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Studies on the microstructure of the positive lead–acid battery plate and its electrochemical reactivity

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It has been shown that the physicochemical properties of PbO_2 in the positive plate of a lead–acid battery relates to the PbO_2 crystal size growth during charge/discharge cycling. It was found that there were two types of PbO_2 present in an uncycled positive plate thermally decomposed into tet-PbO: one with, and the other without, forming β-PbO_x. The degree of crystallinity was found to be lower in the surface layer of PbO_2 crystals than in the interior. The degree of crystallinity of PbO_2 crystals increased with cycling, and at the same time the size of PbO_2 crystals became larger, causing decrease in the specific surface area and surface roughness. It was also concluded that the electrochemical reactivity of the surface layer of PbO_2 was strongly influenced by the properties of the PbO_2 crystal lattice characterized by the formula $PbO_{2-\delta}(xH_2O)$.

1. Introduction

Caulder and Simon reported that the positive plate of a lead–acid battery contained 'amorphous PbO_2' and that PbO_2 became electrochemically inactive as charge/discharge cycles progressed [1–4]. Caulder concluded that the 'amorphous PbO_2' was thermally decomposed into Pb_3O_4 without passing through the intermediate phase of α-PbO_x or β-PbO_x. Hill *et al.* reported that the 'amorphous PbO_2' was present in the amount of 6–29% in a fresh or uncycled positive plate and that the amount increased slightly during repeated discharge and charge cycling [5]. However, Caulder denied the presence of the 'amorphous PbO_2' in 1983 [6]. Caulder proposed the 'hydrogen loss' model where the electrochemical activity of PbO_2 was assumed to be controlled by the amount of hydrogen species which penetrated into the PbO_2 crystal lattice. Recently several researchers have established the presence of hydrogen species as protons or water in the PbO_2 crystals [6–13]. On the other hand, Hill *et al.* concluded that there was no relation between the amount of the penetrated hydrogen species and the capacity loss of the positive plate [14]. Pavlov *et al.* concluded that hydrogen species were found in the hydrolysed surface of PbO_2 crystals which controlled its reactivity [15].

2. Experimental details

2.1. *Methods of manufacturing the test cells*

The positive paste was formed by mixing 1 kg of lead oxide powder (Shimazu-mill oxide; 72% PbO, 28% Pb) with 200 ml H_2SO_4 with a specific gravity of 1.120. Curing proceeded at 35° C and at a humidity of more than 90% for 24 h. The cured positive paste was determined, by X-ray diffraction analysis, to consist mainly of $3PbO \cdot PbSO_4$ and $PbO \cdot PbSO_4$. Formation was carried out at 40° C in dilute H_2SO_4 with a specific gravity of 1.100 and at 13.8 A kg^{-1} for 40 h. The negative pasted plates were also prepared by a similar process. The size of the plates was 58 mm in length and 38 mm in width. The grid was made of a lead alloy containing 0.08% Ca and 0.50% Sn. Two positive plates and three negative plates were assembled into a sealed lead–acid cell with an actual capacity of 4 Ah at 20 h rate, with the composing plates being assembled under a pressure of *ca* 20 kg dm^{-2}.

2.2. *Cycling test and observation method*

Each of the sealed lead–acid cells was cycled to 50% depth of discharge at 40° C. Following a certain number of cycles, the positive plates, in a fully charged state, were removed from the tested cells, washed in water and dried at 55° C. A series of positive active materials were examined by a scanning electron microscopy using JSM-U3 and T-200 (Japan Electron Optical Lab. Ltd) instruments and their specific surface areas were measured by a Quantasorb Surface Area Analyser (Quantachrome Corp.). The positive active material was separated from the grid and ground into a powder form with crystal sizes less than 10 μm in an agate mortar. The powder was subjected to X-ray diffraction analysis using a Geigerflex Rad-IIA (Rigaku Corp.). After the residual PbO and $PbSO_4$ contained in the ground positive active material were respectively dissolved with 5% CH_3COOH and a saturated NH_4COOH solution at 50° C, the thermal decomposition patterns of PbO_2 were studied with a Thermoflex 8085A (Rigaku Corp.). As a test for determining the stability of PbO_2 in dilute H_2SO_4, 10 g of ground PbO_2 was allowed to soak in 100 ml H_2SO_4 with a specific gravity of 1.300 at 50° C for 10 days.

