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An electrochemical and radiotracer investigation on lead dioxide: influence of the deposition current and temperature

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Abstract: The properties of electrodeposited PbO₂ are sensibly influenced by the deposition current and temperature. In particular, tritium radiotracer measurements demonstrated that protons were incorporated into the bulk of an oxide film and on its surface. The degree of hydration increased with increasing current and decreased with temperature, and was related to the morphological characteristics of the oxide, such as roughness measured by changes in the double layer capacity. Conversely, the amount of hydrogen had negligible effects on the number of free carriers as evaluated from Mott–Schottky plots. The hydration degree of the surface seems to be an important factor influencing electrocatalytic processes at high potentials, such as O₂ evolution and O₃ formation. On less hydrated, more crystalline PbO₂ surfaces, the first process was inhibited and accordingly, the second was favored.

Keywords: lead dioxide, tritium, electrodeposition, electrocatalysis.

INTRODUCTION

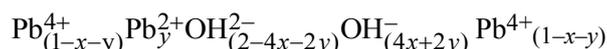
Lead dioxide electrodes have been studied for several years and continue to attract considerable interest from both practical and theoretical points of view. In the field of battery applications, research in lead-acid batteries is still very active,¹ and in particular, recent developments of new soluble lead-acid flow devices appear rather attractive.² A recent review by Li *et al.*³ presents very informative state of the art studies on PbO₂. Despite the enormous amount of work, there is still a considerable debate on some issues, such as the stoichiometry of the oxide (sometimes described as PbO_x) and its influence on electrochemical properties.

The reason of this non-stoichiometry has been attributed to oxygen vacancies, interstitial protons or quasi-free electrons. In the model proposed by Rue-

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tschi and Giovanoli,⁴ vacancies are arranged to form layers (named “internal surfaces”) between crystallographically ordered areas, and the charge due to missing Pb^{4+} would be compensated only by OH^- or by Pb^{2+} and OH^- . Thus, the formula proposed to describe better the composition of PbO_2 is:



The model accounts for the fact that experimental studies report evidence for the presence of Pb(II) and structural water in the PbO_2 lattice. On the one hand, earlier studies remained inconclusive in regards to whether it is fully stoichiometric with respect to oxygen³⁻⁵ or not; on the other hand, according to recent studies based on theoretical calculation,⁶⁻⁸ the conductivity is due to oxygen vacancies.

Different studies agree that electrochemically prepared PbO_2 contains structural water (hydrogen)⁴ and that there is a correlation between the hydrogen content and its electrochemical activity.⁹ The electrochemical behavior of electrodeposited PbO_2 is very sensitive to the preparation method, and the choice of the electrodeposition parameters of play an important role in the control of the morphological characteristics of PbO_2 .¹⁰⁻¹⁵ It seems, however, that there has been insufficient systematic investigations on how the control of different parameters in the electrodeposition of PbO_2 can affect the amount of structural water in the resulting oxide.

In this work, the influence of parameters such as the deposition temperature on the inclusion of tritium into electrodeposited PbO_2 films I discussed. Generally, radiochemical studies can provide useful complementary information in the study of electrochemical reactions.¹⁶⁻²⁰ In addition, the electrochemical behaviors of the obtained films are examined. The starting point was the question raised by Hill several years ago²¹ on a possible connection between structural hydrogen and electrochemical reactions at PbO_2 .

EXPERIMENTAL

Chemicals

Ultrapure acids were obtained from Merck and all other chemicals from Sigma–Aldrich

Equipment

The electrochemical experiments were performed employing an EG&G model 273A potentiostat–galvanostat using EG&G software. Additionally, for impedance measurements, an EG&G model 5210 lock-in amplifier was used. Simulation calculations of the impedance data were realized using the B. A. Boukamp Equivalent Circuit simulation program. Measurements were performed in a conventional three-compartment cell. The counter electrode was a large Pt flag, or a cylindrical Pt gauze surrounding the working electrode in the case of impedance measurements. A saturated calomel electrode (SCE) was used as the reference. This was in contact with the working electrode compartment through a Luggin tip. X-Ray diffraction experiments were performed with an Advance Bruker D8 diffractometer.

Methods

Cyclic voltammetry and impedance measurements were performed with PbO₂ electro-deposited on a Pt wire (geometrical area 0.18 cm²). For the radiochemical experiments, PbO₂ was galvanostatically deposited onto platinized titanium (geometric area 2 cm²). The experimental conditions were adjusted so that the weight of the deposit was constant, and thickness was estimated using the reported density of PbO₂.⁴ Both the activity due to tritium incorporated in the whole films (A_t) and that due to exchange of tritium at the surface (A_s) were measured as described below.

