

Parameters influencing the ratio between electrochemically formed α - and β -PbO₂

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Abstract

The interparticle contact is an important aspect for the capacity of all lead dioxide electrodes. It can be discussed with respect to the ratio of the two lead dioxide phases, α - and β -PbO₂. Of the two phases the α -PbO₂ has a more compact structure compared to the more porous β -PbO₂, resulting in a better contact between the particles. It has previously been shown that different perchlorate salts have an influence on the discharge properties, the self discharge and the active surface area of formed PbO₂. The results were attributed to crystal structure defects caused by the cations and it was suggested that different cations may influence the ratio between α - and β -PbO₂ resulting in different discharge properties. In the present study, structural changes of electrochemically formed lead dioxide were studied as a function of formation time, current, porosity, interparticle contact, and electrolyte cation by X-ray powder diffraction and scanning electron microscopy (SEM). Three different electrode thicknesses 100, 200 and 400 μ m were investigated at two current densities and with four perchlorate salts, KClO₄, NaClO₄, LiClO₄ and HClO₄. The initial results indicate that the ratio of $\alpha/(\alpha + \beta)$ increased when a larger cation was used in the order H⁺ < Li⁺ < Na⁺ < K⁺. The ratio of lead sulfate PbSO₄/ $(\alpha + \beta)$ in the sample seems to decrease both with a decreased cation and with an increased electrode thickness. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

In the well established Planté formation process, the active materials for the lead-acid battery, lead dioxide and porous lead, are created by electrochemical oxidation and reduction of pure lead in diluted sulfuric acid containing potassium perchlorate as a forming agent. In Planté's original process repetitive cycles of oxidation and reduction in pure sulfuric acid created the active material [1]. The addition of a forming agent in the electrolyte accelerated the process by eliminating the risk of a passivating lead sulfate layer to be built up. Much of the work concerning the Planté formation process has therefore been focused on the role of the perchlorate ion in the reaction [2–4]. Very little attention has been paid to the effect of perchlorate salt used in the process. However, in the work by Ahlberg et al. different discharge properties of the

Planté-formed PbO₂ were observed depending on which perchlorate salt was used [5]. Discharge capacity, active surface area and self discharge was found to increase when a perchlorate salt with a smaller cation was used in the order H⁺ > Li⁺ > Na⁺ > K⁺. The results were attributed to defects in the crystal structure caused by the different cations. Since electrochemically formed lead dioxide is nonstoichiometric [6] it seems likely that different cations may be incorporated in the structure causing an impurity effect which in turn stabilized the growth of a particular phase (the α -PbO₂) resulting in different discharge properties [5].

For battery applications it is important to produce lead dioxide with a high discharge capacity and a good ability to collect current. In addition, the contact between the active material and the current collector is an important aspect for the capacity of the battery. These phenomena can be discussed in terms of interparticle contact and porosity. Of the two different lead dioxide phases, i.e., the α - and the β -PbO₂, the former has a more compact structure than β -PbO₂, which results in better contact

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between the particles. The more compact structure makes the α -PbO₂ more difficult to discharge compared to the β -PbO₂ [1]. However, results from the work by Rüetschi showed that when comparing material of equal surface area under conditions of equal acid access, α -PbO₂ showed a higher discharge capacity than β -PbO₂ [6]. Since the size of different cations in the perchlorate-assisted formation of PbO₂ may influence the ratio between α - and β -PbO₂ as suggested earlier [5], it is interesting to investigate how different cations influence the structure of electrochemically prepared lead dioxide.

Planté formation has been proved to be useful in the manufacturing process of thin, semi-bipolar electrodes [7]. By using electrochemical methods to create the semi-bipolar electrodes, the unhealthy handling of lead oxides was eliminated and the electrodes were produced by techniques well known in the electroplating industry.

The main purpose of this work was to study the effects of different perchlorate salts in the Planté formation process, with special attention to the α/β -PbO₂ ratio and porosity to find correlations between different cations and properties of the lead dioxide. The effects of different cations were studied by X-ray diffraction (XRD), scanning electron microscopy (SEM), and BET.

2. Experimental

2.1. Preparation of lead dioxide

The lead dioxide was prepared from pure lead foils (99.95%, Good Fellow) which were converted to active material, i.e., lead dioxide, according to the Planté formation process described in detail by I. Petersson et al. [7].