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3. Results and discussion

3.1. *Properties of PbO_2 in a fresh or uncycled positive lead-acid battery plate*

The formed positive plate was found by chemical analysis to contain 1.65% PbO, 0.36% $PbSO_4$ and 97.99% PbO_2. In the formed positive plate, β-PbO_2 was found dominant by X-ray powder diffraction analysis, and α-PbO_2 in only a small amount. When both the PbO_2 in the uncycled positive plate after formation, and the residual PbO_2 after soaking in the dilute H_2SO_4 solution at 50° C for 10 days, were examined for their physicochemical properties, two remarkable differences were found. Firstly, the residual PbO_2 exhibited a higher relative intensity for each β-PbO_2 X-ray diffraction peak. This suggested that the residual PbO_2, the interior of the PbO_2 crystals, could exhibit a higher degree of crystallinity than that of the surface layer (Fig. 1). Secondly, in the differential thermal analysis curve of the residual PbO_2, the endothermic peak at *ca* 500° C was found to be deeper and the endothermic peak at *ca* 580° C shallower, than those in the PbO_2 before soaking in the dilute H_2SO_4 (Fig. 2). Because in the sample of PbO_2 for thermal decomposition analysis, neither $PbSO_4$ nor PbO was detected by a chemical analysis nor with X-ray diffraction analysis, such changes in the thermal decomposition patterns were not caused by such impurities as $PbSO_4$ and PbO. Decomposition of PbO_2 in the uncycled positive plate was thought generally to occur in the following series of thermal reactions.

$$\alpha\text{- and }\beta\text{-PbO}_2 \xrightarrow{330^\circ C} \alpha\text{-PbO}_x \xrightarrow{426^\circ C} \beta\text{-PbO}_x$$

$$\xrightarrow{498^\circ C} \text{Pb}_3\text{O}_4 \xrightarrow{581^\circ C} \text{tet-PbO}$$

It is noteworthy that the initial PbO_2 in the uncycled positive plate was thermally decomposed almost completely into tet-PbO at *ca* 580° C. On the other hand, the residual PbO_2 after soaking in dilute sulfuric acid solution was thermally decomposed into tet-PbO at *ca* 500° C. It was found that the temperature at which Pb_3O_4 decomposed into tet-PbO was relatively lower for the residual PbO_2 than for the initial PbO_2. The thermal decomposition curve of the residual PbO_2 was found to be very similar to that of the 'amorphous PbO_2', as reported by Caulder and Simon [3], having been thermally decomposed into PbO without forming α-PbO_x or β-PbO_x. It may be assumed that there exists two types of the thermally intermediate phase of Pb_3O_4 which are decomposed into tet-PbO at *ca* 500° C and at *ca* 580° C, respectively. However X-ray powder diffraction data showed that the residual PbO_2 had a higher degree of crystallinity. The residual PbO_2 crystals were soaked in dilute nitric acid at 50° C for 10 days, allowing the surface PbO_2 to gradually react with nitric acid and dissolve into the solution without changing the interior. On examination by scanning electron microscopy, the residual PbO_2 was found to be typically prismatic and highly crystalline.

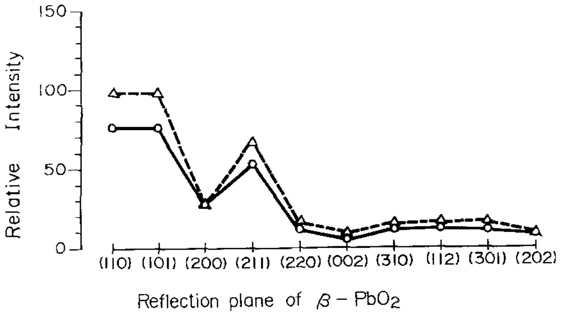

Fig. 1. Change in the relative intensity of X-ray diffraction (XRD) peaks of β-PbO_2 in the uncycled positive plate before and after soaking in the dilute sulfuric acid with specific gravity of 1.300 at 50° C for 10 days.

