

## ELECTRODEPOSITED $\alpha$ -PbO<sub>2</sub> AND $\beta$ -PbO<sub>2</sub> IN SULFURIC ACID: RECHARGE, CYCLING AND MORPHOLOGY

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### Summary

Experiments have shown that a structural transformation,  $\beta \rightarrow \alpha$ , was likely to occur during deep cycling of electrodeposited  $\beta$ -PbO<sub>2</sub> in 8N H<sub>2</sub>SO<sub>4</sub>, and that the appearance of  $\alpha$ -PbO<sub>2</sub>, in formerly pure  $\beta$ -PbO<sub>2</sub>, was responsible for the enhancement of the capacity. The presence of  $\alpha$ -PbO<sub>2</sub> also facilitated the growth process of  $\beta$ -PbO<sub>2</sub> during the charging.

### Introduction

The capacity and the cycle life of lead-acid batteries are strongly dependent on the active material in the positive plate, which consists mainly of  $\alpha$ -PbO<sub>2</sub> and  $\beta$ -PbO<sub>2</sub>. On the other hand, it is known that the performance of positive plate material changes with cycling. Consequently, the effect of cycling has been extensively researched to increase the understanding of the behaviour of cycled lead dioxides. According to several authors [1 - 4], the morphological transformations of the lead dioxides with cycling are responsible for their electrochemical behaviour, while others [5, 6] maintain that there is a relationship between the composition of the positive plate and its performance, stating that the presence of  $\alpha$ -PbO<sub>2</sub> enhances the mechanical strength of the active material. It has been suggested [7], however, that any beneficial effect should not be permanent, since  $\alpha$ -PbO<sub>2</sub>, after conversion to PbSO<sub>4</sub> during battery discharge, reverts to  $\beta$ -PbO<sub>2</sub> upon battery recharge [8 - 13]. Caulder *et al.* [14 - 16] suggested that, in commercial plates, an inactive form of PbO<sub>2</sub> develops in increasing amounts during charge-discharge cycles and that the presence of such a form is responsible for the observed capacity loss. It is to be noted, however, that the identity of the inactive form of PbO<sub>2</sub>, the mechanism by which it forms, and an explanation for its ineffectiveness in the discharge, have yet to be established.

The discharge properties and mechanisms of lead dioxides electrodeposited onto an inert anode material have been studied in considerable detail [17 - 22]. The majority of these studies, however, are concerned with

$\beta$ -PbO<sub>2</sub> in acid media and with  $\alpha$ -PbO<sub>2</sub> in alkaline media [18]. There is little information in the literature on the properties of pure  $\alpha$ -PbO<sub>2</sub> in H<sub>2</sub>SO<sub>4</sub> [23], and almost no work has been reported on the cycling behaviour of pure electrodeposited  $\alpha$ -PbO<sub>2</sub> or  $\beta$ -PbO<sub>2</sub> in H<sub>2</sub>SO<sub>4</sub>. We have already shown that the discharge capacity of a pure electrodeposited  $\alpha$ -PbO<sub>2</sub> electrode is higher than that of a  $\beta$ -PbO<sub>2</sub> electrode under similar experimental conditions [24]. Accordingly, Hill *et al.* [25] have found that the performance and cycle life of the lead-acid battery are improved by increasing the initial proportion of  $\alpha$ -PbO<sub>2</sub> in the positive electrode.

In the present investigation the cyclic behaviour of pure electrodeposited  $\alpha$ -PbO<sub>2</sub> and  $\beta$ -PbO<sub>2</sub> varieties in H<sub>2</sub>SO<sub>4</sub> have been studied and correlated with the morphology of the material.

## Experimental

The two forms of lead dioxide were anodically deposited onto a 3.8 cm<sup>2</sup> platinum planar electrode according to the procedure reported elsewhere [24] and then weighed. In this study the mass of the two forms of PbO<sub>2</sub> were 4.1 mg cm<sup>-2</sup>, corresponding to a deposit thickness of approximately 4  $\mu$ m, assuming the crystallographical density of lead dioxide to be 9.4 g cm<sup>-3</sup>.

