

Short Communication

Heat treatment of α - and β -battery lead dioxide and its relationship to capacity loss

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Abstract

It is well known that lead dioxide contains, what has been called, 'structural water'. Present in the form of OH^- ions replacing O^{2-} ions in the anionic sublattice, the 'structurally bonded' water can be removed by heating, in the temperature range from 150 to 250 °C. In the present study, the discharge capacities of fresh and heat-treated (140 and 230 °C, respectively) α - and β - PbO_2 samples were evaluated in H_2SO_4 solution of 1.28 g cm^{-3} sp. gr. at different current densities of 5 to 40 mA cm^{-2} . It was found that the capacity decreased when structural water was removed. This loss of capacity is important when α - PbO_2 samples are considered. The energy of dehydroxylation was deduced by applying kinetic considerations to thermograms, obtained experimentally. The removal of the OH^- groups from β - PbO_2 needs an energy twice that of the α -form.

Keywords: Batteries; Lead dioxides; Capacity; Heat treatment

1. Introduction

The ability of the lead/acid battery to supply and to store energy depends on the initial electrochemical activity of the material in the positive plate and the rate at which this activity is lost during cycling. The cause of this degradation in performance has been attributed to loss of active material (PbO_2), rearrangement of the microstructure of the active material into a less porous configuration, loss of contact between individual particles of the active material, or of the contact between active material and the current-conducting grid.

The positive active material of lead/acid battery plates consists of a mixture of two PbO_2 modifications: orthorhombic α - PbO_2 and tetragonal β - PbO_2 [1,2].

The formation mechanism of the two crystalline modifications of lead dioxide has been well documented. Orthorhombic α - PbO_2 is the product of cured battery plate electroformation at high pH, and tetragonal β - PbO_2 is formed by electroformation of cured battery plate at low pH [3–7]. Discharge capacities of both modifications have been measured and it has been found that the capacity, in units of Ah g^{-1} of PbO_2 , of α - PbO_2 is lower than that of β - PbO_2 [2,8,9]. However, more recently, it has been shown that α - PbO_2 has a higher inherent capacity than β - PbO_2 [10].

Numerous studies have been reported in the literature concentrating on the differences between chemically and electrochemically prepared lead dioxide. Compared with chemically prepared α - and β - PbO_2 , which are reputed to be electrochemically inactive forms, material prepared by electrochemical formation of positive plates of lead/acid batteries exhibits high electrochemical activity. It was found that, in general, electrochemically prepared lead dioxide is non-stoichiometric, whereas chemically prepared β - PbO_2 is nearly-stoichiometric [11,12]. The origin of the electrochemical activity was essentially linked to the presence of H species. Nuclear magnetic resonance (NMR) [13,14] as well as inelastic [15,16] and quasi-elastic neutron scattering (NQES) studies [17,18] have shown the existence of at least two configurations for the proton in electrochemically active PbO_2 and only one configuration for the inactive, chemically prepared PbO_2 . Hydrogen-combined species were identified in PbO_2 as H_2O and OH^- groups.

Using differential thermal analysis (DTA), Caulder and Simon [19] identified an exothermic peak near 200 °C in battery lead dioxide which was not present in chemically prepared samples. This peak was associated with the presence of combined hydrogen and attributed to the reordering of the lead dioxide lattice with the evolution of oxygen and combined water. During cycling this peak decreased along with the battery plate capacity. A further recent suggestion

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[2,19–22] is that an electrochemically inactive form of β - PbO_2 develops in increasing amounts during charge/discharge cycling and that the loss of activity, is related to the loss of a hydrogen species from the crystal structure of the active dioxide material. In their studies performed on α - and β - PbO_2 chemically prepared, Rüetschi and Giovanoli [23] assumed that the predominant structural defects are due to cation vacancies and Pb^{2+} ions, both requiring charge compensation in the form of OH^- ions, replacing O^{2-} . They concluded that the capacity loss of lead dioxide during cycling can be due to the conversion of (vacancy-rich) α - PbO_2 into (vacancy-free) β - PbO_2 . This results in an increase in crystallite size and in the loss of structural water (hydrogen loss).