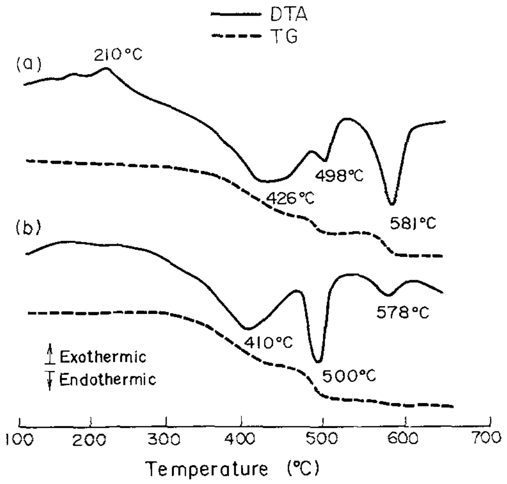

Fig. 2. Change in DTA–TG curve of PbO_2 in the uncycled positive plate before and after soaking in the dilute sulfuric acid with specific gravity of 1.300 at 50° C for 10 days. (Reference sample: α-Al_2O_3, heating rate: 5° C min^{-1}, atmosphere: air.) (a) PbO_2 in the uncycled positive plate before soaking; (b) residual PbO_2 after soaking.

3.2. *Changes in the properties and morphology of PbO_2 during cycling*

Almost the identical phenomena were observed for

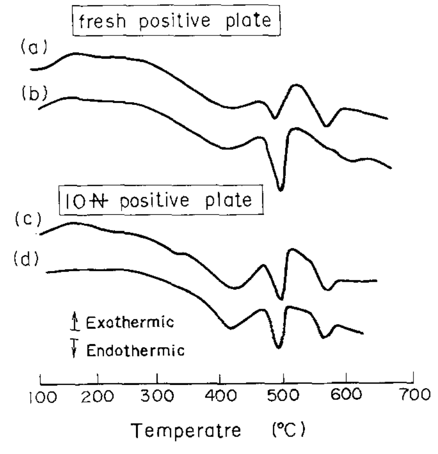

Fig. 3. DTA curves of PbO_2 in the uncycled positive plate and 10-cycled positive plate in the fully charged state and in the fully discharged state. (Reference sample: α-Al_2O_3, heating rate: 5° C min^{-1}, atmosphere: air.) (a) PbO_2 in the uncycled positive plate before first discharge; (b) residual PbO_2 in the fully discharged state after first discharge; (c) PbO_2 in the positive plate before tenth discharge; (d) residual PbO_2 in the fully discharged state after tenth discharge.

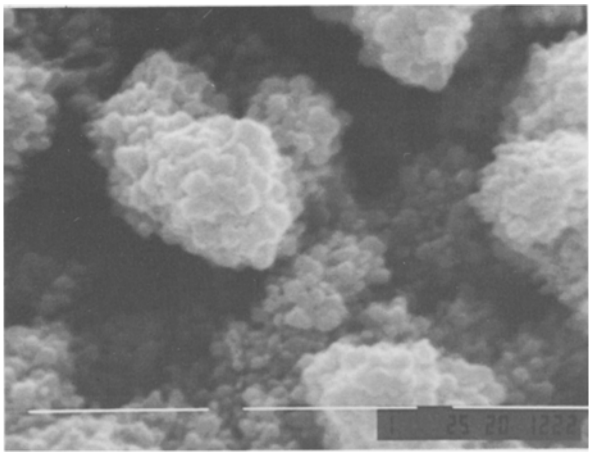

Fig. 4. PbO_2 crystals in the uncycled positive plate. (Each white line corresponds to 1 μm.)