A saturated calomel reference electrode (SCE), was in contact with the solution in the cell through a KCl bridge, and a platinum grid was used as the counter electrode. Otherwise, the circuit is conventionally three electrode, operated either galvanostatically or potentiostatically. It was controlled automatically using a microcomputer. This system, with a special interface, enabled us to study the evolution of the capacity per unit mass of  $\alpha$ -PbO<sub>2</sub> and  $\beta$ -PbO<sub>2</sub> as a function of the number of charge-discharge cycles. The successive operations of discharge at constant current, charge at constant potential, and rest, are shown in Fig. 1.

During the discharge at constant current, the potentials of the lead dioxide electrodes were recorded as a function of the time. After the potential drop from  $E_1$ , which is the potential of the open circuit equilibrium, the discharge was allowed to continue for 10 min. The end of the discharge was

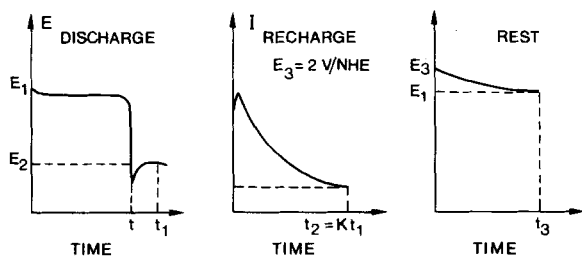


Fig. 1. Automated cycling steps.

taken as  $t_1 = t(\text{at } E_2) + 10 \text{ min}$ , with  $E_2 = 0.95 \text{ V/NHE}$ . When this value was read by the computer, the discharge was automatically terminated and the computer initiated recharge at a constant potential,  $E_3 = 2 \text{ V/NHE}$ . The time for charge was taken as  $t_2 = Kt_1$  with  $K = 1.2$ . The current during the charge was recorded as a function of time. After the charge, the electrodes were rested for  $t_3 \text{ min}$ , which was the time necessary for the electrode to recover to the initial potential  $E_1$ . This rest time depended on the number of cycles and lasted from 15 min to 5 h. When the electrodes had returned to open circuit equilibrium, the next discharge was run.

The morphological aspects of the lead dioxides before and after a number of charge-discharge cycles have been characterized by Scanning Electron Microscopy (SEM). The X-ray analysis of the structural transformations of the electrodeposited lead dioxides submitted to charge-discharge cycles have been performed by mean of a Philips diffractometer using the  $K\alpha$  ray of Cu.

## Results and discussion

### (i) Recharge current profiles of $\alpha\text{-PbO}_2$ and $\beta\text{-PbO}_2$

The current *vs.* time plots for the recharge at constant potential ( $E_3 = 2 \text{ V/NHE}$  (Fig. 1)) after various charge-discharge cycle numbers are shown in Figs. 2 and 3 for  $\alpha\text{-PbO}_2$  and  $\beta\text{-PbO}_2$ , respectively. In both cases, it can be seen that the recharge current passes through a maximum.

If the lead sulphates formed during the discharge were the reactive sites for the  $\text{PbSO}_4 \rightarrow \text{PbO}_2$  electro-conversion process during recharging, one would expect the current to decrease continuously with time, without any maximum. Such a maximum reveals a nucleation process. According to

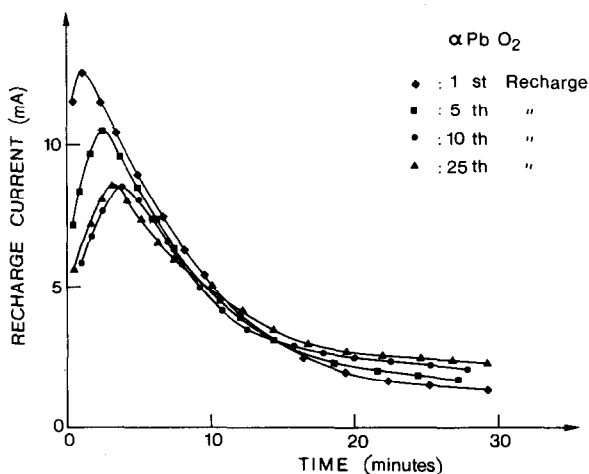


Fig. 2. Recharge current profiles at 2 V/NHE of  $\alpha\text{-PbO}_2$  as a function of the number of charge-discharge cycles.