Hill and Madsen [24] studied β - PbO_2 either prepared chemically or obtained from positive battery plates and suggested that the decline in battery capacity is not a function of the loss of a hydrogen species from the crystal structure of electrochemically active PbO_2 .

According to the literature, the reasons for the influence of preparation conditions on the electrochemical properties as well as the exact origin of the battery failure, i.e., the loss of capacity due to cycling, are not well known and are still subject to controversy.

Consequently, this work focuses on the relationship between heat-treatment of α - and β -battery lead dioxides and capacity loss. In addition, DTA of the two polymorphs was also investigated in the present study.

2. Experimental

2.1. Preparation of samples

PbO_2 samples, α - and β -forms were prepared by electroformation of cured battery plates (with grids cast from a Pb–5%Sb alloy) respectively in alkaline and acidic solutions according to the methods described in Ref. [8].

After washing in running water for several hours to remove excess of NaOH in α - PbO_2 plates and H_2SO_4 in β - PbO_2 plates, respectively, the plates were dried overnight at 110 °C. The quantity of PbSO_4 in the active material was then found to be less than 2%.

Discharge capacity measurements were performed on a set of plates. The active material of the second group of plates was removed, homogenized in a mortar, then treated with hot ammonium acetate solution to remove any PbSO_4 present in the plates. After washing with distilled water and drying in an oven at 110 °C, the material was homogenized a second time in a mortar and served for subsequent analyses.

2.2. Chemical analyses

Pb^{4+} contents were determined for α - and β -samples by iodometric titration using a 645 Multi-Dosimat Metrohm titri-

meter. The total Pb ($\text{Pb}^{4+} + \text{Pb}^{2+}$) and the water content were determined by thermogravimetry.

2.3. Thermal analyses

The thermal decomposition equipment utilized in this investigation was a SETARAM Model RT 3000 DTA and a SETARAM Model PRT 540 thermogravimetric analyser (TG). TG and DTA runs were carried out using very small samples (80 mg) at a heating rate of 10 °C min^{-1} in stationary air, a thermally inert reference sample Al_2O_3 and Pt–10%Rh crucibles were used in the DTA experiments. The activation energies of dehydration (E_1) and dehydroxilation (E_2) of the samples were determined following the method described in Ref. [25].

2.4. Discharge capacity measurements

In order to reproduce the conditions in a lead/acid battery, all measurements were carried out in three-plate cells, each negative plate is at a 1 cm distance from the positive test electrode. An excess of H_2SO_4 with 1.28 g cm^{-3} sp. gr. was provided. Discharge was performed with a current density (5–40 mA cm^{-2}) to an end voltage of 1.75 V and the potential–time curves were recorded. Three categories of plates were tested in this study: (i) fresh α - and β - PbO_2 plates; (ii) α - and β - PbO_2 plates heated at 140 °C for 8 h, and (iii) α - and β - PbO_2 plates heated at 230 °C for 8 h.

3. Results and discussions

3.1. Chemical analyses results

The chemical analysis data are reported in Table 1. Both samples, α - and β - PbO_2 , yield a slight deviation from stoichiometry by showing an apparent oxygen deficiency which is compensated by the presence of OH^- ions. The chemical composition of the samples depends on the method of the specimen preparation (chemical or electrochemical) and on the washing and drying procedures. Following the same methods of preparation Bagshaw et al. [11] gave similar chemical compositions as those found in the authors' laboratory.

