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On the effect of some inorganic additives on the cycle life of the positive electrodes in the lead-acid cell

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The effect of Sb_2O_3, AS_2O_3 and P_2O_5 on the cycle life of the lead–acid cell has been studied with the help of a small cell which avoids the complicating factors encountered in a complete cell. The behaviour of the active mass in absence and presence of different concentration of the additives was compared with the corresponding behaviour of pure α- and β-PbO_2. X-ray as well as microscopic examinations of the active mass were carried out.

It has been shown that Sb_2O_3 (and to a lesser extent AS_2O_3) enhance the oxidation of basic sulphate into α-PbO_2. The latter modification yields double the capacity than that obtained for β-PbO_2.

1. Introduction

The beneficial effect of Sb on the cycle life of the positive plate in the lead–acid cell has been reported by a number of authors [1–7] and various mechanisms have been proposed to explain it. It has been suggested that antimony helps in maintaining a minimum concentration of α-PbO_2 during cycling, which in turn stabilizes the plate structure. Burbank [1] believes that Sb acts as a nucleating catalyst for PbO_2 and inhibits crystal growth. Swets [2] expressed the view that Sb nucleates new α-PbO_2 crystals during charging.

It has been shown [3] that the small particle size, large specific surface area, and prismatic morphology of the PbO_2 crystals were preserved when antimony was present in the plates. Herrman and co-workers [4, 5] recently studied by means of radioactive tracers the migration of antimony in the lead–acid cell. Of the antimony removed from the positive grid during formation (1·5% of the total Sb present), 92% remained associated with the positive plate.

Simon *et al.* [6] observed acicular crystals showing atmospheric etching in cured plates for which 0·1% of Sb_2O_3 had been intentionally added to the paste during mixing. All indications were that this crystal type appeared only when Sb_2O_3 was a constituent of the paste mixture. The authors suggested further investigation of the phenomenon by using various amounts of Sb_2O_3 in the paste and combining this with capacity and life-cycle tests.

Burbank [7] applied the electron microscope to examine the $PbSO_4$ crystals depositing on 5% antimonial lead alloy during discharge of PbO_2 coating in 1·25 sp.gr. sulphuric acid. The morphology (and hence the factors terminating discharge) were compared with those obtained on pure lead.

The aim of the present work was to study the influence of Sb on the cycle life of the positive plate. For this reason a cell was used which does not only warrant high reproducibility [8] but it also avoids complicating factors encountered in a complete cell. The concentration of Sb_2O_3 in the active mass ranged from 0 to 5%.

The behaviour of ball mill oxide – Sb_2O_3 mixtures was compared with that of Sb- free mixtures on the one hand and of pure α- and β-PbO_2 on the other. X-ray and microscopic examination of the active material was conducted. It has been shown that Sb_2O_3 helps in the reduction of particle size of the oxide and enhaces the formation of α-PbO_2.

2. Experimental

The cell used was the same as previously described [8]. Half-gram quantities of the mixtures tested were pressed between a thin graphite layer and a perforated lead disc, 5 cm in diameter. The counter electrode was a lead plate. The potential was measured against Hg/HgSO$_4$/SO$_4^{2-}$ via a Luggin capillary 1 mm apart from the electrode. A valve potentiometer (type E-353) Metrohm, Switzerland was used to measure the potential. The current was kept constant with an electronic constant-current device.

The ground mixture consisted of ball mill oxide (70% PbO and 30% Pb) and acetylene black in the ratio 19 :1 (mix 1). Mixes 2-6 were made up of the ground mixture and Sb$_2$O$_3$, the latter amounting to 0·05, 0·1, 0·5, 1 and 5% of the whole mixture. Mixes 7-11 contained 0·05, 0·1, 0·2, 0·3 and 0·4% As$_2$O$_3$. Other oxides such as Sb$_2$O$_5$ and P$_2$O$_5$ were tested.

Formation was conducted in 2N-H$_2$SO$_4$ at 500 μA cm^{-2} for 6 h before transferring the electrode to a glass vessel containing 10N H$_2$SO$_4$, the counter electrode and Luggin capillary. The electrodes were discharged at 500 μA cm^{-2}. When the step corresponding to the PbO$_2$/PbSO$_4$ couple was completed, the current was reversed. Complete oxidation of PbSO$_4$ formed cathodically was indicated by a potential jump to the oxygen evolution value. Charging was then continued for about 30 min before starting the next cycle.

