

Thermal degradation of α - and β -PbO₂ and its relationship to capacity loss

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Abstract

The thermal degradation of α and β PbO₂ and its relationship to capacity loss was studied using galvanostatic discharge and voltamperometry. The results clearly demonstrate the dramatic effect of the thermal treatment on the capacity of the PAM. The variation of proton diffusion with temperature was determined for both α - and β -PbO₂. The two forms of PbO₂ exhibit different behaviour with regard to water loss. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

The lead–acid battery derives its power from the electrochemical energy released during the conversion of α - and β -PbO₂ to PbSO₄ on the positive plate, and Pb to PbSO₄ on the negative plate. Despite the antiquity of the concept a number of questions regarding the function of the lead acid battery remain unanswered. Among these, are the factors that affect the capacity of the PbO₂ electrode.

Lead dioxide active material has two crystal forms (α and β) in addition to the amorphous phase. It has been also found to contain H₂O and/or H⁺ [1,2]. At least two types of hydrogen are present in electrochemically obtained PbO₂. Different mechanisms for the inclusion of Hydrogen either into the crystal structure of PbO₂ itself [3–5] or on the surfaces of PbO₂ particles [4,6,7] were proposed. Pavlov et al. [8], have proved that PbO₂ particles are complex heterogeneous systems consisting of crystal and amorphous zones. The crystal zones, in which electrons move freely, are interconnected by gel polymer chains forming bridges along which electrons move between the crystal zones. The electrochemical properties of the crystal–gel system depend on the ratio between the gel and crystal zones. The origin of the electrochemical activity of

PbO₂ was essentially linked to the presence of these hydrogen species.

In our previous works [9,10], the results of thermal analyses of both α - and β -PbO₂ showed two distinct exothermic peaks. These were associated with the existence of two types of water: the first one, which disappears at low temperature, is adsorbed on the surface of PbO₂ particles. The second is localised within the crystal structure of PbO₂ itself and is removed at relatively high temperature (230°C). Their drive-off affects considerably the electrochemical properties of PbO₂ and leads to a decrease in the diffusion coefficient of the proton D_H.

The aim of the present work is to show the contribution of each of these two types of water in the process of PbO₂ reduction. The variation of the electrode capacity and the diffusion coefficient D_H with temperature (105–250°C) is determined. Galvanostatic discharge and voltamperometry were used as techniques of investigation.

2. Experimental

2.1. Preparation of PbO₂ active material

The α - and β -forms of PbO₂ 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. [11].

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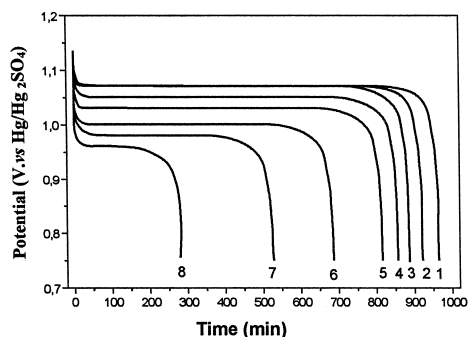


Fig. 1. Potential–time curves for the galvanostatic discharge ($I = -5 \text{ mA cm}^{-2}$) of $\alpha\text{-PbO}_2$ heated at: (1) 105°C; (2) 120°C; (3) 140°C; (4) 160°C; (5) 180°C; (6) 200°C; (7) 230°C and (8) 250°C.

After washing in running water for several hours to remove excess of NaOH in $\alpha\text{-PbO}_2$ and H_2SO_4 in $\beta\text{-PbO}_2$, respectively, the plates were dried overnight at 105°C.

The quantity of PbSO_4 in the active material was then found less than 2%. A set of plates were dried at different temperature in the range 105–250°C. Small electrodes were cut from the α - and $\beta\text{-PbO}_2$ plates and served as working electrodes in the electrochemical cells.

2.2. Electrochemical measurements

The electrochemical measurements were carried out in a three-electrode cell. The working electrode, having a surface area of 1.5 cm^2 , is at 1-cm distance from a rectangular-shaped platinum counter electrode having an apparent surface area of 5 cm^2 . A $\text{Hg}/\text{Hg}_2\text{SO}_4/5 \text{ M H}_2\text{SO}_4$ reference electrode was used. All the experiments were carried out at 25°C. Galvanostatic discharges were performed with a current density of 5 mA cm^{-2} and the potential–time curves were recorded.

The voltammograms were recorded after cycling the electrodes in the 1.2–0.6 V range vs. $\text{Hg}/\text{Hg}_2\text{SO}_4/5 \text{ M H}_2\text{SO}_4$ at different sweep rates ($5\text{--}100 \text{ mV s}^{-1}$). The diffusion coefficient of the proton was estimated from the I_p vs. $v^{1/2}$ equation following the method described in our

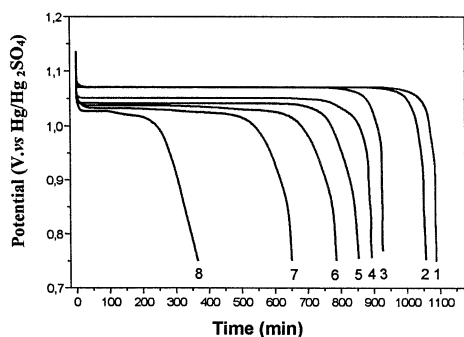


Fig. 2. Potential–time curves for the galvanostatic discharge ($I = -5 \text{ mA cm}^{-2}$) of $\beta\text{-PbO}_2$ heated at: (1) 105°C; (2) 120°C; (3) 140°C; (4) 160°C; (5) 180°C; (6) 200°C; (7) 230°C and (8) 250°C.