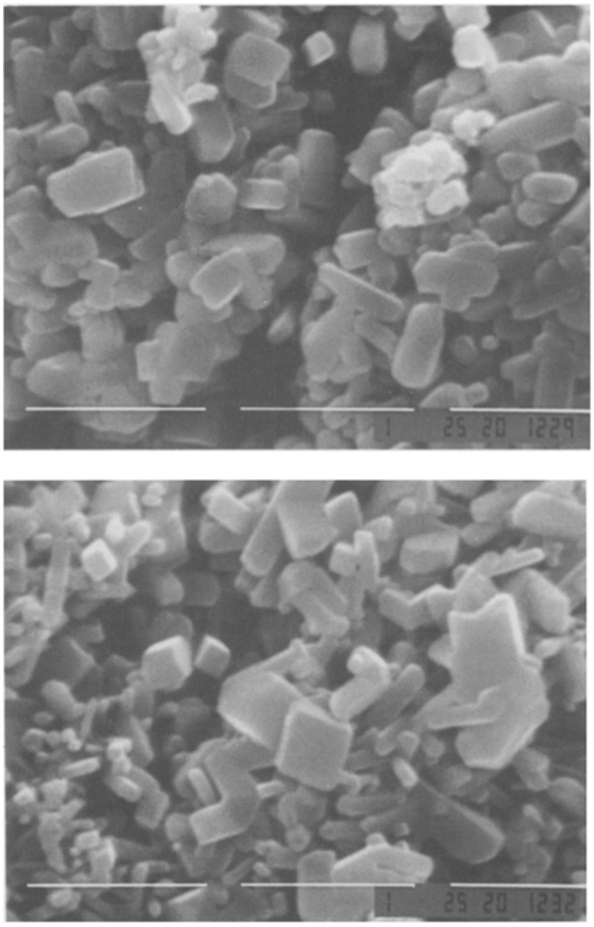

Fig. 5. β-PbO_2 crystals in the positive plate before tenth discharge. (Each white line corresponds to 1 μm.)

the residual PbO_2 in a fully discharged state when the freshly formed positive plate was discharged (Fig. 3). However it was also found that the difference in thermal decomposition patterns between the PbO_2 in a fully charged state and the residual PbO_2 in a fully discharged state became gradually smaller as cycling progressed. It was found that both PbO and $PbSO_4$ remained, throughout the cycling period, in an amount less than 1.0% in the positive active material under a fully charged state, and that no accumulation of PbO and $PbSO_4$ was found. Figure 4 shows the morphology of PbO_2 crystals in an uncycled positive plate. The smallest size was between 0.05 and 0.1 μm. The PbO_2 crystals were found to grow or develop along the c-axis and to be larger than 0.4 μm in length with repeated cycling. It is considered that the rate of growth in crystal size was most rapid in the early stage of cycling as reported by Hill and Madsen [12]. It was found that the PbO_2 crystals became more prismatic and exhibited a higher degree of crystallinity as the size increased. The number of grain boundaries was obviously greater for the PbO_2 crystals in the uncycled positive plate than for those in the positive plate before the tenth discharge (Figs 4 and 5). This decline becomes more distinct with further repeated cycling. The surface roughness of the PbO_2 crystals was found, by scanning electron microscopy, to decrease with enlargement of crystal size which brought about a reduced number of steps, edges and kinks or dislocations on the surface. Because the electrochemical reaction in the positive plate of a lead-acid battery is considered to proceed by a solution-precipitation mechanism, the rate or degree of condensation of the dissolved Pb ions on the surface of PbO_2 crystals is one of the most important factors controlling the rate of electrochemical reaction. When the surface of PbO_2 crystals becomes smoother, the rate of condensation of Pb ions on the surface decreases, because the number of pits or caves on the surface, where the dissolved Pb ions find easily their condensation sites, is thought to decrease. On the other hand, the delayed condensation of dissolved Pb ions is considered to cause a decrease in the rate of reactions for precipitation. In addition, it is generally considered that increase in the size of the PbO_2 crystals causes a decrease in the specific surface area of PbO_2 (Table 1). The decreased specific surface area of PbO_2, which represents a decrease in true reaction surface area of PbO_2, is assumed to cause an increase in current density on the reaction surface, and to eventually cause an increase in the concentration or diffusion overvoltage in the discharge reactions.