The X-ray diffraction patterns were obtained with the aid of a 114·83 mm Philips Debye–Sherrer powder camera and a Philips X-ray unit PW1010, using Co. Rad Fe filter. The exposure time was about 9 h.

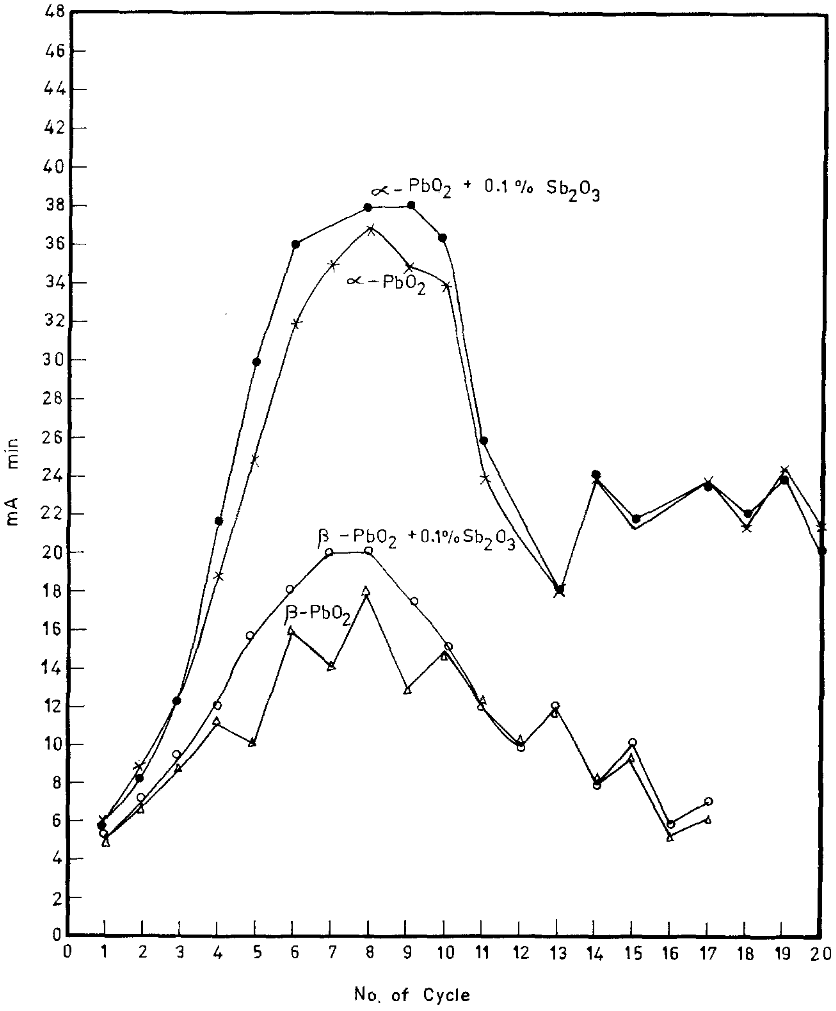

Fig. 1. Capacity against no. of cycle for α- and β-PbO$_2$ with and without Sb$_2$O$_3$.

Specimens of α-PbO_2 and β-PbO_2 were prepared according to the methods describe in references [13] respectively.

Results

Fig. 1 shows capacity – cycle plots for β- and α-PbO_2 with and without 0·1% Sb_2O_3. The curve obtained for pure β-PbO_2 manifests pronounced fluctuations and a gradual increase to a maximum value, whereupon the capacity tends to decrease with cycling. After 17 cycles the capacity drops to zero. The curve showing the addition of 0·1 Sb_2O_3 to β-PbO_2 shows that this results in the disappearance of fluctuations during the first 70% of the cycle life.

Curves for α-PbO_2 show that, both in the presence and absence of Sb_2O_3, fluctuations are absent during the first 13 cycles. It can be also seen that Sb_2O_3 additive brings about a slight increase in the capacity of α-PbO_2. It is also noteworthy that under the same conditions the maximum capacity of β-PbO_2 is slightly more than half (52%) the capacity of α-PbO_2. Moreover, the maximum capacity for the latter persists for 4 cycles as compared with only 2 cycles for the former.