i) For the measurement of A_t , PbO₂ films of different thickness were prepared by electro-deposition at a constant current from solutions of 1 M HNO₃ + 1 M Pb(NO₃)₂. [³H]water (tritium water) was added to the solution to give a radiochemical activity of 5×10⁷ d.p.m. (disintegrations per min). After preparation, the electrodes were washed with dry acetone, dried in an argon flow, weighed and dissolved in H₂O₂/aqueous acetate buffer at pH 5.5. A fixed amount of this solution was added to the scintillating liquid (Insta-gel, Packard), and the radiochemical activity was counted.

ii) For the determination of A_s , the amount of tritium exchanged at the oxide surface, the following procedure was adopted: lead dioxide films having a fixed thickness were prepared in the absence of [³H]water. They were then immersed in solutions containing [³H]water (5×10⁷ d.p.m.) for 60 h; this conditioning time was chosen because separate experiments showed that the uptake of tritium reached a maximum after this period. The samples were thoroughly washed with dry acetone, dried in an argon flow and immersed in the scintillating liquid. The release of tritium in the scintillating liquid was measured as a function of time until the radiochemical activity reached a constant value.

Films of α -PbO₂ were prepared from 2 M NaOH solutions saturated with lead acetate. Ozone analysis was performed mostly by iodometric titration. In some cases, the so-obtained results were checked by the spectrophotometric method measuring the absorption at 254 nm and using an extinction coefficient of 3024 L cm⁻¹ mol⁻¹.

RESULTS AND DISCUSSION

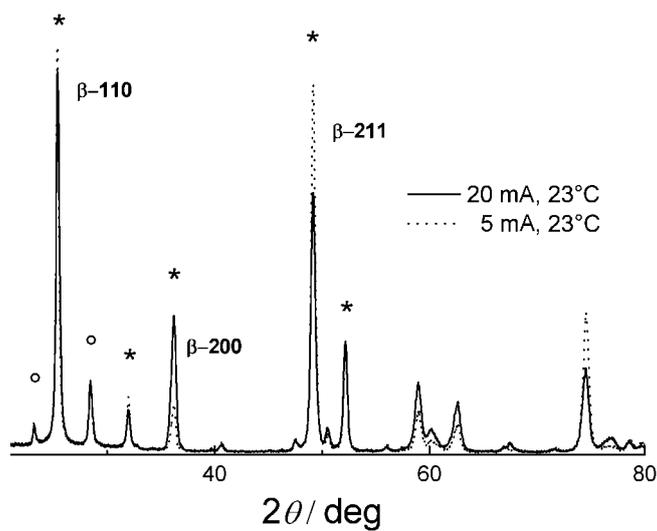
X-Ray characterization

The effect of electrodeposition conditions on the XRD spectra of PbO₂ is shown in Fig. 1. At room temperature, an increase in the constant deposition current does not result in significant changes in the reflection patterns, except for a larger contribution of some higher index planes as the current increased (Fig. 1a). SEM micrographs (Supplementary material) show that at the higher current densities, the films feature crystals without clear crystal edges.

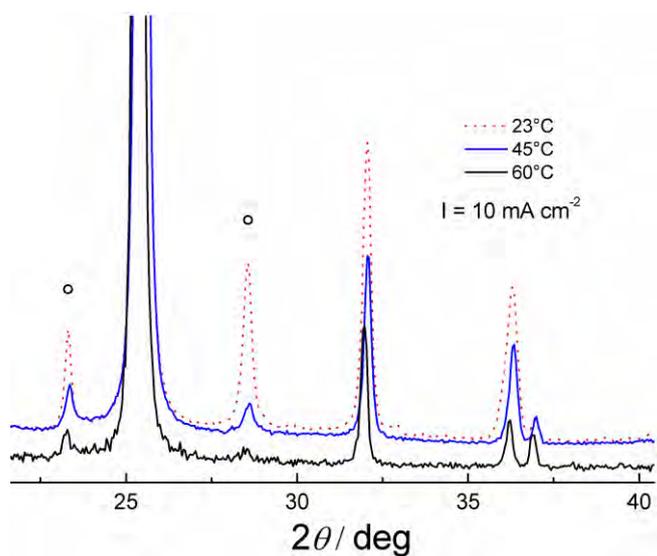
The obtained films consisted of mixture of α - and β -phase PbO₂, with the calculated amount of the former¹⁴ remaining rather constant and less than 10 % of the total PbO₂. The size of the crystallites, calculated from the Scherrer Equation:

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

was also relatively insensitive to current.¹⁴ Using the most intensive β (110) peak, the calculations yielded particle dimensions of 27 and 30 nm for 5 and 20 mA cm⁻², respectively.



(a)



(b)

Fig. 1. a) Effect of the deposition current on the XRD pattern of PbO₂. Peaks marked (*) correspond to β -PbO₂ and those marked (o) to α -PbO₂. Temperature: 23 °C. b) Effect of the deposition bath temperature on the XRD pattern of PbO₂. Peaks marked with (o) correspond to α -PbO₂.