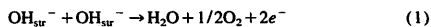
Table 1
Chemical analysis (w/o) of fresh and heat-treated α - and β - PbO_2 samples

Samples	Pb^{4+} (%)	Composition
α - PbO_2	72.48	$\text{PbO}_{1.81}(\text{OH})_{0.097}$
α - PbO_2 heated at 230 °C	70.35	$\text{PbO}_{1.81}$
β - PbO_2	72.76	$\text{PbO}_{1.82}(\text{OH})_{0.071}$
β - PbO_2 heated at 230 °C	70.28	$\text{PbO}_{1.82}$

3.2. Thermal analyses results

The DTA curves of α - and β -PbO₂ are given in Figs. 1 and 2. Both α - and β -PbO₂ gave a first endothermic peak, at 136 °C for α -PbO₂ and 142 °C for β -PbO₂, related to the presence of physisorbed water within the lead dioxide structure.

When increasing the temperature, an exothermic peak appeared, respectively at 234 °C for α -PbO₂ and at 228 °C for β -PbO₂. This peak is associated with the presence of combined hydrogen and attributed to the re-ordering of the lead dioxide lattice under the evolution of oxygen and combined water according to the following decomposition reactions:



The removal of OH⁻ from the lattice can also occur theoretically without O₂ evolution, namely in case of cation vacancy annealing or reoxidation of Pb²⁺ by O, according to:



The loss of combined hydrogen species is accompanied by a decrease in Pb⁴⁺ content for samples heated at 230 °C. In the range of temperature between 250 and 550 °C, three endothermic peaks were recorded for each variety. They correspond to the well-known intermediate oxides, pseudo-cubic α -PbO_x, pseudo-cubic β -PbO_x, and pseudo-tetragonal Pb₃O₄.

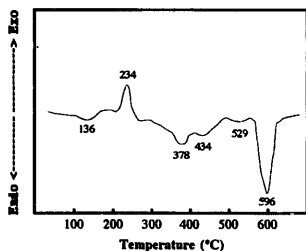


Fig. 1. DTA curve of fresh α -PbO₂.

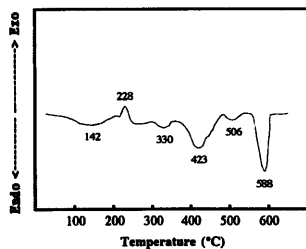


Fig. 2. DTA curve of fresh β -PbO₂.

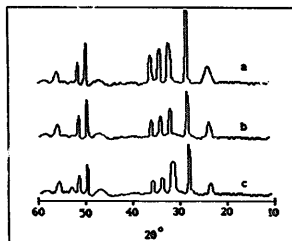


Fig. 3. XRD patterns of: (a) fresh α -PbO₂; (b) α -PbO₂ heated at 140 °C, and (c) α -PbO₂ heated at 230 °C.

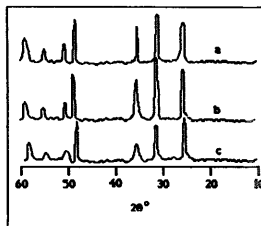


Fig. 4. XRD patterns: (a) fresh β -PbO₂; (b) β -PbO₂ heated at 140 °C, and (c) β -PbO₂ heated at 230 °C.

These phases are reputed to be unstable in H₂SO₄ solutions and they convert easily into α - and β -PbO₂ [9]. A sharp endothermic peak due to the conversion of Pb₃O₄ to PbO appeared at 596 °C for α -PbO₂ and 588 °C for β -PbO₂.

DTA patterns of fresh, and heat-treated samples are given for α - and β -PbO₂ in Figs. 3 and 4. It is shown that removal of physisorbed water and combined hydrogen species does not change the lead dioxide lattice and similar diagrams to those of α - and β -PbO₂ were obtained.

3.3. Discharge capacities results

The results of the capacity measurements for α - and β -PbO₂ samples are illustrated in Figs. 5 and 6, respectively. In these diagrams the capacity of fresh and heat-treated materials is plotted versus current density.

