# On the question of electrochemical activity of differently formed lead dioxides

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## Abstract

Electrochemically and chemically formed lead dioxides show varying electrochemical properties, which has often been discussed in terms of hydrogen content and amorphous phases. These differences in electrochemical activity have always interested research related to their behaviour as the positive active material (PAM) in the lead–acid battery. In this work, the crystallinity and composition of different lead dioxide samples were examined with respect to preparation method. Two electrochemically oxidised samples, one originating from a pure lead foil and the other one from tetra basic lead sulphates (TBLS), were investigated and compared with a commercial chemically prepared lead dioxide. The samples were investigated by X-ray diffraction (XRD) and thermogravimetric analysis (TGA) as a function of temperature in the range of 25–600°C. The experimental results show that only surface bound water is present in the different lead dioxide phases investigated. However, a clear difference between chemically and electrochemically formed oxide is revealed from high temperature XRD (HT-XRD). At high temperatures, a lead oxide sulphate phase is formed in the electrochemically prepared samples, showing the existence of sulphate ions bound to internal surfaces. These ions are believed to facilitate the reduction process of lead dioxide and hence contribute to the electrochemical activity. © 2000 Elsevier Science S.A. All rights reserved.

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## 1. Introduction

The question of the influence of hydrogen, amorphous phases and preparation conditions on the electrochemical activity of $PbO_2$ has been discussed for quite some time. Due to the complexity of the system a general consensus of the problem has not been reached because data from different investigations are sometimes in conflict. The aim of the present investigation is to compare the influence of preparation methods on the composition of the lead dioxide phase formed. The investigated samples were prepared from two types of electrochemically oxidised lead dioxide, one originating from a pure lead foil and the other one from tetra basic lead sulphates (TBLS). As a reference one

commercial chemically prepared $PbO_2$ was also investigated.

The importance of hydrogen in the lead dioxide structure was first pointed out by Caulder et al. [1,2]. From combined capacity measurement and differential thermal analysis they proposed that loss of hydrogen in the active $PbO_2$ mass is accompanied by a capacity loss. An exothermic peak at 200°C and an endothermic peak at 358°C were attributed to an electrochemically active amorphous form of $PbO_2$. From NMR and neutron quasi-elastic scattering it was concluded that water was not trapped in pores but was bound in the structure [2–4]. On heating the sample it was believed that the material became more ordered and crystallised in the common modifications, α- and β-$PbO_2$. Similar results were obtained recently for electrochemically formed α- and β-$PbO_2$ [5,6].

Santoro et al. [4] found changes in the lattice parameters of electrochemically active β-$PbO_2$ compared to the inactive chemically prepared samples. These differences in cell parameters were attributed to the presence of $OH^-$ in the structure. Further, the ratio between lead and oxygen was

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found to be 1:2 and the insertion of hydrogen was therefore suggested to be accompanied by the presence of $Pb^{2+}$ and a general formula for lead dioxide was written,

$$Pb_{1-\frac{x}{2}}^{4+}Pb_{\frac{x}{2}}^{2+}O_{2-x}^{2-}(OH)_x^- \qquad (1)$$

which when re-written, highlights the different domains in the structure, where $PbO_2$ forms crystalline domains and $Pb(OH)_2$ is amorphous [3,4].

$$\left(1-\frac{x}{2}\right)PbO_2 \cdot \frac{x}{2}Pb(OH)_2 \qquad (2)$$

Hill and Houchin [7,8] have attributed the differences in the crystal structure of $PbO_x$ to an abundance of hydrogen in the structure. From their structural model they proposed that electrochemically prepared lead dioxide contains at least two different hydrogen configurations, one similar to that in the water molecule and one interstitial, non-water structure. During cycling, i.e., exposure to alternating oxidising and reducing conditions, the amount of the non-water configuration decreased, and this may result in an increased structural order in the $PbO_x$ lattice.

The presence of $Pb^{2+}$ in the lead dioxide structure was challenged because of its size and the chemical formula of lead dioxide is often expressed as a non-stoichiometric oxide

$$PbO_{2-\delta} \cdot mH_2O \qquad (3)$$

where $\delta$ denotes an oxygen deficiency and m the structural water content [9,10]. Oxygen vacancies, interstitial protons or quasi-free electrons have been suggested as explanations to the disorder of $PbO_x$ [11]. Varma et al. [12] explained the deviation from stoichiometry as a structural disorder in the cationic sublattice that was in accordance with the work of Ruetschi [13] whose crystallographic study of lead dioxide also showed the presence of cation vacancies. On the basis of this cation vacancy model, Ruetschi [13] found the structure of the lead dioxide to be more complicated than the simple chemical expression (3).