The choice of the deposition temperature had a comparatively more pronounced influence. As shown in Fig. 1b, the contribution of the α -PbO₂ polymorph gradually disappeared as the temperature was increased from 22 to 60 °C. These results are in agreement with those reported by Sirés *et al.* for PbO₂ prepared from methanesulfonic acid.²²

Tritium exchange

In the study of electrodeposited PbO₂ under different experimental conditions, tritium radiotracer measurements can, in principle, provide a relatively simple method to obtain information on hydrogen incorporation into the oxide and at its surface. In fact, according to the disorder model of electrochemically grown PbO₂, hydrogen ions on interstitial sites together with quasi-free electrons are considered the dominating disorder centers.²³

The graph displayed in Fig. 2a shows that the total amount of tritium (A_t) incorporated into the whole PbO₂ film was a linear function of thickness. It also showed that the amount of tritium in the more defective α -PbO₂ film was much larger than that observed with β -PbO₂ for the same deposition current and temperature (*cf.* plots 1 and 2). The amount of tritium in the bulk decreased significantly as the deposition temperature was increased to 60 °C, for the same constant current (*cf.* plots 2 and 3). The small amount of the α -polymorph present in the films obtained at room temperature (*vide supra*) does not explain the large decrease in the tritium inclusion brought about by temperature.

In an analogous experiment, the amount of tritium exchanged with the surface (A_s) was determined as described in the experimental section. The results reported in Fig. 2b show the release of tritium as a function of time and temperature from films that had been previously equilibrated in tritiated water for 60 h. It is possible to note that there is a rapid initial exchange which may be referred to as surface proton exchange, followed by a slower process, which is thought to evidence the presence of less accessible protons.¹⁷

The effects of the deposition current and temperature on the radiochemical activity are summarized in Table I. In principle, a number of correlations are possible; for example, one may note that both A_t and A_s increase as the current increased, and that the increase was very pronounced only for samples prepared at room temperature.

Since it could reasonably be expected that A_s would depend on the effective surface area, cyclic voltammetry experiments were performed at different scan rates in the double layer region (1.35–1.45 V) and calculated the capacities as reported in the literature.²⁴ Then the effective areas were estimated by taking the double layer capacity of smooth electrodes (20 $\mu\text{F cm}^{-2}$) as a reference,^{25,26} Examples are given in Table II. It was observed that there is a direct propor-

tionality between the surface radiochemical activity (A_S) and the effective area: both increased with deposition current and decreased with temperature.

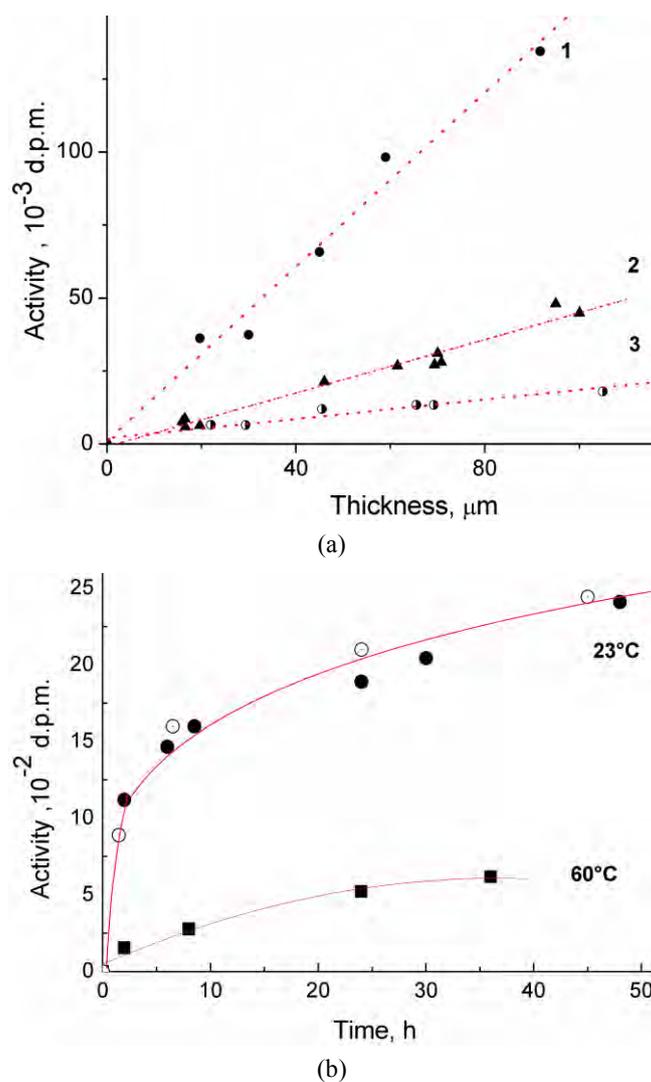


Fig. 2. a) Overall amount of tritium incorporated into $\alpha\text{-PbO}_2$, $t = 23^\circ\text{C}$ (1), $\beta\text{-PbO}_2$, $t = 23^\circ\text{C}$ (2), and $\beta\text{-PbO}_2$, $t = 60^\circ\text{C}$ (3), as a function of film thickness; b) amount of tritium released by $\beta\text{-PbO}_2$ in contact with the scintillating medium after a 60-h contact with tritium water. Samples prepared by electrodeposition at a constant current (10 mA cm^{-2}) onto Pt/Ti substrates. See experimental section for details.