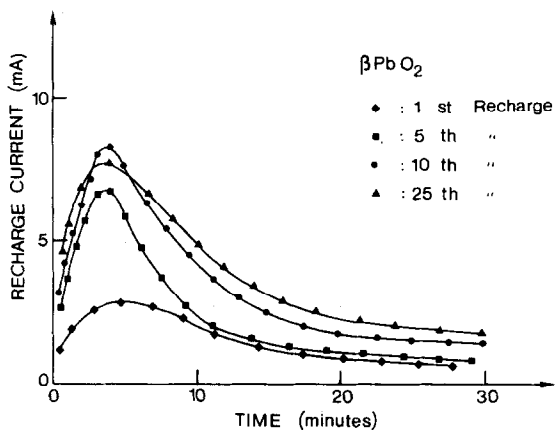


Fig. 3. Recharge current profiles at 2 V/NHE of  $\beta\text{-PbO}_2$  as a function of the number of charge-discharge cycles.

Figs. 2 and 3, one can conceive that at the beginning of the recharge, only some imperfection centers in the sulphate may emit electrons and initiate oxidation to act as nucleation centers for  $\text{PbO}_2$ . Their number and/or size increase with time, making the current density rise to a maximum when, either the lead dioxide crystals overlap or the major part of the lead sulphate has been converted. Similar profiles of recharge currents have been found by Gibson and Peter to occur with battery plates recharged at constant potential [26], in agreement with earlier results given by Dawson *et al.* [4] for the case of a  $\beta\text{-PbO}_2$  electrode.

It is to be noted, however, that there is no work reported in the literature concerning the effect the form of the lead dioxide and the number of cycles had on the recharge current profiles. Our results in Figs. 2 and 3 revealed the great difference between the  $\alpha\text{-PbO}_2$  and the  $\beta\text{-PbO}_2$  forms: the recharge currents of  $\alpha\text{-PbO}_2$  during the first charges are higher than those of  $\beta\text{-PbO}_2$  under the same conditions. This is because the morphology of the lead sulphate, which is formed during the first discharge, is not identical for each variety of lead dioxide, as we have already demonstrated in a previous work [24]. In one case ( $\alpha\text{-PbO}_2$ ), a  $\text{PbSO}_4$  film has been formed, while in another case ( $\beta\text{-PbO}_2$ ),  $\text{PbSO}_4$  has appeared under the form of well localized crystals. Under such conditions, it can then be conceived that the rates of the electro-crystallization process, which characterize the conversion of these lead sulfates to lead dioxide, are quite different. On the other hand, the time to reach the maximum value is less for  $\alpha\text{-PbO}_2$  than it is for  $\beta\text{-PbO}_2$ . From these results, it appears that  $\beta\text{-PbO}_2$  is more difficult to recharge than is  $\alpha\text{-PbO}_2$ . However, this advantage which the  $\alpha\text{-PbO}_2$  has does not persist with an increasing number of charge-discharge cycles, since  $\alpha\text{-PbO}_2$  is converted to  $\text{PbSO}_4$  during discharge and reverts to  $\beta\text{-PbO}_2$  during recharge, a transformation which has been found to occur in battery plates [6]. This enabled us to explain why the recharge current density for  $\alpha\text{-PbO}_2$  at  $t = 0$  and at the

maximum, decreased as the number of the charge–discharge cycles increased (Fig. 2). In other words, the initially pure  $\alpha$ -PbO<sub>2</sub> becomes increasingly more difficult to recharge as the cycle number increases due to the formation of the  $\beta$  form (see below). Beyond the 10th charge, the recharge current profiles of  $\alpha$ -PbO<sub>2</sub> remain unchanged with the number of the charge–discharge cycles. It seems that the conversion rate of  $\alpha$ -PbO<sub>2</sub> to  $\beta$ -PbO<sub>2</sub> decreases as the number of cycles increases. It is possible that the  $\alpha$ -PbO<sub>2</sub>: $\beta$ -PbO<sub>2</sub> ratio reaches a limiting value after a few charge–discharge cycles. This hypothesis is supported by recent results reported by Hill *et al.* [25], who have demonstrated that the conversion of  $\alpha$ -PbO<sub>2</sub> to  $\beta$ -PbO<sub>2</sub> in cycled battery plates is fast only during the first 30 cycles.