Immediately prior to an experiment the lead foil was washed in 8 M HNO₃ (p.a., MERCK) and rinsed in deionized milli-Q water. This was done in order to remove oxides formed by contact with air before the foil was immersed in the electrolyte solution to start the Planté formation process. The lead foils were pretreated cathodically for about 30 min at 1.5 mA cm⁻² in an electrolyte consisting of 0.5 M H₂SO₄ and 0.05 M XClO₄ (X = H, Li, Na, K). The electrodes were then oxidized and reduced galvanostatically in the same electrolyte at 10 mA cm⁻² to desired thickness (400, 200, 100 μ m). After the reduction process, the perchlorate ions were removed from the electrodes by rinsing with deionized milli-Q water, and finally the positive electrodes were completely oxidized to PbO₂ in 1 M H₂SO₄. After the formation process, the electrodes were dried before the lead dioxide was removed and kept in an oxygen-free environment until use. The equipment for the Planté formation process consisted of a microprocessor-controlled unit, a power supply, and a multimeter, and it was designed to send alternate anodic and cathodic currents through the cells. The time and the current density for each step in the process could be adjusted manually.

2.2. X-ray powder diffraction (XRD)

A powder X-ray diffractometer SIEMENS (D5000) using CuK α as radiation source was used for identification of the phases. Measurements were made at 0.019° intervals of 2 θ over the range 15–65° with a count-time of 8 s at each step. If necessary, large grains or flakes in the lead dioxide powder were ground before identification.

2.3. Scanning electron microscopy (SEM)

To keep the original structure of the porous lead dioxide electrodes for the SEM study, the electrodes were rinsed, dried, and vacuum-impregnated in epoxy resin before a cross section could be made. The epoxy binds the porous lead dioxide in its original positions during the investigation. After about 24 h a cross section was made and polished before the morphology of the lead dioxide electrode was characterized by scanning electron microscopy (JEOL JSM-5300).

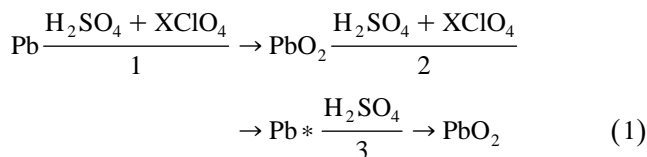
2.4. Specific surface area (BET)

The internal specific surface area (BET) was determined by measuring the low-temperature nitrogen adsorption using a FlowSorb II 2300 (Micromeritics).

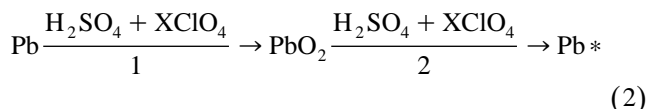
The lead dioxide powder used in the BET study was used directly without any pretreatment.

3. Results and discussion

The Planté formation process as used in the present work can be described by the following sequences for the positive electrode,



and for the negative electrode,



where X = K⁺, Na⁺, Li⁺ and H⁺, and Pb* = spongy lead.

In this study the effects of the four different cations, i.e., K⁺, Na⁺, Li⁺ and H⁺ were investigated in the perchlorate assisted formation of lead dioxide. Previously it was suggested that different cations influence the structure of electrochemically formed lead dioxide [5], but no structural evidence was given. In the present study, X-ray

diffraction was used to determine changes in the ratio between α - and β - PbO_2 as a function of charging current (layer thickness), charging time, porosity, and electrolyte cation.

Samples of lead dioxide were removed following step 1 and 3 in sequence (1) and (2) in the Planté formation process because i) the structure of the lead dioxide is altered during cycling and ii) any formed α - PbO_2 is converted to β - PbO_2 during this process [1,8]. The original Planté formation process was performed in pure sulfuric acid with a current density of $1\text{--}3 \text{ mA cm}^{-2}$ and at a temperature of $16 \pm 1^\circ\text{C}$ [1]. The process was further developed by adding a forming agent to the electrolyte which eliminated the risk of forming a passivating lead sulfate layer. However, to increase the rate of this rather time consuming process and make it interesting from a manufacturing point of view Berghult et al. increased the current density to 10 mA cm^{-2} and performed the experiment at room temperature [9]. The results from this study showed that even with a high current density, a uniform formation was sustained. This was confirmed in the present study by SEM investigations. In Fig. 1a a cross-section