In the work of Pavlov et al. [14–18] it was suggested that lead dioxide particles, formed from basic lead sulphates, are complex heterogeneous systems composed of crystal zones surrounded by amorphous lead hydroxide. The amorphous zones, which are described as a gel-like substance, consist of hydrated lead dioxide, $Pb(OH)_2$ and the crystal zones consist of $PbO_2$. Further, these investigations show the existence of a dynamic ion exchange process between the crystalline and the amorphous zones of the particles as well as between the lead dioxide particle and the solution. In these investigations, the formation of the positive active material (PAM), starts from basic lead sulphates and as much as 30% of the lead dioxide was claimed to be hydrated and amorphous. The exchange reaction between ions in the electrolyte and PAM was also investigated and discussed in terms of changes in the crystallinity by intercalation [15].

In the present investigation, X-ray diffraction (XRD) was used to study changes in crystallinity and phase transformation of $PbO_2$ as a function of temperature. These experiments were complemented by thermogravimetry analysis (TGA) to follow mass changes due to water loss and phase transition. The results show that sulphate ions are enclosed in the electrochemically formed oxide and are revealed at high temperatures as a lead oxide sulphate phase. Only small amounts of water were detected and were attributed to surface bound water.

## 2. Experimental

### 2.1. Preparation of PbO₂

#### 2.1.1. PbO₂ prepared from lead foil

The lead dioxide was prepared from pure lead foils (99.95%, Good Fellow) according to the Planté formation process described in detail by Petersson et al. [19].

In order to remove lead oxides formed from oxidation of lead in air, the lead foil was washed in 8 M $HNO_3$ (p.a., Merck) and rinsed in deionised milli-Q water before the foil was immersed in the electrolyte solution to start the Planté formation process. The lead foils were initially pretreated cathodically for about 30 min at 1.5 mA cm$^{-2}$ in an electrolyte consisting of 0.5 M $H_2SO_4$ containing 0.05 M $KClO_4$. The electrodes were then oxidised and reduced galvanostatically in the same electrolyte at 10 mA cm$^{-2}$ to desirable thickness, corresponding to the oxidation of 400-, 200- and 100-μm lead foil. After the reduction process, the perchlorate ions were removed from the electrodes by rinsing with deionised milli-Q water, and finally the positive electrodes were completely oxidised to $PbO_2$ in 1 M $H_2SO_4$. After the formation process the electrodes were assembled to 2 V laboratory cells, using a conventional pasted lead electrode (Tudor Nol, Sweden) as counter-electrode, and stabilised by three discharges at 22 mA cm$^{-2}$ in 5 M $H_2SO_4$. After the stabilisation cycling, the electrodes were rinsed with deionised milli-Q water, acetone and dried before the lead dioxide was removed from the foil for further examination.

#### 2.1.2. PbO₂ formed from TBLS, 4PbO · PbSO₄

A paste was prepared by mixing commercial 4PbO · PbSO₄ powder with water and $H_2SO_4$ to give a paste with a density of 4.2 g cm$^{-3}$. The mixture was stirred at 80°C for 1 h, spread over a pure lead grid and cured at 40°C for 72 h [15]. The plate was then electrochemically oxidised to $PbO_2$ in 1 M $H_2SO_4$. After the formation process, the electrode was assembled to a 2 V unit using a commercial pasted lead electrode (Tudor Nol) as counter-electrode, and stabilised by five charge–discharges cycles. After the cycling, the electrode was rinsed with deionised milli-Q water, acetone and dried at 80°C for 1 h before the active material was removed from the grid for further examination.

## 2.2. Characterisation methods

### 2.2.1. X-ray powder diffraction (XRD, HT-XRD)

An X-ray powder diffractometer (Siemens D5000) using CuK$\alpha$ as radiation source and a position sensitive detector (PSD) was used for identification of the different phases. Measurements were made at 0.018° intervals of 2$\theta$ over the range of 15–60° with a count-time of 10 s of each step.