With respect to the evolution of the recharge current profiles of  $\beta$ -PbO<sub>2</sub> during cycling, Fig. 3 shows that the recharge current density both at  $t = 0$  and at the maximum increased with the cycle number. This probably reflected an increase in the number of adequate growth centers for PbO<sub>2</sub> on PbSO<sub>4</sub> which were formed during the discharge. Since it has been found [27, 28] that the current due to the growth depends on the number of growth centers according to the relation:

$$I = BNt^n \quad (1)$$

where  $N$  is the number of growth centers,  $t$  the time,  $B$  the constant governing the crystal growth, and  $n$  depends upon the type of nucleation. According to Abyaneh and Fleischmann [29], in the case of two dimensional nucleation,  $n$  may vary in the range between 1 and 2.

Moreover, it has been demonstrated [28] that the number of growth centers changes, being given by:

$$N = N_0[1 - \exp(-At)] \quad (2)$$

where  $A$  is the nucleation constant.

According to these equations, our results in Figs. 2 and 3 show that the number of growth centers is greater with  $\alpha$ -PbO<sub>2</sub> than with  $\beta$ -PbO<sub>2</sub>. Therefore, the build up of  $\beta$ -PbO<sub>2</sub> in initially pure  $\alpha$ -PbO<sub>2</sub> with cycling, is a factor responsible for the increased difficulty involved in recharging of  $\alpha$ -PbO<sub>2</sub> as the cycle number increases.

For the case of initially pure  $\beta$ -PbO<sub>2</sub>, X-ray analysis after 12 charge–discharge cycles clearly showed the formation of  $\alpha$ -PbO<sub>2</sub> (Fig. 4). Before cycling neither of the  $\alpha$ -PbO<sub>2</sub> peaks was visible in the spectrum. This formation was accompanied by a corresponding increase in the charge current (Fig. 3). Taking into account the previous observations, it is thought that the presence of  $\alpha$ -PbO<sub>2</sub> in the initially pure  $\beta$ -PbO<sub>2</sub> favours the charge of the latter. This observation agrees with the work reported by Pavlov and Iordanov [30] concerning the growth process of the anodic layer during the potentiostatic oxidation of lead in sulfuric acid. These authors claimed that the Pb<sup>2+</sup> ions are oxidized to  $\beta$ -PbO<sub>2</sub> at the  $\alpha$ -PbO<sub>2</sub> solution interface.

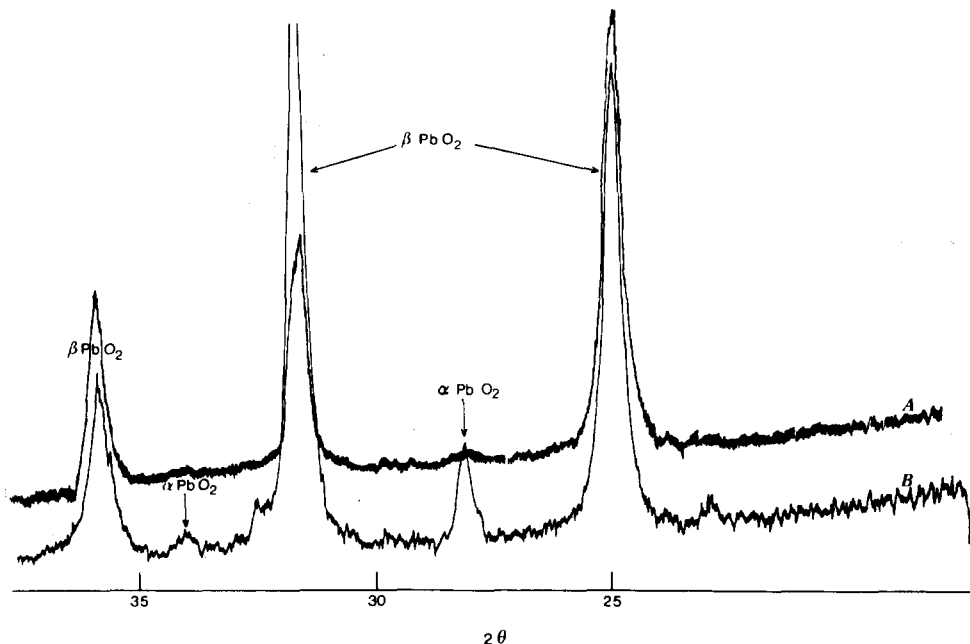


Fig. 4. X-ray analysis of an initially pure  $\beta\text{-PbO}_2$  electrode before (A) and after 12 charge-discharge cycles (B).