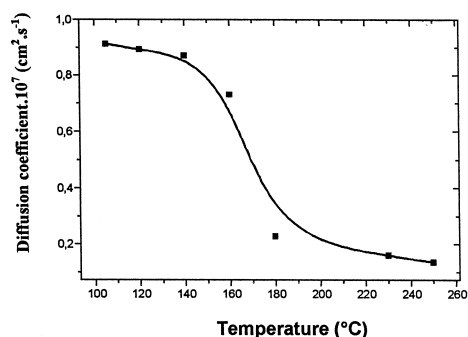


Fig. 3. Diffusion coefficient D_H vs. temperature for $\beta\text{-PbO}_2$.

previous work [10]. I_p and v are, respectively, the current at the peak and the sweep rate.

3. Results and discussions

Galvanostatic discharge curves are shown, respectively for α - and $\beta\text{-PbO}_2$, in Figs. 1 and 2, referring to the first discharge after filling the cell. Both α - and $\beta\text{-PbO}_2$ showed a potential plateau at 1.07 V due to the conversion of PbO_2 to PbSO_4 . As the temperature increases, the progressive removing of water causes an increase in the ohmic drop and the value of the potential plateau shifts down. The ohmic drop is higher when $\alpha\text{-PbO}_2$ is considered, however, the contribution of hydration water in the conductivity is important.

In addition, the drive-off of water is associated with a decrease in the capacity of PbO_2 . This decline in capacity becomes prominent when PbO_2 is heated at 180°C and more. The loss of structural water seems to affect more the capacity of $\alpha\text{-PbO}_2$.

The effect of thermal degradation of PbO_2 on the kinetics of proton diffusion is illustrated in Figs. 3 and 4 for β - and $\alpha\text{-PbO}_2$, respectively. In both cases, it appears that the progressive dehydration of PbO_2 has a great influence on the diffusion coefficient of the proton in PbO_2 .

However, the shape of the curves shows that this effect differs from one variety to another.

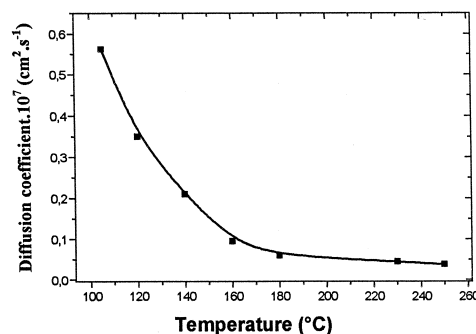


Fig. 4. Diffusion coefficient D_H vs. temperature for $\alpha\text{-PbO}_2$.

In the case of β -PbO₂ (as shown in Fig. 3), the dependence of D_H with temperature can be expressed according to three zones: we observe a slight variation of D_H in the zone of temperature 105–140°C, range of temperature corresponding to the loss of physisorbed water, followed by an important drop in the value of D_H in the zone 140–200°C. This zone corresponds to the removing of structural water. Beyond 200°C the value of D_H remains almost constant. In contrast, in the case of α -PbO₂ (as shown in Fig. 4) the increase of the temperature causes a gradual decrease of D_H , which reaches a constant value for the temperatures more than 200°C.

4. Conclusion

The hydration water, present on the surface or localised in the PbO₂ particles, plays an important role in the process of discharge of α - and β -PbO₂.

The results showed that heating affects considerably the electrochemical properties of α - and β -PbO₂. The loss of water is associated with a change in the electrical resistance, this results in a decrease in the capacity and the conductivity of PbO₂. When only physisorbed water is removed, little loss in capacity is observed for both α - and β PbO₂. On the contrary, the removing of 'structurally bonded' water seems to affect considerably the capacity of the two forms of PbO₂. It has more effect on the capacity of the α than the β form.

The kinetics of proton diffusion in PbO₂ are different from one variety to another. The value of D_H shows a significant variation with the temperature of heating PbO₂.

In the case of β -PbO₂, the loss of physisorbed water provokes little change in the value of D_H . On the contrary,

when α -PbO₂ is considered, an important decrease in the value of D_H is noticed. The removing of structural water causes a considerable change in the value of D_H for β -PbO₂, whereas a slight variation for α -PbO₂ is recorded. This difference in the behaviour of α - and β -PbO₂ with regard to water loss can be attributed, on one hand, to the nature and the repartition of these hydrogen components in the amorphous zones and to the difference existing in the structure of the two polymorphs of PbO₂ on the other hand. However, the presence of the two forms in PAM is necessary for the performance and cycle life of lead acid battery. β -PbO₂ determines the capacity and α assures the electrical conductivity.

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