It was generally observed that high currents favor the formation of PbO_2 films that are less stoichiometric. Additionally, under these conditions, oxygen

evolution could occur and lead to an increase in the microporosity of the coating, and, as a consequence, the exchange of tritium between the films and the environment occur more easily due to the large number of lattice defects and morphological disorder.¹⁷ Conversely, more compact, less defective surfaces are formed at high temperature,^{22,27} which explains why a smaller amount of hydroxyl species was present in the surface region as well as across the film.

TABLE I. Amount of tritium incorporated into α -PbO₂ ($t = 23$ °C) and β -PbO₂ ($t = 23$ and 60 °C) electrochemically grown onto platinized Ti substrates (2 cm^2) at a constant current (10 mA cm^{-2})

Deposition current, mA cm^{-2}	$t / \text{°C}$	
	23	60
Surface activity ($A_s/100$), d.p.m.		
5	11.04	3.82
10	18.8	5.89
20	30	7.3
30	35.4	8.2
40	38	9.32
Total activity ($A_t/100$), d.p.m.		
5	17.8	16.45
10	31.2	30.3
20	47	33.3
30	62	35
40	74.2	33.25

TABLE II. Double layer capacities and roughness factors as a function of PbO₂ deposition current and temperature

Deposition current, mA cm^{-2} (temperature, °C)	Capacity, mF	Roughness factor	Effective area, cm^2
5 (23)	1.75	87.5	15.8
5 (60)	0.685	34.2	6.15
20 (23)	4.6	230	41.4
5 (23), α -PbO ₂	30	1500	270

Electrochemical characterization

Electrodeposited PbO₂ is reported to be a narrow band gap semiconductor with high electron conductivity due to non-stoichiometry, which varies with preparative conditions.^{7,28} Often the Hall effect is used to determine the number of free charges. However, reasoning that useful information was obtained from Mott–Schottky analysis for conductive materials, such as Sb–SnO₂²⁹ and boron-doped diamond,³⁰ the capacities of the prepared PbO₂ films were calculate from their impedance and the data was plotted according to:

$$\frac{A^2}{C^2} = \frac{2}{q\epsilon\epsilon_0 N} \left(E - E_{fb} - \frac{kT}{q} \right) \quad (2)$$

where q is the electron charge, A is the area, ϵ_0 is the vacuum permittivity, ϵ is the dielectric constant of PbO_2 , taken as 3.91,⁷ and E and E_{fb} are the applied and flat-band potentials, respectively. A plot of A^2/C^2 vs. E should give a straight line, the slope of which is inversely proportional to the number of carriers N . Straight lines were indeed observed with a positive slope (n -type conductivity) for PbO_2 (5 mA, 23 °C) and PbO_2 (5 mA, 60 °C) from which the calculated values of N were 6×10^{21} and $8 \times 10^{21} \text{ cm}^{-3}$, respectively. The data are the same within experimental error and so there is no apparent correlation with tritium/proton incorporation as a function of temperature. The results are not completely unexpected, and in fact, Ruetschi and Giovanoli drew attention to this type of experimental findings several years ago.⁴ On the other hand, the effect of current density is more conspicuous as seen in the example of experimental plots of Fig. 3. In the case of PbO_2 (20 mA, 23 °C), The Mott–Schottky plots are non-linear, which could be due, for example, to a high number of defects³¹ and/or porosity.³² It is noteworthy that hydration was also observed to cause non-linearity in Mott–Schottky plots.³³