Fig. 1 also shows that in the case of α-PbO_2 the capacity, after dropping from the maximum value, fluctuates about a more or less constant value which is higher than the maximum capacity reached by β-PbO_2. For the latter, on the other hand, the corresponding mean capacity continues to decrease with cycling.

Figs. 2 and 3 show plots of capacity against number of cycles for mix 1 to 11 (see Experimental).

The curve obtained for mix 1 [Fig. 2(a)] displays pronounced flutucations throughout. After 10 cycles the capacity drops to zero. Although curve (b) (mix 2) possesses nearly the same shape as curve (a), it is slightly shifted toward higher capacities. Curve (c) (mix 5) shows that the capacity increases linearly for 10 cycles and then decreases for another 5 cycles before fluctuations set in. Curves (d) and (e) possess a nearly similar shape as that obtained for mix 5. The fluctuations start after 15 and 19 cycles respectively. Curve (f) (mix 6) almost overlaps with curve (a). Fig. 2 shows that the capacities are highest at 0·1% Sb_2O_3 and decrease with further increase or decrease in the additive content.

Fig. 3 shows the capacity–cycle plots obtained

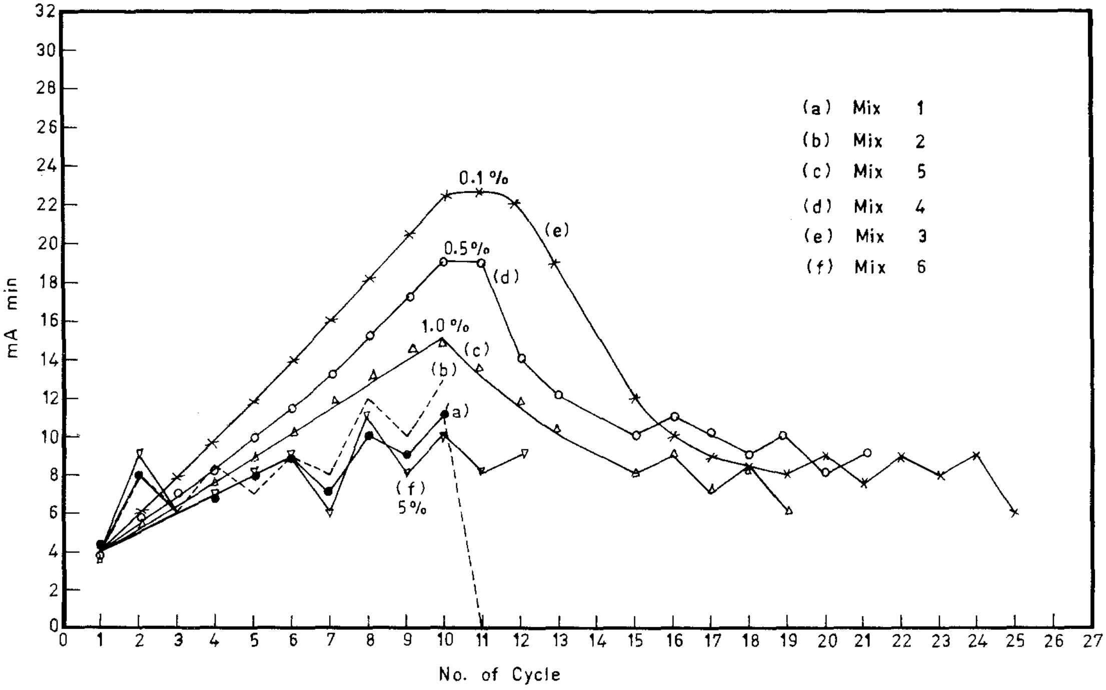

Fig. 2. Capacity against no. of cycle for mixes (1–6).