The same diffractometer was used for the high temperature XRD (HT-XRD) measurements, although equipped with a special platinum sample holder. This holder serves as heating device by a computer controlled thermocouple regulating the (elevated) sample temperature. The lead dioxide sample was heated from 25°C to 600°C with a rate of 2°C s$^{-1}$ and with an equilibrium time of 4 min before the diffraction scans were recorded. Scans were taken at 25°C, 50°C, 75°C, 100°C, 120°C, 150°C, 200°C, 250°C, 300°C, 400°C, 500°C and 600°C and 0.4 g of each lead dioxide sample was used.

### 2.2.2. Neutron diffraction

Neutron diffraction was used as a complement to the X-ray powder diffraction measurements to try to discriminate between water present in the pores and water in the structure of the lead dioxide. The neutron diffraction experiments were performed with the medium-resolution neutron powder diffractometer (NPD) situated at the R2 Reactor, Studsvik, Sweden. The wavelength of the neutron beam was 1.47 Å, and the 2$\theta$ range covered was 4.00° to 139.92°, with a step-length of 0.08°.

### 2.2.3. Thermogravimetric analysis

In order to study if there was water present in the sample, TGA was performed. A thermobalance/DTA instrument Setaram TAG 24 s 16 was used to record changes in sample weight as a function of temperature and eventual phase transitions associated with chemical reactions. The lead dioxide sample was heated from 25°C to 600°C with a rate of 0.5°C min$^{-1}$ using both $O_2$ and $N_2$ atmospheres.

## 3. Results and discussion

The existence of an amorphous phase in the positive active mass was put forward by Caulder et al. [1,2] based on both NMR studies and differential thermoanalysis. In a number of studies the difference in the intensity of the diffraction peaks between electrochemically and chemically prepared lead dioxide has been interpreted as the existence of an amorphous phase in the electrochemically formed sample [14–16,18]. However, a difference in intensity is not a sufficient evidence for the existence of an amorphous phase as discussed earlier [20]. By mild heating in vacuum (60°C) for 1–2 h or drying in air for a long period of time (> 24 h), a slight change in the diffraction

signal was observed, indicating that the water trapped in the pores is removed in the drying procedure. In order to study this effect in a systematic way both TGA and XRD were made as a function of temperature. In these experiments the lead dioxide samples were heated from 25°C to 600°C.

### 3.1. X-ray powder diffraction (XRD, HT-XRD)

For the chemically formed $PbO_2$, the diffractogram obtained at room temperature shows only the presence of $\beta$-$PbO_2$, with four main peaks in the 2$\theta$ range investigated (Fig. 1). The diffractogram remains unchanged with increasing temperature up to 300°C. At 400°C, a marked decrease in the $\beta$-$PbO_2$ reflections can be observed together with some new peaks showing the beginning of the phase transformation. The reflections at 28.3°, $\sim$33° and $\sim$47° are in good agreement with the non-stoichiometric lead oxide, $PbO_{1.55}$, and the reflection at 46° is due to platinum from the sample holder. Further heating to 500°C leads to the formation of $Pb_3O_4$ and small amounts of PbO. At 600°C, only PbO is observed, but with the short equilibrium time used in the experiments only a minor part is transformed to the high temperature orthorhombic form. These phase changes are in agreement with common knowledge [21]. Also for $PbO_2$ formed from TBLS, only the $\beta$-phase was observed at room temperature (Fig. 2). The reflections at 39.8° and 46° correspond to platinum from the sample holder. In contrast to the chemically formed $PbO_2$ only a small change in phase composition is observed at 400°C and there is no sign for formation of the non-stoichiometric lead oxide. At 500°C, large amounts of tetragonal PbO is formed together with $Pb_3O_4$. An interesting feature appears at 600°C where a lead oxide sulphate phase, $Pb_5O_4SO_4$ is formed in addition to tetragonal and orthorhombic PbO. Thus, it is quite clear that sulphate ions are retained in the lead dioxide structure after formation.