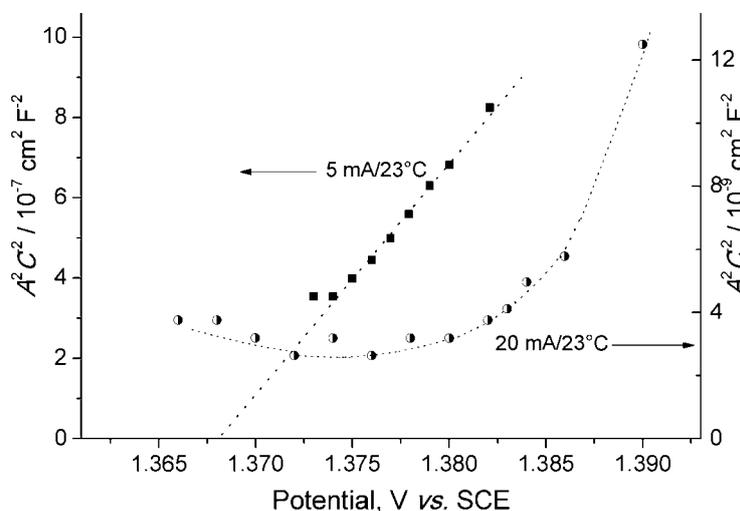
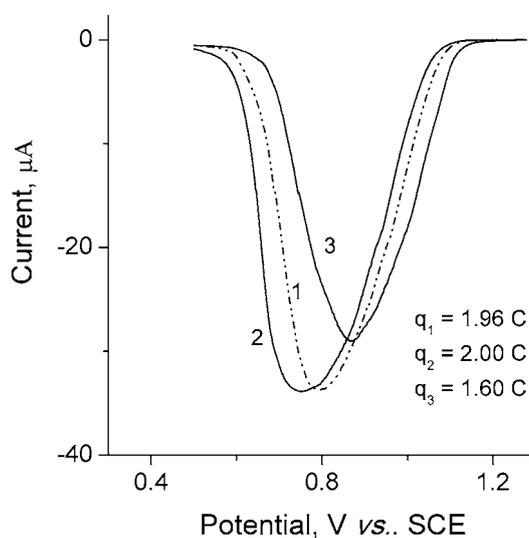


Fig. 3. Mott–Schottky plots for PbO_2 electrodeposited at 5 and 20 mA cm^{-2} at a temperature of 23 °C.

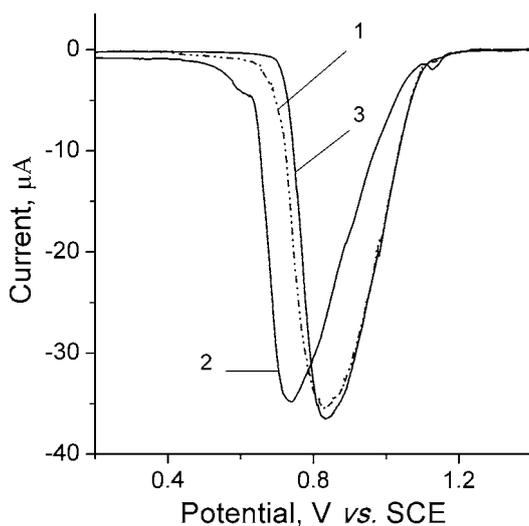
In the literature, reduction of PbO_2 electrodeposited under different conditions has been investigated frequently in order to gain insight into activity related to film morphology. Thus, for example, films with structural characteristics such

as accessibility to species in the electrolyte and fast surface and subsurface exchange of protons are expected to be more easily reduced.¹²

The results reported in Fig. 4a are first scan linear sweep voltammetry curves for the reduction of different PbO_2 samples in HClO_4 . The scan was started at 1.5 V, where no faradaic process occurs, and HClO_4 were chosen in order to avoid effects of strong adsorption of the anions. It appears that reduction occurred at more positive potentials when the films were obtained at relatively high currents;



(a)

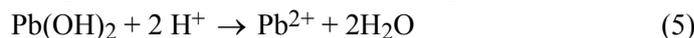
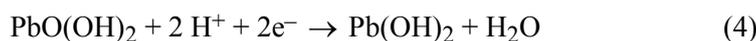
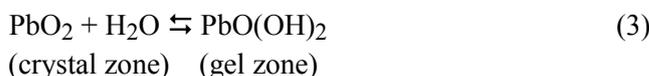


(b)

Fig. 4. Linear sweep voltammetry curves for the reduction of PbO_2 prepared under different experimental conditions: 1) 5 mA cm^{-2} , $23 \text{ }^\circ\text{C}$; 2) 5 mA cm^{-2} , $60 \text{ }^\circ\text{C}$; 3) 20 mA cm^{-2} , $23 \text{ }^\circ\text{C}$; a) first scan experiments after preparation and b) after polarization of the electrodes at 1.95 V for 1200 s. Scan rate: 5 mV s^{-1} . Electrolyte: 1 M HClO_4 .

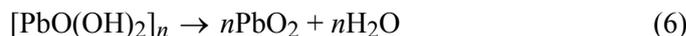
conversely, an increase in the deposition temperature shifted the reduction process to more negative potentials. Films of pure α -PbO₂ were more readily reduced, typically at ≈ 0.95 V. The lower reduction charge q_3 (Fig. 4a) is likely due to a lower electrodeposition efficiency at high currents, because of the occurrence of O₂ evolution.¹⁰ Qualitatively, the described behavior seemingly parallels the defective structure of films, as also shown by the tritium uptake experiments.