of a $400 \mu\text{m}$ thick, fully Planté formed electrode, with sodium as a cation, can be seen. The electrode has a structure of acicular crystals of lead dioxide (grey) and the spacing of the crystals (black) permits unimpeded circulation of electrolyte through the electrode structure. Also, as can be seen from this figure, the formed lead dioxide layer is uniformly distributed over the electrode. The important contact between the underlying lead foil (white) and the porous lead dioxide layer (grey) is tight which also can be seen in Fig. 1b. Three different electrode thicknesses, 100, 200 and $400 \mu\text{m}$, were investigated to study the effects of formation conditions and porosity on the lead dioxide phases. To obtain the different thicknesses the same current density was used while the formation time was changed. The weight change of the electrodes before and after each formation was used to determine the current utilization. The results from this gravimetric measurement showed that the formation process was performed with almost 100% conversion for all the four cations. Thus, the thicknesses 100, 200 and $400 \mu\text{m}$, which are referred to throughout the text, corresponds to the conversion of 100, 200 and $400 \mu\text{m}$ of the lead foil, respectively.

3.1. X-ray powder diffraction

The α - and β - PbO_2 phases were identified in the samples by X-ray powder diffraction. Recently the positive lead dioxide active mass (PAM) has been treated as a gel-crystal system composed by crystal zones surrounded by amorphous lead hydroxide [10–13]. In these investigations the formation of the PAM starts from basic lead sulfates 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 [11]. In the present work the lead dioxide originates instead from pure lead according to the procedure described earlier in this paper. The crystallinity of this oxide was tested by comparing its X-ray spectra with that of chemically formed β - PbO_2 (p.a., MERCK). The intensity of the diffraction peaks for the electrochemically formed lead dioxide was found to be lower compared to those for the chemically formed β - PbO_2 , in agreement with earlier findings [10–13]. However, a difference in intensity is not a sufficient evidence for the existence of an amorphous phase. The same effect can be obtained if water is trapped in the porous lead dioxide structure. Samples were therefore dried by different procedures. By mild heating in vacuum (50°C) for 1–2 h or by drying in air for long time ($> 24 \text{ h}$) the contribution from the apparent amorphous phase diminishes. This indicates that water trapped in the pores are removed in the drying procedure.

Neutron diffraction was also used to try to discriminate between water in the pores and water in the structure of the lead dioxide. Hill [8] and Hill and Houchin [14] have proposed that electrochemically prepared lead dioxide con-

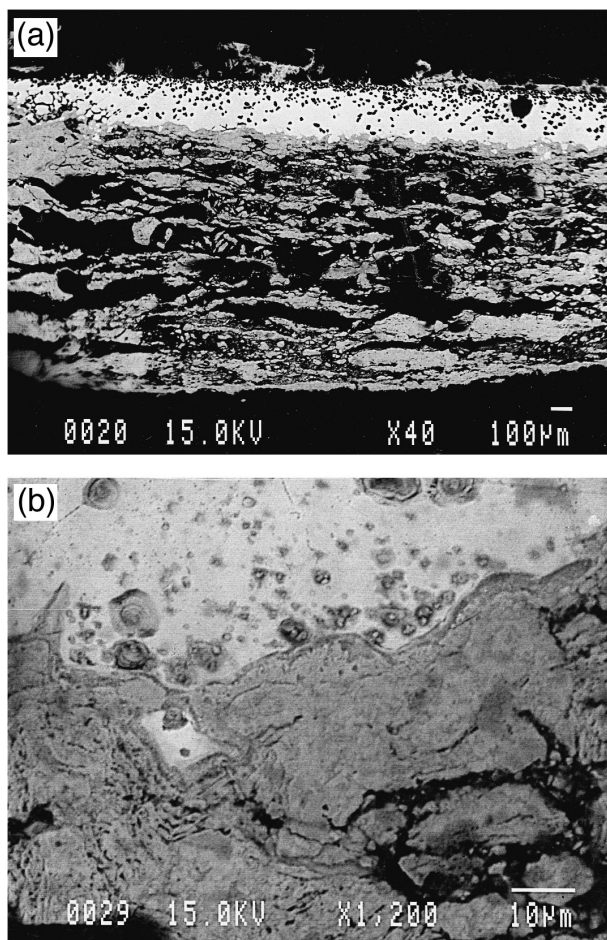


Fig. 1. (a) Cross section of a $400 \mu\text{m}$ thick Planté formed electrode with potassium as cation. (b) Enlargement of the interphase between lead and lead dioxide in the electrode.

tains at least two different hydrogen configurations, one similar to that in the water molecule and one interstitial, non-water structure. However, not even in this case a discrimination was possible. Examination of the X-ray diffraction spectra show that the peak widths are larger for the electrochemically formed lead dioxide compared to the chemically formed β -PbO₂. 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. The two samples were therefore also examined by SEM and a clear difference in the appearance was observed. The chemically formed β -PbO₂ had a more homogeneous structure compared to the electrochemically formed oxide, which contained crystals of varying size.

