the presence of α-PbO_2. In these cases, the XRD peaks essentially at $2\theta = 25.4$ and 32.0 radians for the (1 1 0) and (1 0 1) planes, respectively, of the β-PbO_2 and at $2\theta = 28.5$ radians for the (1 1 1) plane of the α-PbO_2 appear in varying proportions, in addition to some other low intensity peaks. In order to estimate the ratio of the α- and β-modifications of the lead dioxide deposited at different current densities, the procedure of Dodson [19] was employed. The ratio of the relative intensity of the (1 1 1) plane of α-PbO_2 (J_α) to the average of relative intensities of the (1 1 0) and (1 0 1) planes of β-PbO_2 ($J_{\beta 1}$ and $J_{\beta 2}$, respectively) is proportional to the percentage ratio of the α-PbO_2 (W_α) in the mixture.

$$\frac{2J_\alpha}{J_{\beta 1} + J_{\beta 2}} = KW_\alpha \qquad (6)$$

The proportionality constant (K) was calculated using the XRD peak intensities of a known mixture of the α- and β-modifications of the PbO_2. Using the value of K (equal to 0.0139 per wt%), the percentage of the α-modification present in the PbO_2 prepared at several current densities was calculated and is shown in Fig. 4. The quantity of α-PbO_2 decreases with increase in current density. At practical PbO_2 deposition current densities (10–20 mA cm^{-2}), the presence of α-PbO_2 is in the range 10–15%.

The present results provide a quantitative estimation of the α-PbO_2 as an impurity in electrodeposited β-PbO_2 and also confirm the qualitative observations

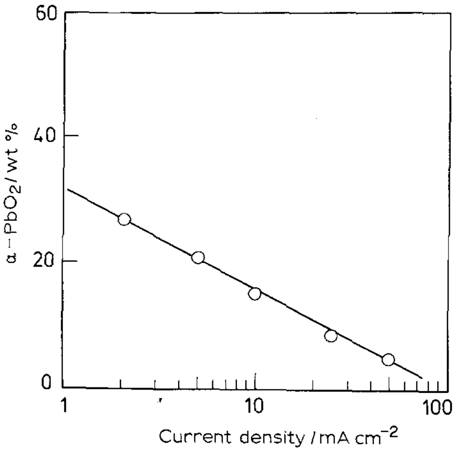

Fig. 4. Quantity of α-PbO_2 codeposited with β-PbO_2 from 0.5 M lead nitrate solution at 60° C as a function of current density.

[16, 17] on the influence of current density. Similarly, the ratio of α-PbO_2 to β-PbO_2 was higher in the positive plate of a lead acid accumulator, when the formation current density was lower [19]. The contradictory results given above are probably due to variations in the other parameters such as concentration of Pb^{2+}, acid strength, other ions, temperature, mode of agitation etc., of the deposition process.

3.4. *Voltammetric studies*

When subjected to potential cycling between 0.30 and 1.50 V against SCE in a neutral electrolyte, the β-PhO_2 electrode exhibits an irreversible anodic current peak at about 1.10 V due to the oxidation of PbO to PbO_2 [1]. If, however, the lower limit of the potential range is raised to 0.60 V or higher, the oxidation peak is absent and charging current alone flows at the electrode. In the present studies, the voltammetric response of the electrode in neutral 0.2 N sodium nitrate solution is shown in Fig. 5.

From the charging curves of the β-PbO_2 electrode prepared at any current density, the double layer capacitance (C_d) was calculated. Assuming that time constant is negligible at potentials greater than 0.70 V and also any contribution of pseudo capacitance is absent, the charging current density (i_c) can be approximately related to the scan rate (dE/dt) as

$$i_c \simeq C_d \frac{dE}{dt} \qquad (7)$$

On integration of Equation 7, the double layer capacitance is related to the voltammetric charge (q).

$$C_d \simeq \frac{q}{E_s - E_i} \qquad (8)$$

where E_i and E_s are the initial and final potential limits of the scan. The C_d thus calculated is an average value in the potential range studied. The dependence of q

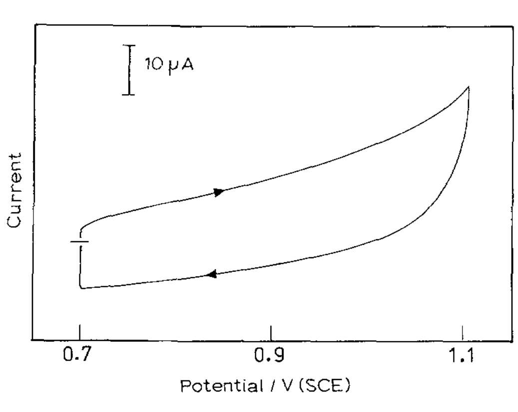

Fig. 5. Cyclic voltammogram of β-PbO_2 (50 μm) deposited on Pt (0.5 cm^2) at a current density of 1 mA cm^{-2}, in 0.2 M sodium nitrate solution at 20° C in a nitrogen atmosphere.

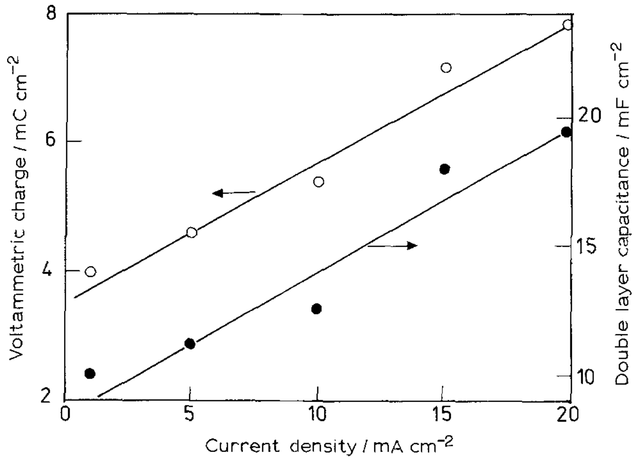

Fig. 6. Cyclic voltammetric charge (○) and double layer capacitance (●) of β-PbO_2 (50 μm) deposited on Pt (0.5 cm^2), in 0.2 M sodium nitrate solution at 20° C under a nitrogen atmosphere as a function of the deposition current density.