3.3. *Thermal decomposition pattern of β-PbO_2 in the failed positive active material*

Figure 6 shows the X-ray powder diffraction patterns of the failed positive active material. It indicates that only traces of α-PbO_2 and $PbSO_4$ were detected. The thermal decomposition pattern of the PbO_2 in a failed positive plate was found to be similar to that of a chemically prepared PbO_2 as suggested by Caulder and Simon [3]. This means that the PbO_2 in the failed positive plate is thermally decomposed into tet-PbO

Table 1. Observed specific surface area (B.E.T.) of PbO_2 in the positive lead-acid battery plate

	Specific surface area ($m^2 g^{-1}$)
After formation	6.1
10 ₦	5.3
After failure	1.9

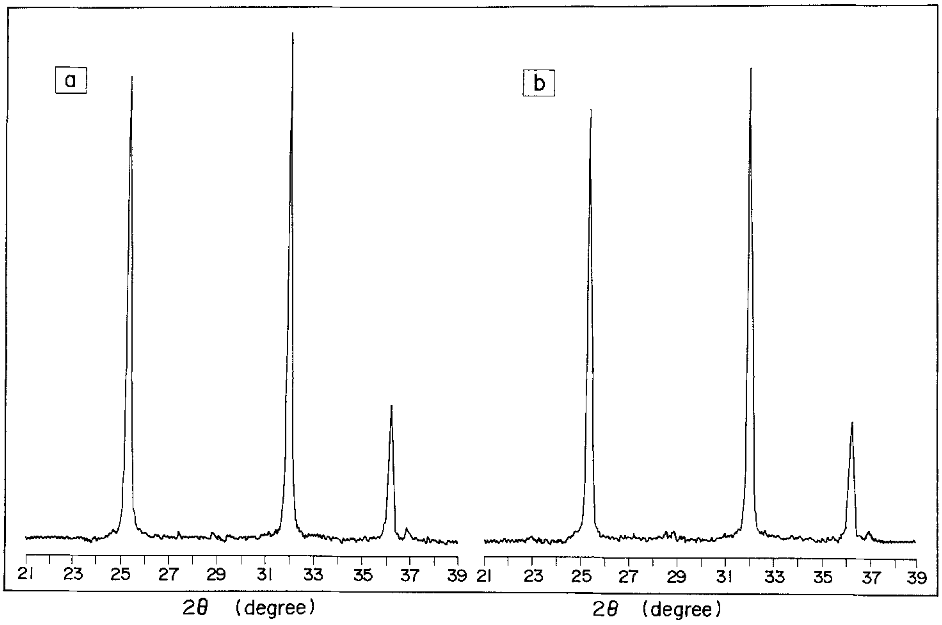

Fig. 6. X-ray powder diffraction patterns (Cu-K_α radiation) in the failed positive active material. (a) 228 ~~N~~; (b) 558 ~~N~~.

without forming β-PbO_x as an intermediate phase (Fig. 7).

$$\beta\text{-}PbO_2 \xrightarrow{338^\circ C} \alpha\text{-}PbO_x \xrightarrow{462^\circ C} Pb_3O_4 \xrightarrow{590^\circ C} \text{tet-PbO}$$