From these different analyses it was not possible to prove or disprove the existence of an amorphous phase and in the present investigation we have treated the electrochemically formed lead dioxide as crystalline. Though a quantitative determination of each phase was not possible, a semi-quantitative treatment was made by comparison of the ratio of the peak area between the different phases in each sample. The peak area was determined using integration of the peaks when corrected for background. When comparing the ratio of the different lead dioxide phases the amount of the particular phase was related to the total amount of lead dioxide in the sample, $\alpha/(\alpha + \beta)$ and $\beta/(\alpha + \beta)$. Also the amount of lead sulfate in the sample was related to the total amount of oxides, $\text{PbSO}_4/(\alpha + \beta)$. When discussing the ratio of PbSO_4 in these reactions it is important to consider the charging of the electrodes. An increase in the $\text{PbSO}_4/(\alpha + \beta)$ ratio is likely to be an

effect of an inefficient formation process, so conclusions about this ratio should be drawn with caution. Fig. 2 shows two spectra, one with the two lead dioxide modifications, α and β , and a minor lead sulfate peak, and the other one when a larger ratio of lead sulfate is present in the sample. The peaks at 28.6 and 47.5° (α -PbO₂), 32.6 and 49° (for β -PbO₂) and 26.7 and 43.7 (PbSO₄) were used for integration of the respective phase. By this method some very general conclusions about the trends in the ratio between the different phases could be gained. The perchlorate-assisted PbO₂ formation was characterized by X-ray powder diffraction following the completion of step 1 and 3 in sequence 1 and also after a repetitive cycle of step 1, i.e., three oxidations instead of one.

3.2. α -PbO₂

Following the first oxidation step, i.e., step 1 in sequence (1), with a current density of 10 mA cm⁻² the ratio of $\alpha/(\alpha + \beta)$ increased when a larger cation was used in the order $\text{H}^+ < \text{Li}^+ < \text{Na}^+ < \text{K}^+$ for both the 200 and the 400 μm electrode, Fig. 3. However, for the 100 μm electrode this trend was broken after sodium, and with potassium perchlorate the ratio between α - and β -PbO₂ was slightly less than for sodium perchlorate, Fig. 3. A larger cation refers to the anhydrous ionic radii which indicates that the cation is either built in the oxide structure or strongly adsorbed, losing its hydration shell. The same relationship between the two lead dioxide phases was found when the current density was changed to 3 mA cm⁻². However, a reduction of the current density involves a longer formation time and this results in an increase of the ratio between α - and β -PbO₂ compared to