For the Planté-formed $PbO_2$, a more complex diffraction pattern was observed at room temperature (Fig. 3). Firstly, both $\alpha$- and $\beta$-$PbO_2$ appear in this case [20]; the



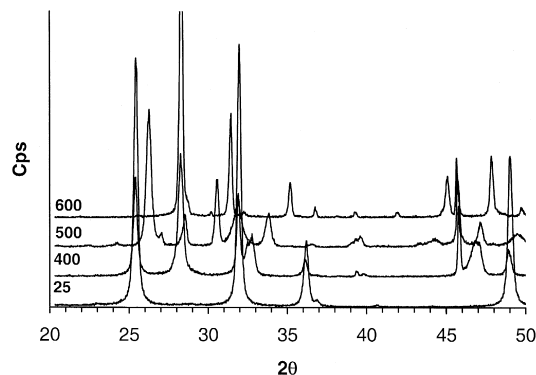Fig. 1. X-ray diffractograms for chemically formed $PbO_2$. The numbers in the figure refer to the temperature given in degrees centigrade (°C).
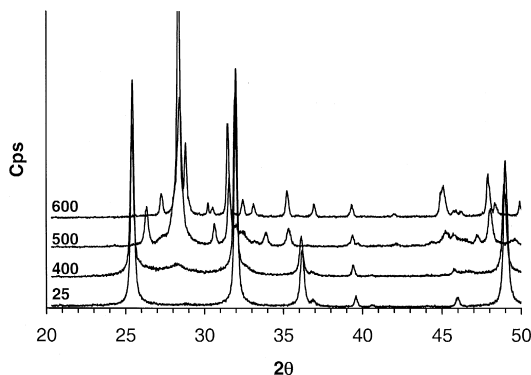
Fig. 2. X-ray diffractograms for PbO$_2$ formed from TBLS. The numbers in the figure refer to the temperature given in degrees centigrade (°C).

characteristic peaks for α-PbO$_2$ are at 28.5° and 34.3°. Secondly, the shoulder noticed at the left side of the β-PbO$_2$ at 25.4° can be attributed to a trace of lead carbonate, for example $2PbCO_3 \cdot PbSO_4 \cdot Pb(OH)_2$. Also, Fourier transform infrared spectroscopy (FTIR) measurements on this sample show the presence of traces of carbonate and sulphate bound in solid phase [22–24]. At 300°C, this phase and α-PbO$_2$ have decomposed to form tetragonal PbO. A non-stoichiometric oxide is partly formed at 400°C, but undergoes further phase changes as the temperature is increased. At 500°C, several phases co-exist, $Pb_3O_4$, $Pb_5O_4SO_4$, tetragonal PbO, and orthorhombic PbO. Finally, at 600°C $Pb_3O_4$ is transformed to PbO in both its modifications. The lead oxide sulphate phase is also stable at this temperature.

The differences in the temperature behaviour of the different samples are related to the existence of sulphate in the lead dioxide structure. The formation process for both TBLS and the Planté-formed lead dioxide takes place in sulphuric acid and it is reasonable that sulphate can be captured in the porous structure. However, even after careful rinsing with water, sulphate is still present within the oxide grains. Sulphate or hydrogen sulphate may be electrostatically bound to the lead dioxide surface, making it difficult to remove by normal rinsing. The final formation process took place in 5 M sulphuric acid and at such a concentration the hydrogen sulphate is prevalent. The surface of the oxide is positively charged by adsorption of protons and this positive charge is counterbalanced by the hydrogen sulphate ions. Thus, together with the sulphate group there will also be some hydrogen in the oxide. It has been assumed that sulphuric acid adsorption increases the amorphisation of the lead dioxide particles [14].

In the Planté-produced lead dioxide, more sulphate is retained in the structure. This can be attributed, on the one hand, to the presence of a lead carbonate sulphate phase and on the other hand to the larger surface area of the lead dioxide formed by this procedure. An examination of the XRD spectra showed that the peak widths for chemically formed lead dioxide and lead dioxide formed from TBLS

are approximately the same while the peak width for the lead dioxide formed from a lead foil was nearly twice as large. This indicates that the grain size is smaller for the electrochemically formed lead dioxide and part of the material may be X-ray amorphous, i.e., the grain size is beyond Bragg's limits so that no clear reflection pattern can be obtained.