(ii) *Effect of cycling on the capacity per unit mass of lead dioxide*

Figure 5 represents the capacity per unit mass of the  $\alpha$  and  $\beta$  varieties of lead dioxide during cycling under the charge-discharge conditions previously described (see the Experimental section).

It can be seen that the effect cycling had on these varieties of lead dioxide was quite different. In the case of the  $\alpha\text{-PbO}_2$  electrode, its capacity per unit mass increased only after the first charge, then decreased progressively as a function of the charge-discharge cycle number, while in the case of the  $\beta\text{-PbO}_2$  electrode, a continuous increase in the capacity per unit mass has been observed during the first 10 cycles. Therefore, the difference in the capacity values tends to become less than it was during the first cycles.

It was also found that these varieties of lead dioxide, which had radically different microstructures before the first discharge (Fig. 6(a) and (b)), were all transformed into almost identical microstructures after 40 charge-discharge cycles (Fig. 6(c) and (d)). This transformation probably resulted from the structural change, as shown in Fig. 4. It seems, therefore, that there is a correlation between the structural changes and the discharge capacities of the lead dioxides.

As mentioned above, the conversion of  $\alpha\text{-PbO}_2$  to  $\text{PbSO}_4$  during discharge and of the partial conversion of  $\text{PbSO}_4$  to  $\beta\text{-PbO}_2$  during charge was a well known fact [8 - 13]. This means that the initially pure  $\alpha\text{-PbO}_2$  phase

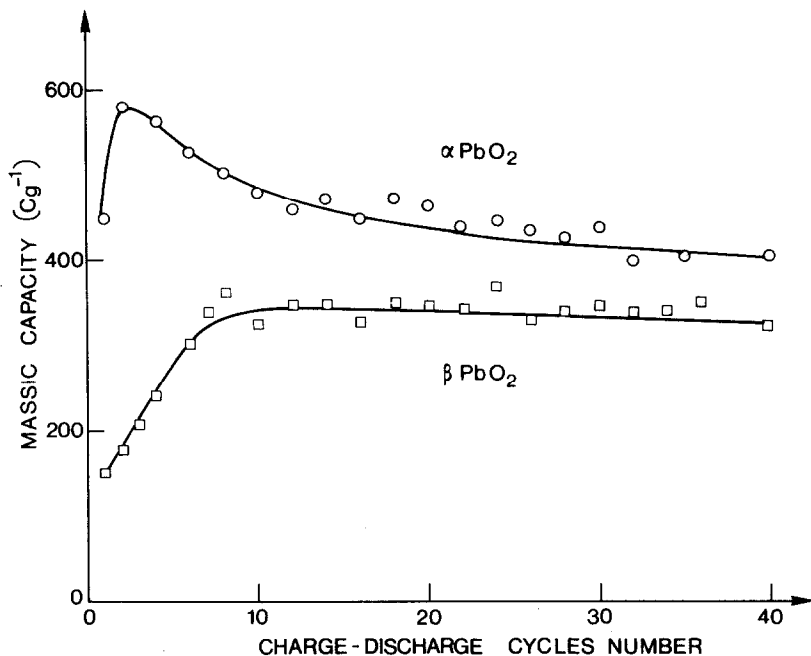
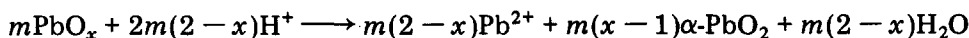