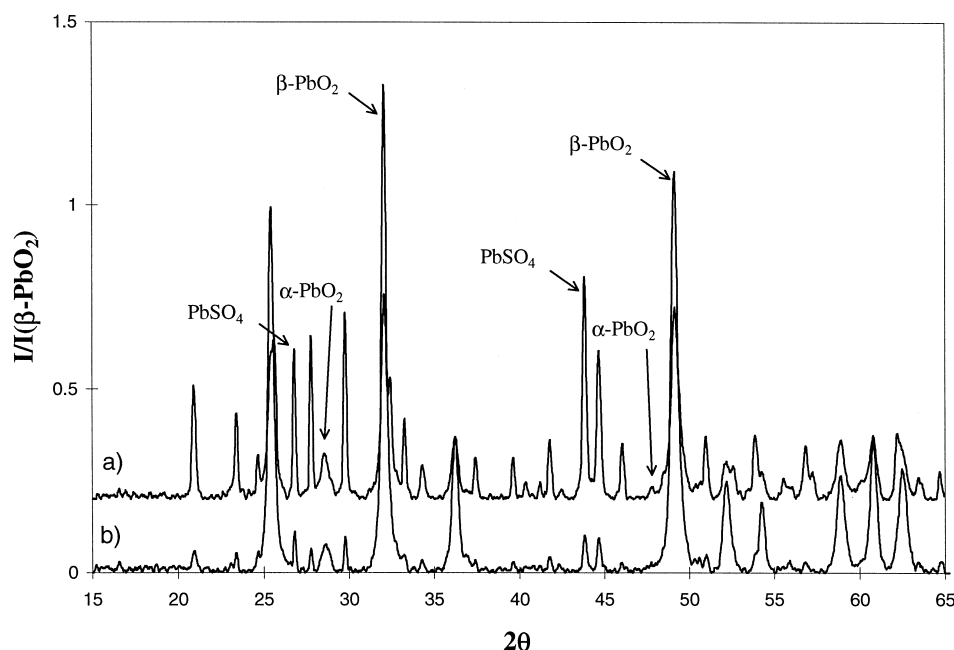


Fig. 2. X-ray powder diffraction, using CuK α radiation, of the two different lead dioxide phases, α - and β -PbO₂, and lead sulphate.

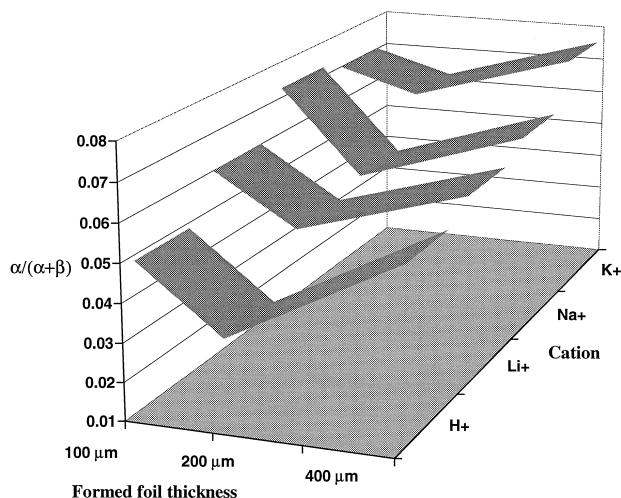


Fig. 3. The ratio of $\alpha/(\alpha + \beta)$ -PbO₂ for the three different electrode thicknesses and for the four different electrolyte actions, following the first oxidation step. Current density 10 mA cm⁻².

the earlier experiment with 10 mA cm⁻², Fig. 4. A possible explanation is that a longer time with lower charging current favors the solid-state oxidation by allowing for mass transfer. Thus a larger amount of α -PbO₂ is formed in the first step with a lower current density.

When oxidation steps 1 and 2 in sequence (1) were repeated three times in the same electrolyte with a higher current density the ratio of α - to β -PbO₂ increased with the size of the cation for all the three thicknesses, Fig. 5. Even in these experiments the effect of a longer formation time was seen and the $\alpha/(\alpha + \beta)$ -PbO₂ ratio increased with a longer formation time, i.e., with a thicker electrode.

Following step 3, i.e., after the complete Planté formation, the α -PbO₂ content increased for the three electrodes

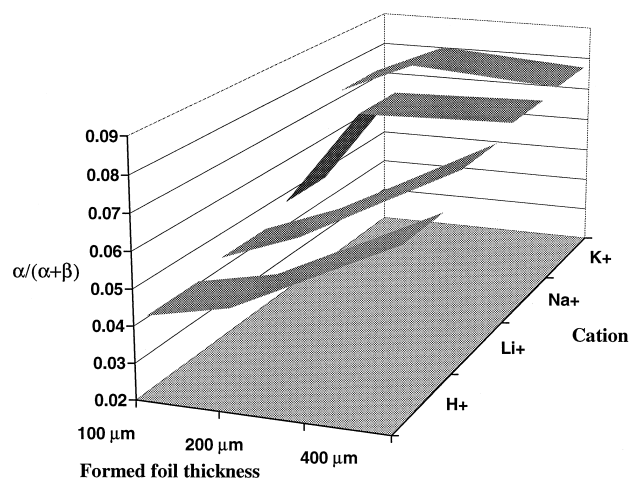


Fig. 5. The ratio of $\alpha/(\alpha + \beta)$ -PbO₂ for the three different electrode thicknesses and for the four different electrolyte actions, after repetitive cycling of steps 1 and 2 in sequence (1). Current density 10 mA cm⁻².

with the size of the cation up to sodium, while for potassium a smaller peak area ratio was obtained, Fig. 6. This was similar to the results found for the 100 μ m electrode following oxidation step 1. When the electrode thickness was reduced from 400 to 100 μ m, i.e., when the electrodes were formed for a shorter period of time, the ratio of α - to β -PbO₂ increased, the reverse of what was found following the three oxidations of steps 1 and 2.