A decline in the electrode capacity for both α - and β -samples with increasing current density is recorded. This decline in capacity becomes important when the temperature increases. The loss of capacity (calculated from the data of Figs. 5 and 6) versus current density is plotted in Fig. 7. The results show that, when only physisorbed water is removed, little loss in capacity is obtained for both the α - and β -samples. On the contrary, the loss of OH⁻ groups seems to affect the capacity of the two electrodes considerably. It affects more the capacity of α - than the β -form. The discrepancy

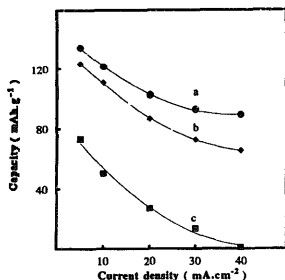


Fig. 5. Discharge capacity vs. current density: (a) fresh α -PbO₂; (b) α -PbO₂ heated at 140 °C, and (c) α -PbO₂ heated at 230 °C.

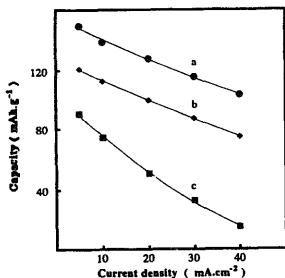


Fig. 6. Discharge capacity vs. current density: (a) fresh β -PbO₂; (b) β -PbO₂ heated at 140 °C, and (c) β -PbO₂ heated at 230 °C.

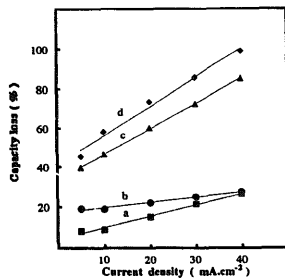


Fig. 7. Capacity loss vs. current density: (a) α -PbO₂ heated at 140 °C; (b) β -PbO₂ heated at 140 °C; (c) β -PbO₂ heated at 230 °C, and (d) α -PbO₂ heated at 230 °C.

between the values increases linearly with current density. This difference in the behaviour of the two forms of PbO₂ with regard to the loss of OH⁻ species can be explained that these hydrogen combined species are localised within the two structures. In their study Boher et al. [17] found an anisotropy of the OH...O bonds in the (PbO₆) octahedra chains which are oriented differently in the α - and β -structures. The

Table 2
Dehydration and dehydroxilation activation energies and constant rates of OH⁻ loss of α - and β -PbO₂ samples

Samples	Activation energy, E_1 (kcal mol ⁻¹)	Activation energy, E_2 (kcal mol ⁻¹)	Rate constant of OH ⁻ loss, k , at 473 °K (min ⁻¹)
α -PbO ₂	25.3	73.2	1.98
β -PbO ₂	23.1	150.5	0.13

values of the dehydroxilation activation energy for the two polymorphs are given in Table 2. It is shown that the value obtained for β -PbO₂ is twice that for the α -form.

The activation energy of dehydroxilation is composed of two terms: the energy of structural water decomposition and the sum of the diffusion energies in the crystal and in the powder.

Changes in activation energy may be attributed to differences in diffusion energy in the crystal, since the samples considered here have similar particle size (50 μ m). Consequently, the removal of OH⁻ species from β -PbO₂ lattice is very slow and needs more energy.

The values of rate constant of OH⁻ loss, determined at the same temperature 200 °C (average temperature at which the OH⁻ groups disappear) for the two varieties appear to confirm this hypothesis.

4. Conclusions

The studied discharge capacities of electrochemically active α - and β -PbO₂ in presence of H₂SO₄, showed that structural water plays an important role in determining the discharge capacity. The OH⁻ loss affects considerably the capacity of both α - and β -PbO₂, it affects more the capacity of α -PbO₂. These changes in capacity loss with regard to the removal of structural water was attributed to the way that these hydrogen-combined species are localised within the two structures. The dehydroxilation activation energy was calculated for the two varieties, the results gave a value for β -PbO₂ which is twice that of the α -form. The thermal decomposition mechanism of structural water and the study of the PbO₂ electrode using a solid protonic conductor electrolyte will be of a great interest to demonstrate the contribution of the OH⁻ groups in the mechanism of PbO₂ reduction.

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