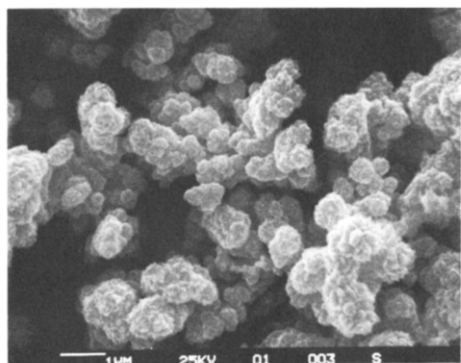
Fig. 5. Effect of the number of cycles on the capacity per unit mass of the  $\alpha$  and  $\beta$  varieties of  $\text{PbO}_2$ .

enriches progressively with the  $\beta$ - $\text{PbO}_2$  phase with cycle number. This enrichment was accompanied by a corresponding decrease in capacity (Fig. 5) and it is likely that the  $\beta$ - $\text{PbO}_2$  was responsible for this. The conclusion supports our previous observations [24] and is in good agreement with the recent results of Hill *et al.* [25] concerning the correlation between the  $\alpha$ - $\text{PbO}_2$  content in the positive plates and the performance of the lead-acid batteries. According to these authors [25], the decrease in capacity was the result of the conversion of  $\alpha \rightarrow \beta$  forms during cycling.

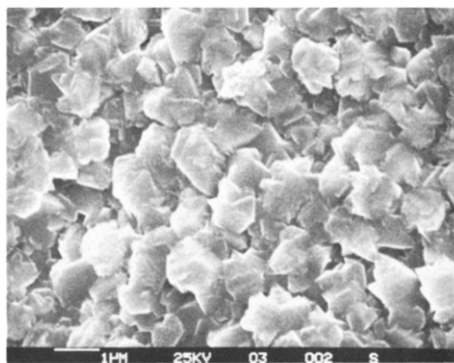
For the  $\beta$ - $\text{PbO}_2$  case, as shown in an earlier work [24], a second plateau around 0.3 - 0.4 V/NHE was reached at the end of a discharge step, and this was ascribed to the formation of lead monoxide ( $\text{PbO}$ ) and lower oxides ( $\text{PbO}_x$ ). These lower oxides ( $\text{PbO}_x$ ) could produce  $\alpha$ - $\text{PbO}_2$  in concentrated  $\text{H}_2\text{SO}_4$  according to



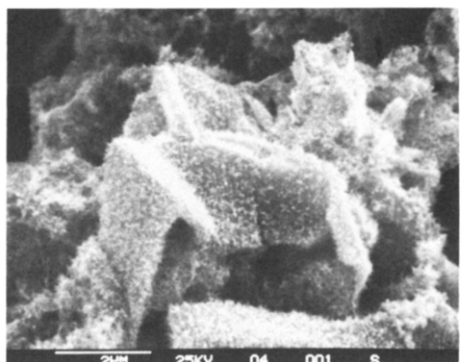
Such a disproportionation was claimed by Burbank [32], then confirmed by Rüttschi [33] on the basis of purely chemical reactions. Whilst these suggestions are probably true, it would be expected that, under our experimental conditions, the cycling would produce an enrichment of  $\alpha$ - $\text{PbO}_2$  in formerly pure  $\beta$ - $\text{PbO}_2$  as a function of the cycle number. These results (Figs. 4 and 5) lead us to believe that the appearance of  $\alpha$ - $\text{PbO}_2$  was



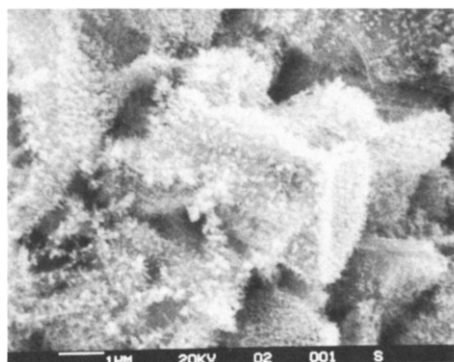
(a)



(b)



(c)



(d)

Fig. 6. (a)  $\alpha$ - $\text{PbO}_2$  before discharge; (b)  $\beta$ - $\text{PbO}_2$  before discharge; (c)  $\alpha$ - $\text{PbO}_2$  after 40 charge-discharge cycles; (d)  $\beta$ - $\text{PbO}_2$  after 40 charge-discharge cycles.

likely to be responsible for the enhancement of the capacity. This observation showed the important role of  $\alpha$ - $\text{PbO}_2$  during the repeated charge-discharge cycles.