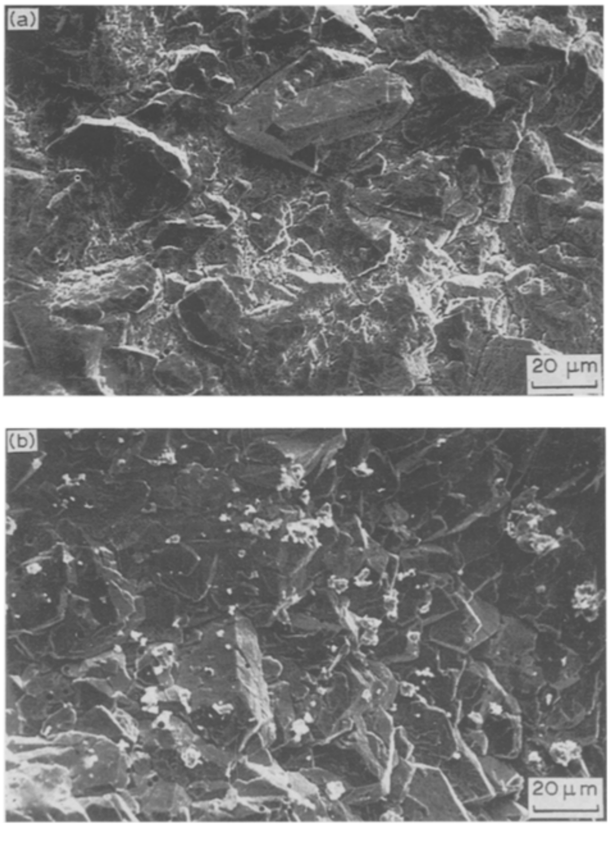

Fig. 7. SEM photographs of 0.5 mm thick β-PbO_2 deposited from 0.5 M lead nitrate (60° C) at a current density of (a) 1 mA cm^{-2} and (b) 50 mA cm^{-2}.

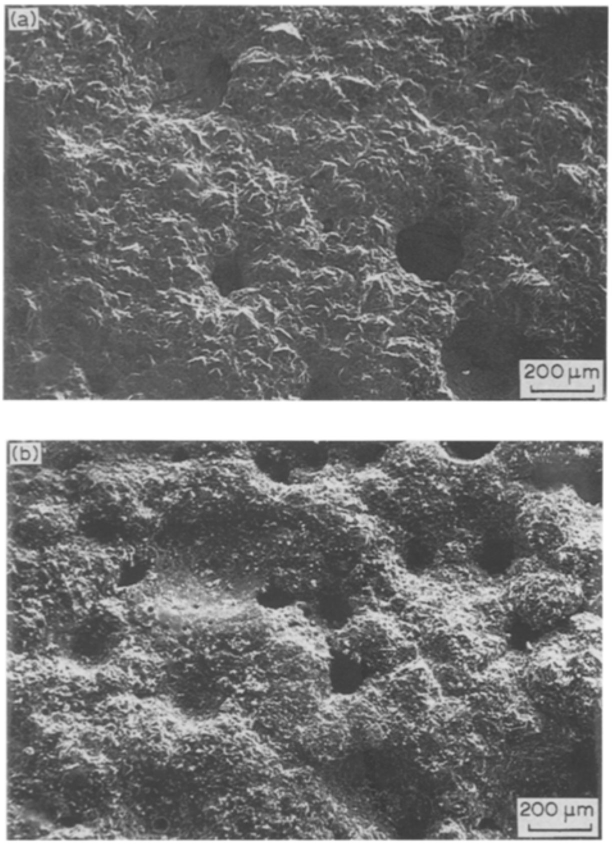

Fig. 8. SEM photographs showing pores on 0.5 mm thick β-PbO_2 deposited from 0.5 M lead nitrate (60° C) at a current density of (a) 25 and (b) $50\,mA\,cm^{-2}$.

and C_d calculated from the voltammograms recorded at $20\,mV\,s^{-1}$ scan rate in the potential region 0.70–1.10 V, on the deposition current density is shown in Fig. 6. It can be seen that the voltammetric charge and therefore the double layer capacitance of the β-PbO_2 electrode increase with the deposition current density. As the thickness of the β-PbO_2 is maintained constant at all current densities the enhancement of the charge and the double layer capacitance can be attributed to increase in surface roughness and therefore the surface area of the electrode.

The increase in true surface area was clearly seen when the lead dioxide was examined by SEM (Fig. 7). The surface of PbO_2 deposited at $1\,mA\,cm^{-2}$ consisted of crystals of large size with surface non uniformity, whereas there were a large number of small crystals spread uniformly throughout the surface if the current density was $50\,mA\,cm^{-2}$. At current densities $25\,mA\,cm^{-2}$ or higher, however, the PbO_2 became porous (Fig. 8) due to oxygen bubbles on the surface during the course of the deposition. It may also be seen in Fig. 8, that the crystal size was larger on PbO_2 deposited at $25\,mA\,cm^{-2}$ rather than at $50\,mA\,cm^{-2}$.

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