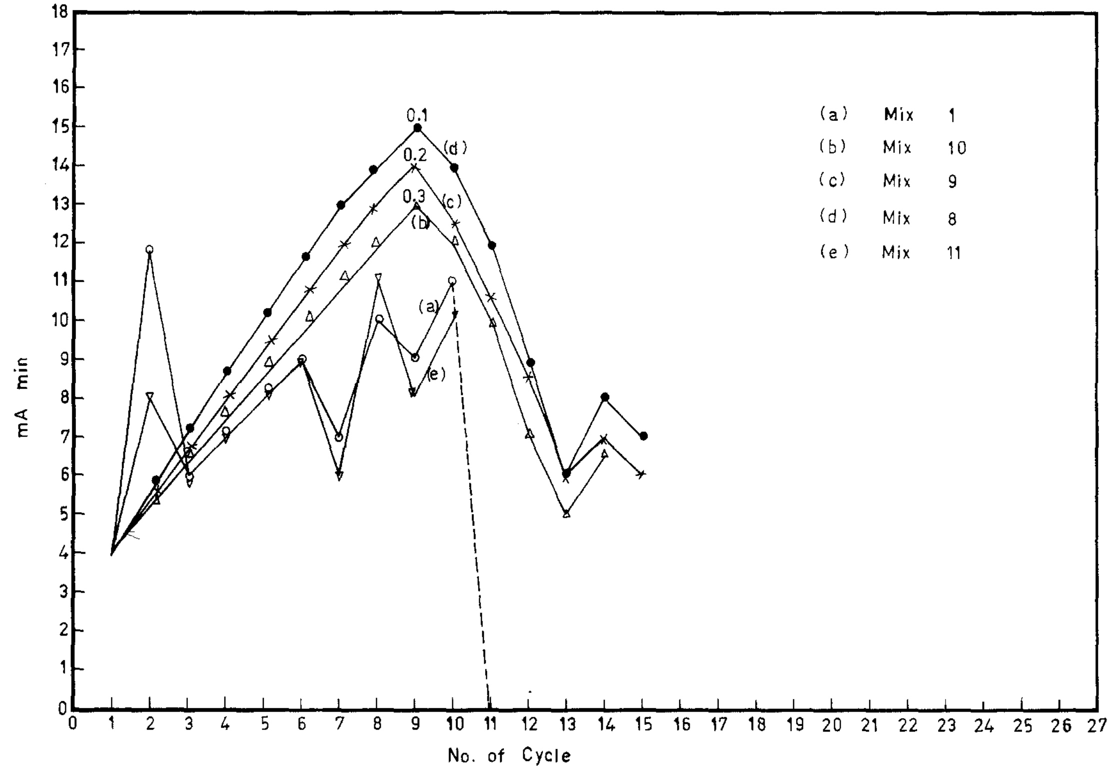

Fig. 3. Capacity against no. of cycle for mixes (7–11).

for mixes 7 to 11 containing As_2O_3 oxides. Curves (b), (c) and (d) possess a shape similar to that obtained for Sb_2O_3 oxide. Fluctuations set in after 13 cycles. Curve (e) of mix 11 displays pronounced fluctuations.

As in the case of Sb_2O_3 the capacities are highest at 0·1% and decrease with further increase in As_2O_3 comparison of Figs. 2 and 3 reveals that the maximum capacity, the capacity–cycle product and the effective range of concentrations are higher for Sb_2O_3 than for As_2O_3.

The influence of Sb_2O_3 and As_2O_3 on the morphology microstructure of PbO_2 is demonstrated by Fig. 4. It can be clearly seen that the Sb_2O_3-free samples contain some large crystals which are absent from the corresponding active material containing Sb_2O_3.

The pentoxides of antimony and phosphorous were found to be ineffective. The curves were nearly similar to that obtained for mix 1.

Fig. 5 shows the X-ray diffractions patterns obtained for charged mixtures as well as for prepared α- and β-PbO_2. It is shown that the characteristic line of α-PbO_2 can be detected in the patterns for the charged mixtures and that its relative intensity is highest for the mixture containing 0·1% Sb_2O_3.

Discussion

The foregoing results show clearly the irreproducibility of surface area of β-PbO_2 after each cycle. Antimony trioxide may help in enhancing nucleation at the expense of growth. Dawson *et al.* [10, 11] suggested that in H_2SO_4 solutions Sb is present as the anions $Sb\,(SO_4)_2$, $SbOSO_4^-$ and $Sb_3SO_4^{3-}$. These ions may adsorb on the growing nuclei preventing them from reaching relatively large sizes. This effect helps in increasing and stabilizing the capacity.