Experiments with films that had previously been used as electrodes for O₂ evolution in HClO₄ at high potentials showed that the only detectable effect was that of temperature (Fig. 4b). A possible explanation is that a gel layer is rapidly formed on PbO₂ in contact with water,¹ which is involved in the reduction process:³⁴



The influence of gel formation and its involvement in the cyclic voltammetry behavior of PbO₂ electrodes in H₂SO₄ solutions was discussed in a recent EQCM investigation by Pech *et al.*³⁵

One may speculate that the contribution of the crystal zones remains more pronounced even after polarization at high positive potentials. According to Pavlov,³⁶ however, equilibrium (3) is reversible and washing the electrode restores the crystalline zones



and since the present experiment was *ex situ*, it does not appear likely that gel formation could explain the observed behavior. Alternatively, following electrolysis at high current densities, re-deposition of PbO₂ occurred with the formation of small crystallites on the surface, as proposed by Thanos and Wabner.³⁷

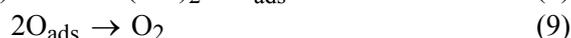
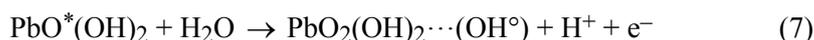
Thus, experiments were performed in dilute H₂SO₄, analogous to those described in Fig. 4 (Supplementary material). The obtained results agreed with those reported earlier in this paper and with the conclusion of Devilliers *et al.*³⁸ that reduction of PbO₂ constituted of larger, more regular crystallites is more difficult.

Electrocatalytic behavior

The results presented so far demonstrated that the preparation method determines the amount of hydrogen incorporated within PbO₂ films and influences the electrochemical behavior. The connection between these experimental aspects is probably the non-stoichiometry of the films.³⁹

Continuing with the characterization, again three types of PbO_2 electrodes, prepared at different temperature and constant current, were examined in order to assess the effects of these parameters on the O_2 evolution process.

Oxygen evolution proceeds in the gel-layer (*vide supra*) through the following elementary steps:



where $\text{PbO}^*(\text{OH})_2$ is an active center located in the hydrous layer and OH° is a hydroxyl radical bound to an active center. Thus, it is to be expected that the thickness of this layer would exert an important influence on this electrochemical process and indeed, it was reported that it lowers the potential of O_2 evolution.⁴⁰ Unfortunately, there is presently no convincing evidence of an influence of the preparation method on the degree of gel-layer formation; the interesting EQCM study by Pech *et al.*³⁵ did not explore the effects of varying the electrodeposition conditions of PbO_2 .

In the present study, the O_2 evolution was mainly investigated by impedance spectroscopy, and the results obtained by fitting the data according to the equivalent circuit displayed in Fig. 5 are reported in Table III. In this circuit, R_{ct} is the electron transfer faradaic resistance; R_{p} is the resistance associated to desorption of oxygen radical intermediates; C_{dl} is the known double layer capacity; C_{p} is related to the pseudo-capacitance, *i.e.*, to the potential dependence of the steady state coverage by reaction intermediates and is hence related in an important way to electrocatalysis. The number “ n ” appearing in the tables refers to the behavior of the constant phase element¹⁸ and has a value of 1 for a pure capacity.

A comparison of the data at a fixed potential shows that electrodeposition at high current or temperature causes a decrease and an increase, respectively, of both R_{ct} and R_{p} . In all cases $R_{\text{p}} > R_{\text{ct}}$, which seemingly indicates to a mechanism in which desorption of intermediates (reaction (8)) is slow. As reported before:¹⁸

$$\log(R^{-1}) = \log(bi^\circ) + bE \quad (10)$$

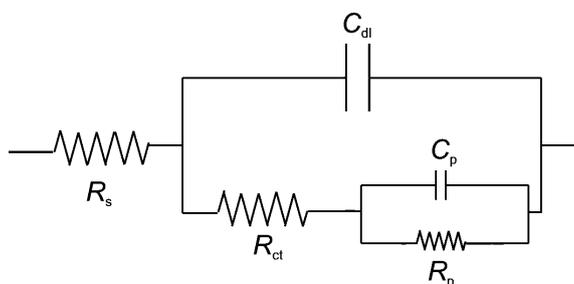


Fig. 5. Scheme of the equivalent circuit used for fitting the impedance data.

and the Tafel slope b can be obtained from plots of $\log(R^{-1})$ vs. potential. In effect, Fig. 6 shows that there is quite good agreement between the steady-state polarization plots of E vs. $\log I$ (Fig. 6a) and $\log(R_p^{-1})$ plots (Fig. 6b), at least at potentials below 1.9 V. At more positive potentials, R_p decreases rapidly and reaction (8) becomes faster. Indeed, according to MNDO calculations⁴¹ based on the hydroxylate cluster model $Pb_3(OH)_{12}(H_2O)$, electron transfer producing OH radicals and their removal from the surface to give (O) species requires almost the same energy: 685.3 and 712.5 kJ mol⁻¹, respectively.