On the other hand, Faber established that the chemically produced PbO_2, with relatively higher specific surface area, was not necessarily inactive electrochemically, and concluded that hydrogen was not able to be present in the PbO_2 crystal lattice with 'PbO_6' octahedra packed precisely [16]. It may be assumed that in PbO_2 in the positive plate, in the early stage of cycling, oxygen does not easily diffuse through the crystal lattice during its thermal decomposition due to similar constraints imposed by the crystal lattice. As Pb_3O_4 is considered to be the most stable phase in which Pb^{2+} ions and Pb^{4+} ions co-exist, formation of α-PbO_x or β-PbO_x may be related to the delay of diffusion of oxygen during its thermal decomposition. This suggests a possibility that protons or water, which exist in the crystal lattice of PbO_2, hinder the diffusion of oxygen or attract oxygen. There are probably several types of PbO_2 with different thermal decomposition paths, as explained by Gillibrand and Halliwell [17, 18]. However, the thermal decomposition pattern of PbO_2 before the 228th discharge cycle was found to be very similar to that before the 558th discharge. It has not yet been confirmed why the test cell with an almost identical positive plate exhibited a cycle life twice as long as the other. This suggests that capacity loss of a positive plate of the lead–acid battery cannot be explained solely by the change that takes place in the thermal decomposition of PbO_2, considered to be related to a reordering or stabilization of PbO_2 crystal lattice. An increase in contact resistance at the interface between crystals of PbO_2 in the positive active material could perhaps be an additional factor.

3.4. *Morphologies of β-PbO_2 crystals in the failed positive active material*

After the failure of the positive plate, sizes of PbO_2 crystals were found to exceed 2 μm, about 40–50 times that of the smallest crystals of PbO_2 in an uncycled

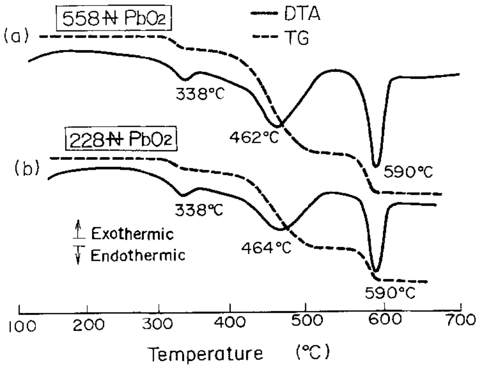

Fig. 7. DTA–TG curves of β-PbO_2 in the failed positive plates. (Reference sample: α-Al_2O_3, heating rate: 5°C min^{-1}, atmosphere: air.) (a) β-PbO_2 in the failed positive plate before 558th discharge; (b) β-PbO_2 in the failed positive plate before 228th discharge.

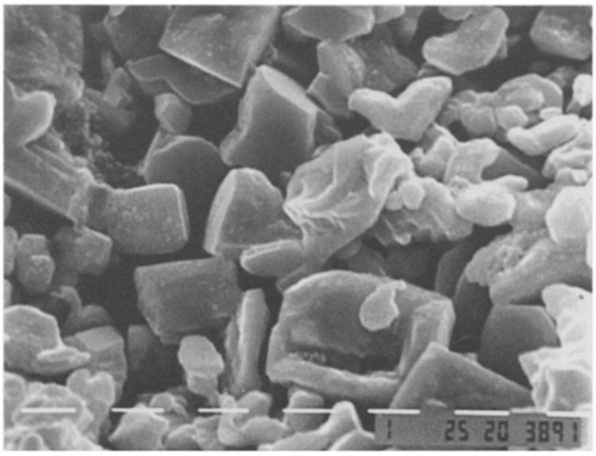

Fig. 8. β-PbO_2 crystals in the failed positive plate which are about 40–50 times larger than the initial crystals in the uncycled positive plate. (Each white line corresponds to 1 μm.)