### (iii) Morphology and discharge capacity of lead dioxides

It is generally recognized that the morphology of the porous electrodes is important for their proper functioning. It is interesting to note, however, that the correlation between the morphology and the performance of lead dioxides remains to be clarified. Although a substantial number of papers deal with this problem, it is not yet known with certainty what exact shape and size of the  $\text{PbO}_2$  crystals favour a high discharge capacity. According to some authors [34, 35], prismatic  $\text{PbO}_2$  is beneficial, but the precise mechanism of this action remains to be studied; others [36] maintain that the presence of the reticulate structure improves the capacity of lead dioxides. Such a structure was not observed by Hughel and Hammar [37].

On the other hand, it has been shown that the coralloid  $\text{PbO}_2$  structure was responsible for the loss of capacity [16], although such a structure



appears to be ideal for a porous electrode. Moreover, Voss and Freundlich [38] have clearly demonstrated that the discharge capacity of lead dioxide was not proportional to its BET surface area. It is, therefore, difficult to attribute the difference in the behaviour of the two modifications of  $\text{PbO}_2$  entirely to the difference in their morphology [31]. It seems, however, that the capacity of  $\text{PbO}_2$  is connected with the content of hydrogen species, as suggested by Caulder *et al.* [15]. This concept is probably true, since no hydrogen species has been found in chemically prepared  $\beta\text{-PbO}_2$  [14, 40], which is known to be an unsatisfactory battery electrode [14, 41, 42]. More recently Moseley *et al.* [40], using inelastic neutron scattering and chemical analysis, have shown that the content in hydrogen species is higher in  $\alpha\text{-PbO}_2$  than in  $\beta\text{-PbO}_2$ . These results agreed with those of Jorgensen *et al.* [39].

According to these works, it might be expected that the difference in the behaviour of the two forms of  $\text{PbO}_2$  in the present investigation results from their hydrogen content. This might explain why their structural transformation during cycling is one of the major factors governing the capacity change under repeated cycles.

## Conclusion

Both the alpha and beta electrodeposited varieties of  $\text{PbO}_2$  investigated in this work have exhibited a structural transformation during cycling. This transformation was accompanied by changes in the capacity. Taking into account the overall results, and others in the literature, it can be concluded that during cycling, the discharge capacity of  $\alpha\text{-PbO}_2$  decreases and that of  $\beta\text{-PbO}_2$  increases, due to the bulk transformation of one variety into the other. The occurrence of  $\alpha\text{-PbO}_2$  with cycling in formerly pure  $\beta\text{-PbO}_2$  under our experimental conditions is a factor responsible for the enhancement of the capacity of this variety; its presence also facilitated the growth process of  $\beta\text{-PbO}_2$  during charging. It seems that the  $\alpha\text{-PbO}_2$  crystals might act as growth centers for the transformation of  $\text{PbSO}_4$  into  $\beta\text{-PbO}_2$ , as suggested by Pavlov *et al.* [30].

By contrast, the presence of  $\beta\text{-PbO}_2$  in formerly pure  $\alpha\text{-PbO}_2$  is responsible for the loss in capacity of this variety with cycling.

The difference in behaviour of the two forms of  $\text{PbO}_2$  is probably derived from their hydrogen content, as pointed out by different authors [39, 40]. These chemical entities would be necessary for a high electrochemical reactivity, as suggested by Caulder and co-workers [15], even though the role of these chemical entities in the mechanism of discharge has not yet been fully elucidated.

The experimental results presented in this paper highlighted the beneficial effect of  $\alpha\text{-PbO}_2$ . This leads us to believe that the presence of this variety in the lead-acid battery positive materials is necessary for better performance. It is noteworthy that we suggested this idea in 1981 [24], and that it agrees with findings recently reported by Hill *et al.* [25].

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## List of symbols

$A$	Nucleation constant
$B$	Constant governing the crystal growth
$I$	Recharge current
$N$	Number of growth centers at time $t$
$N_0$	Total number of growth centers
$t$	Time of recharge

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