TABLE III. Impedance spectroscopy data for PbO_2 prepared under different experimental conditions. Electrolyte: 1 M $HClO_4$

E/V	R_s/Ω	R_{ct}/Ω	R_p/Ω	$C_{dl}/10^{-3} F (n)$	$C_p/10^{-3} F (n)$
5 mA cm ⁻² , 23 °C					
1.65	1.12	11.25	932.8	1.72 (0.92)	1.20 (1.0)
1.70	1.96	10.53	443.7	1.92 (0.96)	1.17 (1.0)
1.75	1.45	8.90	150.2	1.88 (0.94)	1.13 (1.0)
1.80	1.13	8.57	41.3	1.84 (0.93)	1.05 (1.0)
1.85	1.13	6.25	18.4	1.62 (0.94)	1.10 (1.0)
1.90	1.15	3.80	11.4	1.30 (0.96)	1.25 (1.0)
1.95	1.12	2.17	8.0	0.88 (1.0)	1.05 (1.0)
2.00	1.10	1.78	4.31	0.83 (1.0)	1.69 (0.90)
2.05	1.10	1.68	2.24	0.58 (1.0)	1.27 (0.90)
5 mA cm ⁻² , 60 °C					
1.75	1.07	17.65	206.4	1.45 (0.98)	0.55 (1.00)
1.80	1.20	15.20	91.15	1.38 (0.96)	0.42 (1.00)
1.85	1.18	10.17	47.20	1.24 (0.95)	0.50 (0.92)
1.90	1.14	3.78	33.15	1.03 (0.98)	0.72 (0.85)
1.95	1.00	1.16	15.07	1.36 (0.98)	0.97 (0.85)
2.00	1.00	1.06	4.95	1.10 (1.00)	1.41 (0.84)
2.05	1.18	1.40	2.55	0.77 (1.00)	1.91 (0.84)
20 mA cm ⁻² , 23 °C					
1.70	0.86	6.05	111.6	3.60 (0.92)	2.02 (0.98)
1.75	0.86	5.6	47.15	3.50 (0.91)	2.00(1.00)
1.80	0.88	4.15	15.25	3.00 (0.92)	2.30 (0.95)
1.85	0.88	2.3	8.92	1.70 (0.98)	2.92 (0.92)
1.90	0.87	1.46	6.10	1.42 (1.00)	2.42 (0.93)
1.95	0.87	2.29	2.89	1.36 (0.97)	3.35 (1.00)
2.00	0.88	1.42	1.36	1.36 (1.00)	6.40 (0.85)
2.05	0.90	1.07	0.85	1.30 (1.00)	9.3 (0.83)

Ozone formation is an important reaction occurring on PbO_2 at relatively high potentials, in parallel with O_2 evolution⁴² (reaction (9)):



and the efficiency of O_3 generation evidently depends on the coverage and stability of O_{ads} ; the recombination process (reaction (9)) that forms an oxygen

molecule ensures a gain in energy of $891.2 \text{ kJ mol}^{-1}$.⁴¹ In this context, it is noteworthy that the stability of O is reported to be higher on less defective oxide surfaces,¹⁸ which would correspond to the less hydrated PbO_2 (5 mA, 60 °C) samples prepared in the present work.

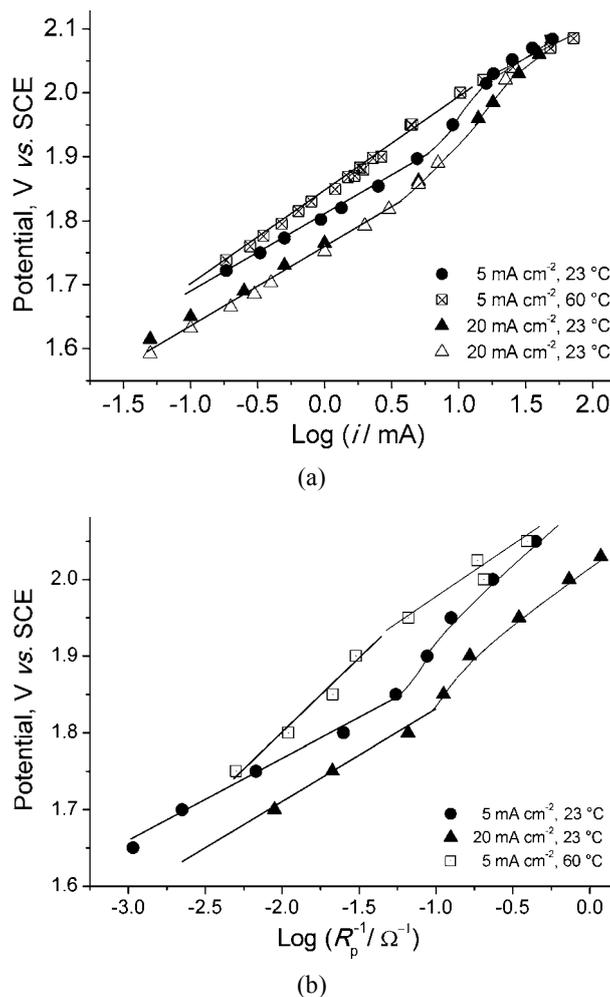


Fig. 6. Effects of PbO_2 preparation parameters on: a) E vs. $\log I$ from quasi steady-state data; b) E vs. $\log(1/R_p)$ from impedance data. Electrolyte: 1 M HClO_4 .