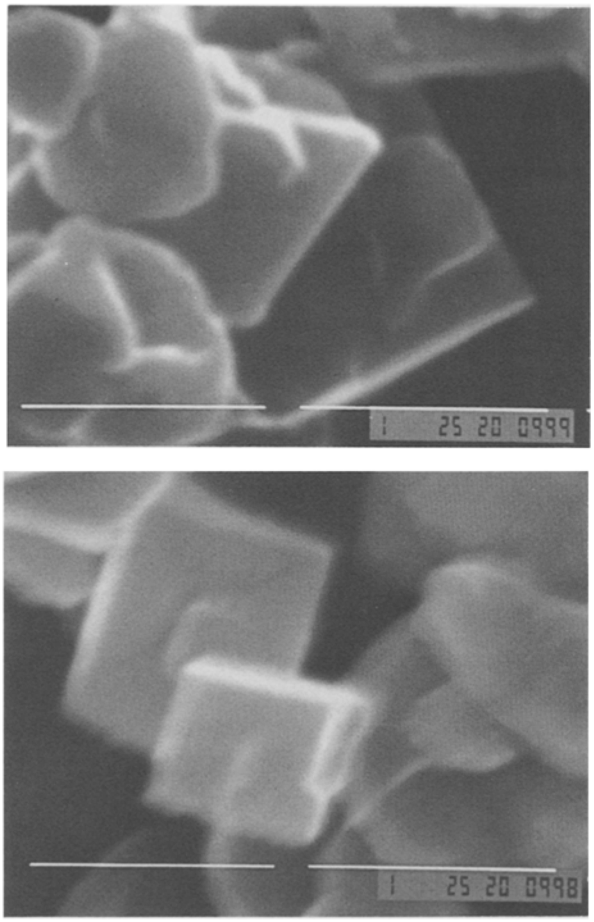

Fig. 9. β-PbO_2 crystals with the smallest size in the failed positive plate. Observed are the traces of the spiral growth on the surface of PbO_2 crystals. (Each white line corresponds to 1 μm.)

positive plate (Fig. 8). Figure 9 shows that the PbO_2 crystals with the smallest size in the failed positive plates are at least 10 times that in an uncycled positive plate. Traces of spiral growth appear on their surface. It is assumed, as the most possible mechanism for growing size of the PbO_2, that numerous PbO_2 crystals of smaller size are bound together, leading toward conglomeration in larger crystals in a similar manner as occurs in the sintering process for pottery. For the case of a flooded lead-acid cell, Pavlov and Bashtavelova concluded that an 'agglomerate' structure was transformed into a 'crystalline-type' structure which led to softening and shedding of the positive active material, causing an eventual failure [19]. Thus, in the case of the flooded lead-acid cell, it is, in general, difficult to observe the grown PbO_2 crystals of size larger than 1 μm even in the failed positive plate. On the other hand, no shedding occurs in the case of a sealed lead-acid cell, because its positive and negative plates are kept assembled under a relatively high pressure, contacting with the separator tightly in the container. Thus the 'crystalline-type' structure further continues to develop in a positive plate, even after the positive active material is very soft. Then it may be assumed that a degree of transformation into the 'crystalline-type' structure in the positive plate is relatively higher in a sealed lead-acid cell than in a flooded lead-acid cell and that PbO_2 crystals can grow appreciably to crystal sizes larger than 2 μm in a sealed lead-acid cell until it finally fails. Figure 10 shows the change in the rate of transformation of PbO_2 to $PbSO_4$ after soaking of 10 g of the ground PbO_2 in 100 ml H_2SO_4 with a specific gravity of 1.300 at 50° C for 10 days. The stability of PbO_2 crystals in the failed positive plate was found to be at least 10 times that in an uncycled positive plate after an electrochemical formation. Increase in the stability of PbO_2 crystals may represent decrease in their electrochemical activity. In addition, it was observed that in the failed positive plate there existed among some of the largest PbO_2 crystals, twin crystals with enlarged sizes (Fig. 11). The presence of PbO_2 twin crystals in a failed positive active material suggests that the electrochemical stability of PbO_2 crystals may be greatly influenced by the sizes of the crystals and the chemical stability of their surface layers. Chemical stability of PbO_2 crystals may be controlled by the degree of crystallinity of the surface layer of PbO_2. The mechanism controlling the activity of the surface layer of PbO_2 crystal is not yet fully known. Pavlov *et al.* and Hill *et al.* assumed that hydrogen was found in the hydrolysed surface of the PbO_2 crystals: that is, hydration of the surface Pb^{4+} ions of PbO_2 crystals played an important role in their electrochemical reactivity [14, 15]. It may be that stability or electrochemical activity of PbO_2 in H_2SO_4 is controlled strongly by the properties of the crystal lattice in the surface layers of PbO_2 as characterized by the concept of $PbO_{2-\delta}(xH_2O)$ as explained by Pohl and Rickert [20], Pohl and Schlectriemen [21] and Pohl and Atlung [22, 23].