In order to compare the different samples two quantification procedures were tested. Firstly, the intensity of the diffraction peaks was measured as a function of the sample weight. However, no correlation between the sample weight and the intensity of the peaks was obtained. Secondly, 10 wt.% Si was added as an internal standard. Also in this case quantification failed, probably due to a "matrix effect". When the X-ray beam reaches the sample, it will penetrate a less dense sample deeper than a denser one. The experiments show that the intensity of the silicon peak differed between the samples and from a weighing of the three samples it was noticed that the lead dioxide originating from the lead foil was much denser than the two other samples. However, although the X-ray beam penetrates a smaller distance in the denser sample the peak intensity for silicon was higher, indicating that the silicon particles accumulates on top of the more easily packed sample.

For the three different materials used in the present investigation, no changes in the diffractograms were noticed up to a temperature of 300–400°C, where the phase transformation starts. This strongly indicates that also the electrochemically produced lead dioxide is crystalline in nature. This is in agreement with some earlier studies, where annealing at different temperatures up to 200°C was not found to change the diffractogram [4]. In contrast to this, Pavlov et al. [14–16,18] claimed the existence of an amorphous phase by comparing the intensity of the diffraction peaks for chemically and electrochemically prepared PbO$_2$. One of the samples used in the present study was prepared from TBLS according to the description by Pavlov and Balkanov [15]. Only minor changes in the intensity of the diffraction peaks were observed, compared to the
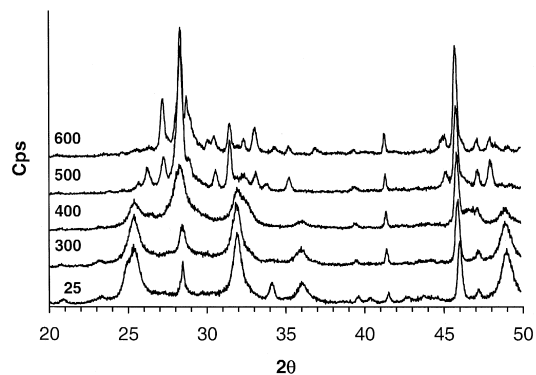


Fig. 3. X-ray diffractograms for PbO$_2$ prepared from lead foil. The numbers in the figure refer to the temperature given in degrees centigrade (°C).

chemically prepared sample. However, for the Planté-formed sample a large decrease in the intensities was observed, accompanied by a broadening of the peaks, which show that the size of the crystallites is smaller.

## 3.2. Thermogravimetric analysis

A thermobalance was used to measure the weight loss as a function of temperature. In contrast to earlier findings [1,2,5,6], no accentuated peaks were observed in the diagram before the phase transformation started. However, in the quoted references a lead–antimony grid was used for the positive electrode. It is well known that antimony will be present in the positive mass as a hydrated oxide and the amount of water in the oxide increases with increasing antimony content of the alloy [25]. For pure lead approximately 10% water was observed in agreement with our results, while for a Pb 20% Sb alloy, as much as 30% hydration was found [25].

A small decrease in the sample weight was, however, observed at temperatures up to 200°C. By assuming that this weight loss is due to loss of water, the amount of water in the material can be estimated. The mole fraction of water found for the chemically prepared $PbO_2$ was 8.8%, while for electrochemically prepared samples (Planté formation), value between 11% and 16% were obtained. The same values were obtained in both $O_2$ and $N_2$ atmospheres. The similarities between the chemically and electrochemically formed samples with respect to the water content show that water is bound to the surface. The smaller crystal grains and hence larger surface area of the electrochemically formed sample may cause the somewhat larger content of water in this material.

## 3.3. Neutron diffraction

In order to discriminate between water trapped in the pores and water bound in the structure of the lead dioxide, neutron diffraction measurements were done. A comparison between the chemically prepared lead dioxide and the electrochemically prepared sample originating from pure lead show the same general features as observed in XRD, i.e., smaller peak heights and broader peaks for the electrochemically formed sample. Another difference between the two samples is the level of the background. The background of the electrochemical sample is larger indicating a higher degree of bound hydrogen in the structure or a larger amount of amorphous material.