3.3. β -PbO₂

Since β -PbO₂ is dominating, the ratio $\alpha/(\alpha + \beta)$ is in all cases < 0.1 , i.e., the error in the ratio $\beta/(\beta + \alpha)$ is normally larger than the changes. A few exceptions were

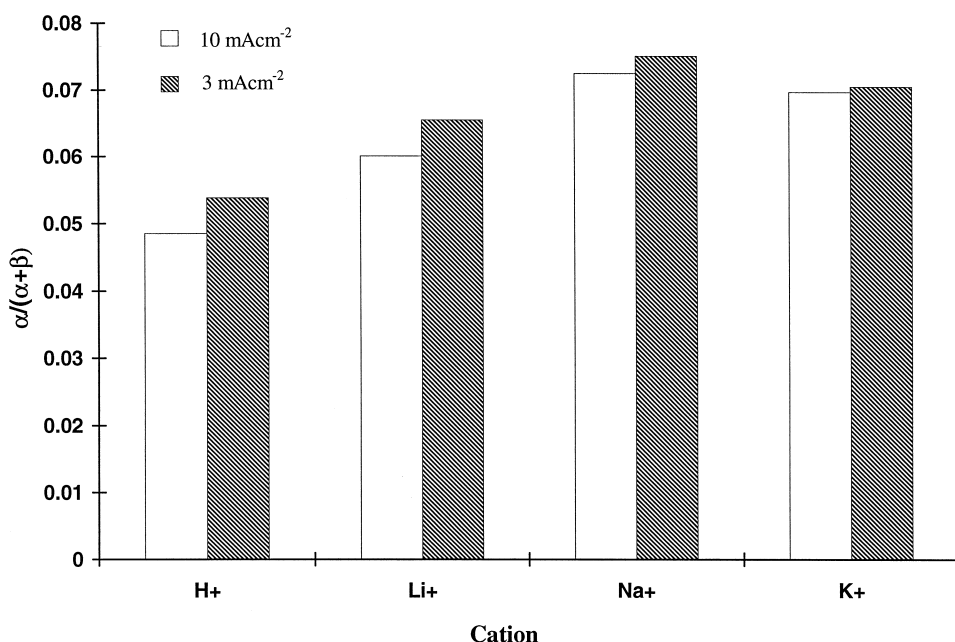


Fig. 4. A comparison between two different current densities 3 and 10 mA cm⁻² for a 100 μ m electrode following oxidation step (1).

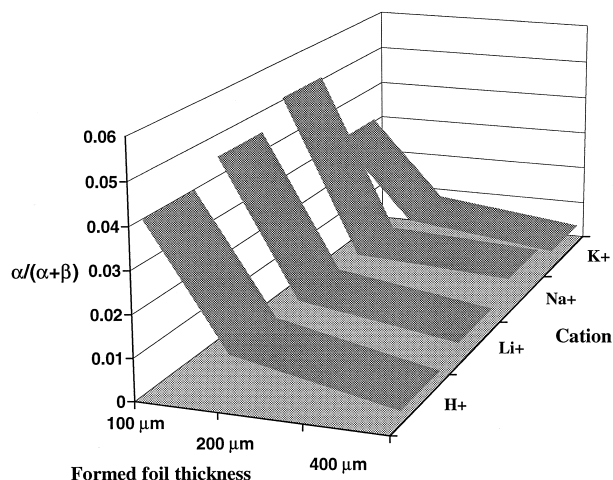


Fig. 6. The ratio of $\alpha/(\alpha + \beta)$ -PbO₂ for the three different electrode thicknesses and for the four different electrolyte actions, following the complete formation with a current density of 10 mA cm⁻².

noted. A lower content of β -PbO₂ was found following the complete Planté formation for the 100 μm electrode. The same effect was seen for the 200 μm electrode, however not as clear as in the 100 μm case.

3.4. PbSO₄

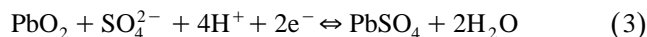
The ratio of lead sulfate, i.e., PbSO₄/($\alpha + \beta$), seems to decrease both with a decreased cation size and with an increased electrode thickness. For the 100 μm electrodes the ratio of PbSO₄/($\alpha + \beta$) was higher and, just like the β -PbO₂ case, this effect was most pronounced following reaction 3. This can be explained by considering the porosity of the layers. The porosity of the oxide increases with the thickness and thus electrolyte can have access to a much larger area of the electrode. This will facilitate the oxidation to β -PbO₂. Using the compact density technique a porosity measurement of the three electrode thicknesses (100, 200 and 400 μm) was made with potassium as a cation. The measurement showed an increase in porosity with increasing layer thickness and the value of the porosity was about 14% for 100, 19% for 200 and 27% for the 400 μm electrode [7].