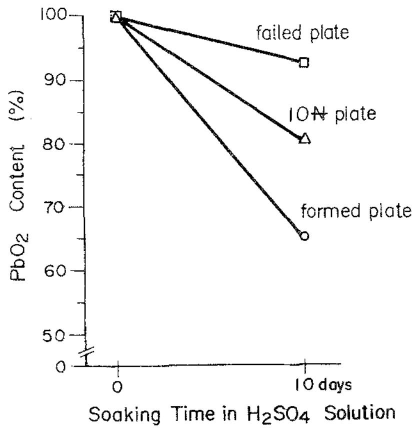

Fig. 10. Decrease in the content of PbO_2 in the positive active material after soaking in the dilute sulfuric acid with specific gravity of 1.300 at 50° C for 10 days.

4. Conclusion

The results obtained in this work confirm a correlation between the electrochemical activity or stability of PbO_2 in dilute H_2SO_4 and the process of growth or development of PbO_2 crystals in the positive plate of the lead-acid battery during charge and discharge cycles. It may be concluded that: (1) there exist, in an uncycled positive plate, two types of PbO_2 that are found thermally decomposed into tet-PbO: one with, and the other without, forming β-PbO_x as an inter-

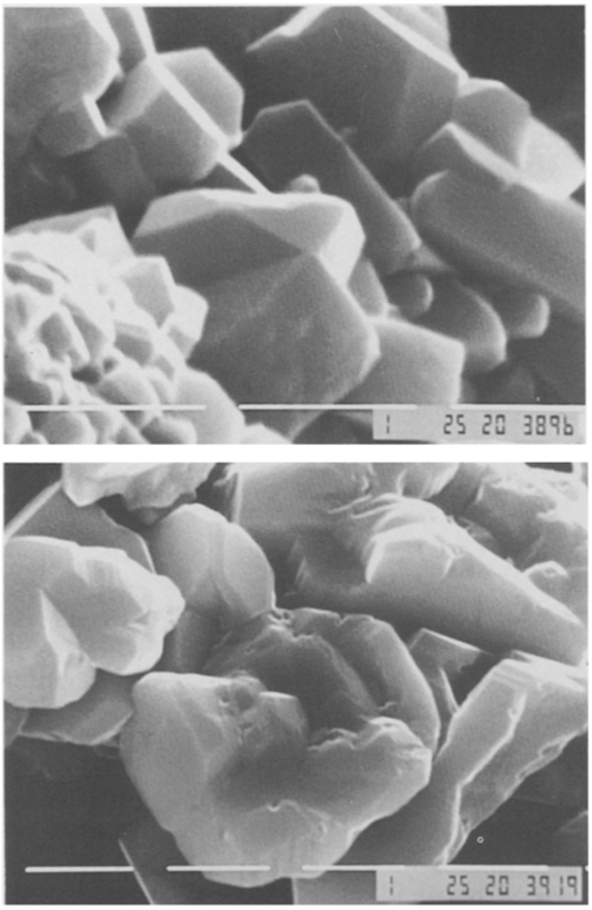

Fig. 11. PbO_2 crystals which exhibit the morphology of the twin crystals with an enlarged size. (Each white line corresponds to 1 μm.)

mediate phase; (2) the surface layers of PbO_2 crystals have a lower degree of crystallinity than the interior in the case of the uncycled positive plate; this difference in the degree of crystallinity was observed to gradually disappear with repeated cycling; (3) the stability of PbO_2 increases as the size of the PbO_2 crystals becomes larger, causing a decrease in specific surface area and surface roughness of the PbO_2 crystals; (4) decrease in the electrochemical activity or 'inactivation' of PbO_2 in a failed positive plate is greatly influenced by the growth in size of the PbO_2 crystals and at the same time by the increase in the degree of crystallinity of the surface layers of PbO_2 crystals; (5) the electrochemical reactivity of the surface layer of PbO_2 is strongly influenced by the stability of the PbO_2 crystal lattice, characterized by the concept of $PbO_{2-\delta}(xH_2O)$.

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