The data on the effect of temperature on O_3 formation shown in Fig. 7 confirmed the above reasoning. In addition, it was shown previously¹⁸ that for $E > 1.95 \text{ V}$, the current–potential curves reached a stable profile after relatively long polarization times. These results were confirmed in the present work for

samples prepared at room temperature, while those deposited at 60 °C did not exhibit such a time dependence. A tentative explanation might be that in the latter case, corrosion is less pronounced and the equilibrium in reaction (3) is shifted to the left; this conclusion would agree with the results of Fig. 4.

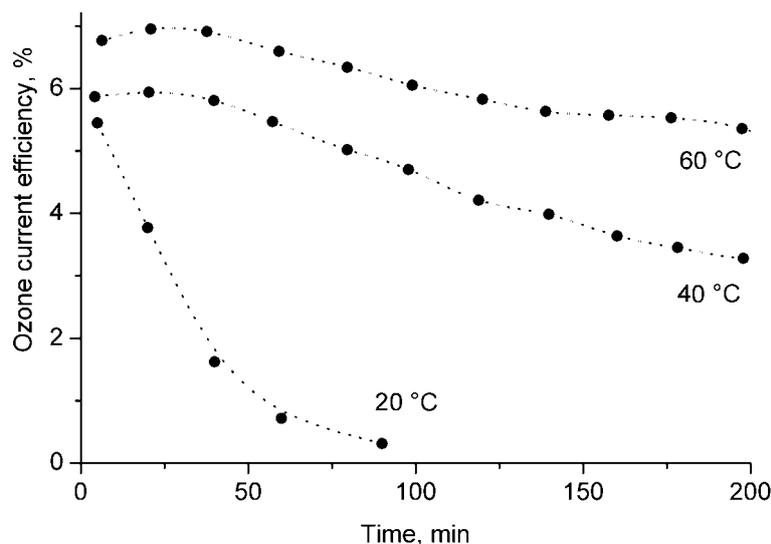


Fig. 7. The effect of the PbO₂ electrodeposition temperature on the current efficiency of ozone electrogeneration in 0.5 M H₂SO₄ as a function of time of operation at 0.5 A cm⁻².

CONCLUSIONS

Herein, an investigation into some aspects of the influence of current and temperature on electrodeposited PbO₂ has been presented. In particular, tritium radiochemical studies provide unequivocal evidence for the presence of structural water in the bulk of the oxide film and not only on its surface. In battery studies, the role of the hydrogen content in the PbO₂ lattice has been an issue for years and is still in focus these days.

We find, In accordance with the conclusions of Hill,²¹ it was found that the amount of hydrogen in PbO₂ has no direct influence on the electrochemical and electrocatalytic behavior. However, the degree of hydrogen/tritium incorporation provides information on changes in the chemico-physical characteristics. In particular, it is related to PbO₂ morphological defects, which in turn influence electrocatalytic processes, such as O₂ and O₃ generation. In this regard, the hydration degree of the surface seems to be an important parameter, the control of which could affect the efficiency of electrocatalytic oxidation processes. Probably, the question that requires further investigation is a more quantitative analysis of the relationship between degree of bulk hydration and that of the surface.

SUPPLEMENTARY MATERIAL

Figures S1–S3 are available electronically at <http://www.shd.org.rs/JSCS/>, or from the corresponding author on request.

ИЗВОД

ИСПИТИВАЊЕ ОЛОВО(IV)-ОКСИДА ЕЛЕКТРОХЕМИЈСКИМ МЕТОДАМА И МЕТОДОМ ИЗОТОПСКИХ ОБЕЛЕЖИВАЧА: УТИЦАЈ СТРУЈЕ ТАЛОЖЕЊА И ТЕМПЕРАТУРЕ

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На својства електродепонованог PbO₂ значајно утичу струја таложења и температура. Мерења са трицијумом као изотопским обележивачем показују да су протони инкорпорирани и у маси оксидног филма и да се налазе на његовој површини. Степен хидратације се повећава са повећањем струје, а опада са температуром, што је повезано са морфолошким карактеристикама оксида као што је храпавост која је одређена преко капацитивности двојног слоја. Супротно, количина водоника занемарљиво утиче на број слободних преносилаца наелектрисања израчунат из Mott–Schottky дијаграма. Изгледа да је степен хидратације површине важан фактор за електрокаталитичке процесе на високим потенцијалима као што су издвајање O₂ и стварање O₃. На мање хидратисаним, више кристалиничним PbO₂ површинама први процес је инхибиран, а у складу са тиме, други фаворизован.

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