Three different parameters that influence the results are considered in the discussion.

3.5. Current–time

At small current densities, i.e., slow reaction rate, no other reactions than formation of lead dioxide occurs. A long formation time also allows for slower processes to take place, i.e., enables the species to find the most suitable positions in the structure. The oxide layer has time to ‘relax’ and reach the equilibrium state, resulting in a dense and stable layer. When the reaction rate is increased

and the formation time reduced, more tension and disorder are likely to be found in the oxide layer, and one would expect that this change favors the formation of α -PbO₂. However, initially the opposite was found experimentally, as shown in Fig. 4, which indicates that other factors are of more importance. At high current densities, O₂ may be formed initially by a side reaction. The formed oxygen may cause cracks in the oxide structure and this in turn will result in a more porous oxide structure, especially close to the surface. Also the passivation reaction (3),



depends on the current density and becomes faster when the current density increases. As soon as a passivating PbSO₄-layer is formed on the surface it plugs the pores and prevents further reaction, leaving an unreduced core of PbO₂. As the current density is increased the passivation reaction becomes faster due to the formation of much smaller PbSO₄ crystals, resulting in a higher degree of coverage [15].

3.6. Porosity–interparticle contact

Porous oxides have a higher content of β -PbO₂, while a more dense oxide has a higher α -PbO₂ content. Depending on the method used for preparation of the lead dioxide the initial ratio of α - and β -PbO₂ in a sample will vary [16]. Discharge capacity and porosity of the lead dioxide electrodes is often discussed with respect to the ratio of the two lead dioxide phases, α - and β -PbO₂, in the electrodes. In these electrodes the β -PbO₂ is the major phase, even in electrochemically prepared lead dioxide, and if any α -PbO₂ is present it is usually irreversibly converted to β -PbO₂ during cycling [8]. The conversion of (vacancy rich) α -PbO₂ to (vacancy free) β -PbO₂ will result in an increase in crystallite size. An increase in crystallite size, as influenced by the charge and discharge rate, results in a loss of interparticle contact, and this is a problem since this contact is essential for good electrode performance [7,17,18]. Recently it was shown that interparticle contact is more important than porosity as the capacity limiting effect [7]. The less porous the active material, the better is the chance for good interparticle contact and a thinner, less porous electrode has a higher discharge capacity than a thicker, more porous electrode. Imperfections in the contact pattern between the particles may result in difficulties for electron movement, necessary for discharging. The increase in discharge capacity may be attributed to a higher content of α -PbO₂ in the thinner electrodes compared to a thicker and more porous electrode. In the present study the amount of α -PbO₂ increased with the size of the cation, but also with the thickness of the sample in step (1). However, after completion of the formation, step (3), the amount of α -PbO₂ decreased with the thickness. In the first formation step, lead dioxide is formed directly from the lead foil, which means that the 400 μm

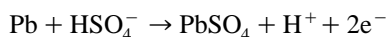
electrode has 4 times as long formation time as the 100 μm . During the formation, the electrolyte is consumed, further reaction is limited by pore diffusion, and there is a pH increase close to the active material. It has been shown that the basic environment stabilizes the $\alpha\text{-PbO}_2$ [19]. Thus, a longer formation time favors the build up of the basic environment and thereby the formation of $\alpha\text{-PbO}_2$. During cycling, $\alpha\text{-PbO}_2$ is converted to $\beta\text{-PbO}_2$ [1,8] and this process is facilitated by the access of electrolyte. The electrolyte can penetrate the more porous 400 μm electrode to a greater extent than the less porous 100 μm , favoring the oxidation of $\beta\text{-PbO}_2$ in the thicker electrodes.

3.7. Electrolyte cation

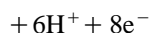
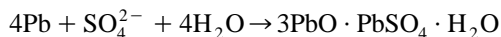
In a previous paper the influence of different cations on the discharge capacity, self discharge and active surface area was clearly shown and it was suggested that the ratio between α - and $\beta\text{-PbO}_2$ was decisive for the performance [5]. It was further shown that the correlation was related to the radii of the anhydrous cations, which means that the cations are either incorporated in the oxide structure or strongly adsorbed. The effect remains in pure sulphuric acid solution after reduction to Pb and reoxidation to PbO_2 . This indicates that the topography of the formed layer has large impact on the properties.