Neutron powder diffraction has previously been used to correlate electrochemical activity to differences in lattice parameters between differently prepared lead dioxides [4]. The changes in the lattice parameters of electrochemically active $\beta$-$PbO_2$ compared to the inactive chemically prepared samples were attributed to the presence of $OH^-$ in the structure. Further, the ratio between lead and oxygen was found to be 1:2 and the insertion of hydrogen was

therefore suggested to be accompanied by the presence of $Pb^{2+}$, which resulted in the formulation of the lead dioxide phase according to Eqs. (1) and (2). It should be possible to verify the existence of $OH^-$ groups by FTIR measurements and therefore spectra were recorded for the three different lead dioxide samples. A metal bound hydroxide group has a typical stretching vibration in the range of 3700–3500 $cm^{-1}$, independent of the nature of the metal ion [26]. For chemisorbed $OH^-$ groups, even higher wave numbers are observed and in both cases very sharp peaks generally appear. However, our FTIR measurements only show a broad band at 3400 $cm^{-1}$ and a small band at 1640 $cm^{-1}$, which can attributed to vibrations of chemisorbed and physisorbed water, respectively [24]. Thus, the presence of hydroxide in the structure could not be verified. Since the bands at 3400 and 1640 $cm^{-1}$ are present in all of the lead dioxides investigated, it can be concluded that the water molecules are mostly chemisorbed. Further, in the TGA, a small continuous decrease in the weight is found on heating to 200°C, which can be assigned to loss of chemisorbed water. The absence of lead hydroxide is also in accordance with the XRD results. In air, lead hydroxide dehydrates in the temperature interval 130°C to 145°C to form the monoxide [27], but we observed no formation of PbO at these temperatures.

## 3.4. Surface-bound sulphate ions

When a metal oxide is exposed to water, surface hydroxyl groups are formed by dissociative adsorption of water molecules and the surface will exhibit acid–base properties. In general, the understanding of the acid–base behaviour is based on the combination of a site-binding model including electrostatic interactions relating the concentration of hydrogen ions in the solution to its local concentration in an electric field [28]. Thus positively, neutral and negatively charged surface sites are present dependent on pH of the solution. No information on the electrokinetic or acid–base properties of $PbO_2$ has been found in the literature, but for the structurally related $TiO_2$, the point of zero charge is located between 5 and 6 [29]. In the strongly acidic solution used in the formation process (5 M $H_2SO_4$), the surface of lead dioxide will be positively charged and must be counterbalanced by negatively charged anions from solution. Anions can form different types of surface complexes but commonly the anion is bound to the oxide surface by an ion-exchange reaction yielding an inner sphere complex, as illustrated for a tentative reaction involving $PbO_2$.

$$\equiv \overset{IV}{Pb}\,OH° + OSO_3H^- + H^+ \rightleftharpoons \equiv \overset{IV}{Pb} - OSO_3H + H_2O$$

$$(4)$$
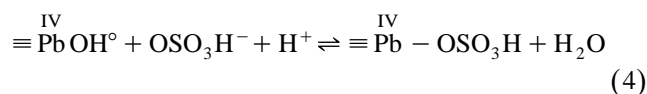
This reaction takes place at the surface. Since the electrochemical path involves the formation of lead sulphate as an intermediate stage, some of the sulphate will be trapped in the lead dioxide structure by adsorption. It

should be noted that lead sulphate is not present in the samples from the beginning and thus the sulphate ions are trapped in the structure without chemical reactions. When the lead dioxide is reduced, by increasing the temperature, the trapped sulphate ions react to form a basic lead sulphate.

The presence of sulphate ions in the lead dioxide phase is interesting since these ions readily can participate in the reduction reaction without previous diffusion. It is well known that the activity of electrochemically formed $PbO_2$ is large compared to the chemically prepared oxide. This has mainly been attributed to hydration of the electrochemically formed material and to the presence of an amorphous phase [1–3,5–9,13–18,25] but in an early study [30] also the importance of adsorbed sulphuric acid was reported. The results obtained in the present investigation indicate that the presence of surface bound sulphate ions may be important for the electrochemical activity. The fact that hydrogen disappears from the lead dioxide upon cycling may be accompanied with the formation of an electrochemically inactive lead sulphate.

## 4. Conclusions

· From the TG experiments, it was concluded that only surface bound water was present in the three differently prepared lead dioxide samples investigated.

· HT-XRD shows a clear difference between chemically and electrochemically formed samples. In the latter samples, a lead oxide sulphate phase was observed together with PbO, while in the chemically formed sample only PbO was detected.

· These results are discussed in terms of a surface bound sulphate ion, which might be important for the discharge reaction, explaining the difference in electrochemical activity between chemically and electrochemically formed oxide.

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