In the present paper it is shown that the α - to $\beta\text{-PbO}_2$ ratio increases with increasing cation radius, keeping other parameters constant. In order to discuss the effect of cations on the oxidation of Pb, the reaction mechanism has to be considered. Recently a new potential-pH diagram for anodic films on Pb in sulphuric acid was evaluated, where the activity of different species was taken into account [20]. The overall reaction mechanism can be written:

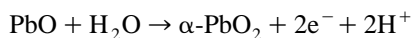
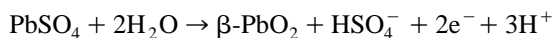
Initial oxidation



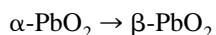
Film growth



Further oxidation



Further reaction



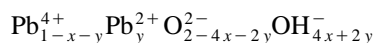
Lead sulphate passivates the lead surface and further oxidation of lead takes place by transport of SO_4^{2-} -ions

through the lead sulphate layer. A potential gradient is created and, in order to retain electroneutrality in the growing layer, hydrogen ions are transported to the bulk electrolyte. In consequence, the pH in the inner part of the layer will increase and stable basic lead sulphate and lead monoxide will be formed [20]. The existence of lead monoxide has for example been proved by photoelectrochemical measurements [21–25]. Further oxidation of lead monoxide and basic lead sulphates results in the formation of $\alpha\text{-PbO}_2$, while $\beta\text{-PbO}_2$ is formed by oxidation of lead sulphate and by conversion of the unstable α -modification. In the presence of perchlorate ions, active dissolution of lead takes place in the form of localized corrosion [26].

In the alkaline environment at the metal/oxide interface the oxide is negatively charged and it is reasonable to believe that cations adsorb on the oxide surface and influence the oxide growth or eventually become incorporated in the structure. It has been shown that the lead sulphate layer is only partly permeable to K^+ [27], thus preventing the cation to migrate to the bulk electrolyte. This probably holds also for Li^+ and Na^+ since the hydrated radii of these actions have similar size. However, the increasing ratio between α - and $\beta\text{-PbO}_2$ in the order $\text{H}^+ < \text{Li}^+ < \text{Na}^+ < \text{K}^+$ might reflect the ability to migrate through the lead sulphate layer. Other factors that might influence the α - to $\beta\text{-PbO}_2$ ratio are the adsorption and the ability to become incorporated in the crystal structure.

3.8. Incorporation in the structure

Lead dioxide has often been expressed as a nonstoichiometric oxide with the general formula $\text{PbO}_{2-\delta} \cdot m\text{H}_2\text{O}$, where δ denotes an oxygen deficiency and m the structural water content [1,17]. Oxygen vacancies, interstitial protons of quasi-free electrons have been suggested as responsible for the disorder in $\text{PbO}_{2-\delta}$ [28]. However, Varma et al. explained the deviation from stoichiometry as a structural disorder of the cationic sublattice [29]. According to the proposed structure of the defective lead dioxide [6], cation vacancies were suggested:



where x is the cation vacancy fraction and y is the fraction of Pb^{2+} ions present with respect to the total number of cationic sites. In the highly defective $\alpha\text{-PbO}_2$ it is possible that instead of Pb^{2+} , other actions can be incorporated in the lattice and influence the stability.

3.9. Adsorption

Adsorption of cations might influence the growth rate and thereby the crystal size. This behavior is well known in the formation of zirconium dioxide from alkaline solutions. In the presence of sodium ions, the growth rate is lowered and the tetragonal modification is stabilized by the formation of small crystallites [30]. In the present case the

effect of the cation is retained even after reduction to lead and subsequent oxidation in sulphuric acid. This strongly indicates that the topography of the lead layer is decisive for the discharge properties.

4. Conclusions

- The amount of α -PbO₂ in perchlorate-assisted formation of PbO₂ was found to depend on the formation current, the thickness of the layer and the cation of the perchlorate salt.

- The α - to β -PbO₂ ratio increased with lower formation current and with increasing size of the cation ($H^+ < Li^+ < Na^+ < K^+$). These results are discussed in relation to the reaction mechanism of the lead oxidation in sulphuric acid.

- It is suggested that the cations influence the formation of α -PbO₂ either by adsorption or by incorporation in the lattice.

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