The absence of fluctuations and rapid increase in capacity with cycling observed for α-modification must be ascribed to a rapid increase in surface area with the charge–discharge process. This behaviour may find explanation in the results published recently by Simon *et al.*, [6]. The authors

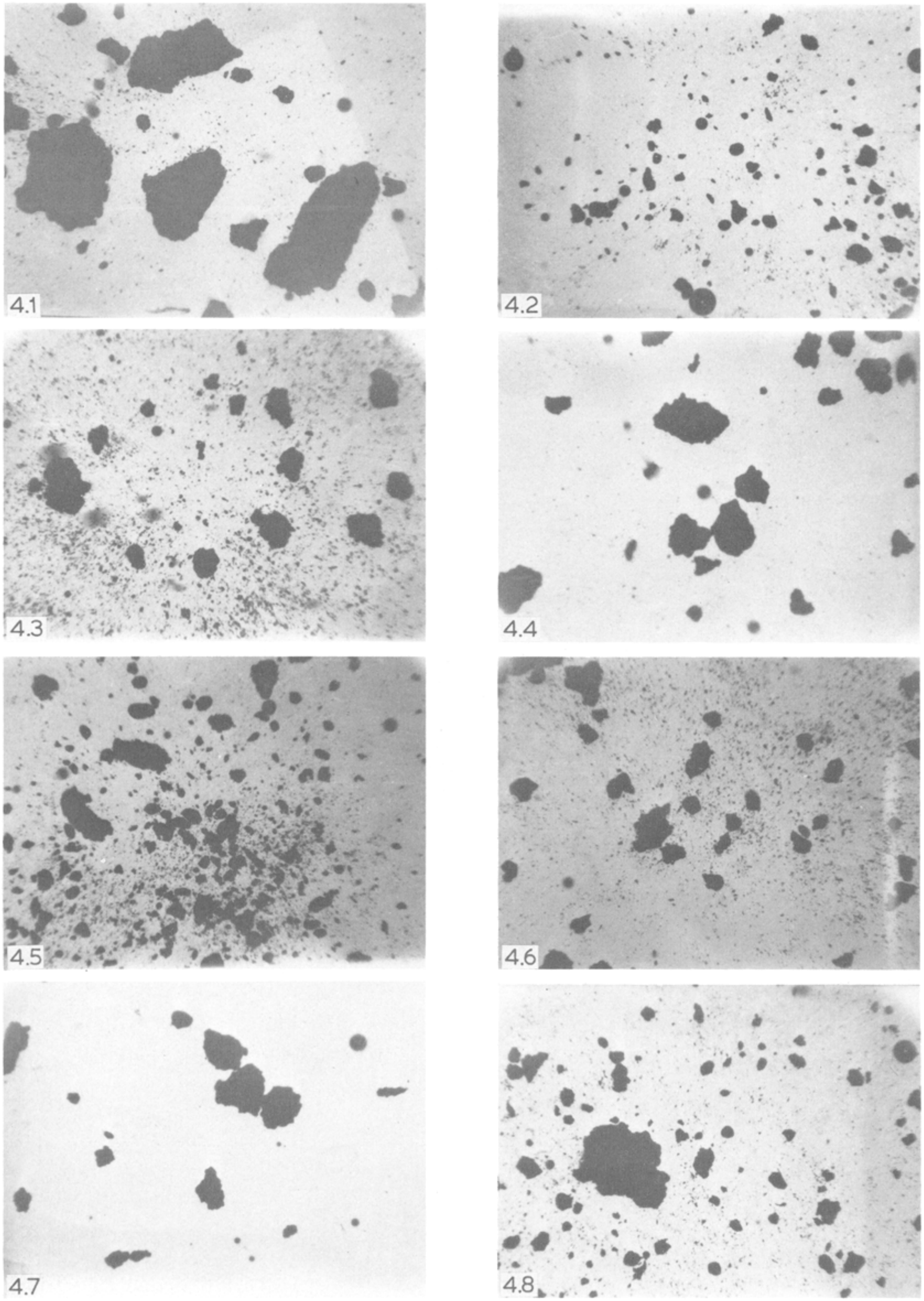

Fig. 4. The morphology microstructure of different mixtures after 9 cycles. 4.1 = mix 1; 4.2 = mix 3; 4.3 = mix 5; 4.4 = mix 6; 4.5 = mix 8; 4.6 = mix 9; 4.7 = mix 10; 4.8 = mix 11.

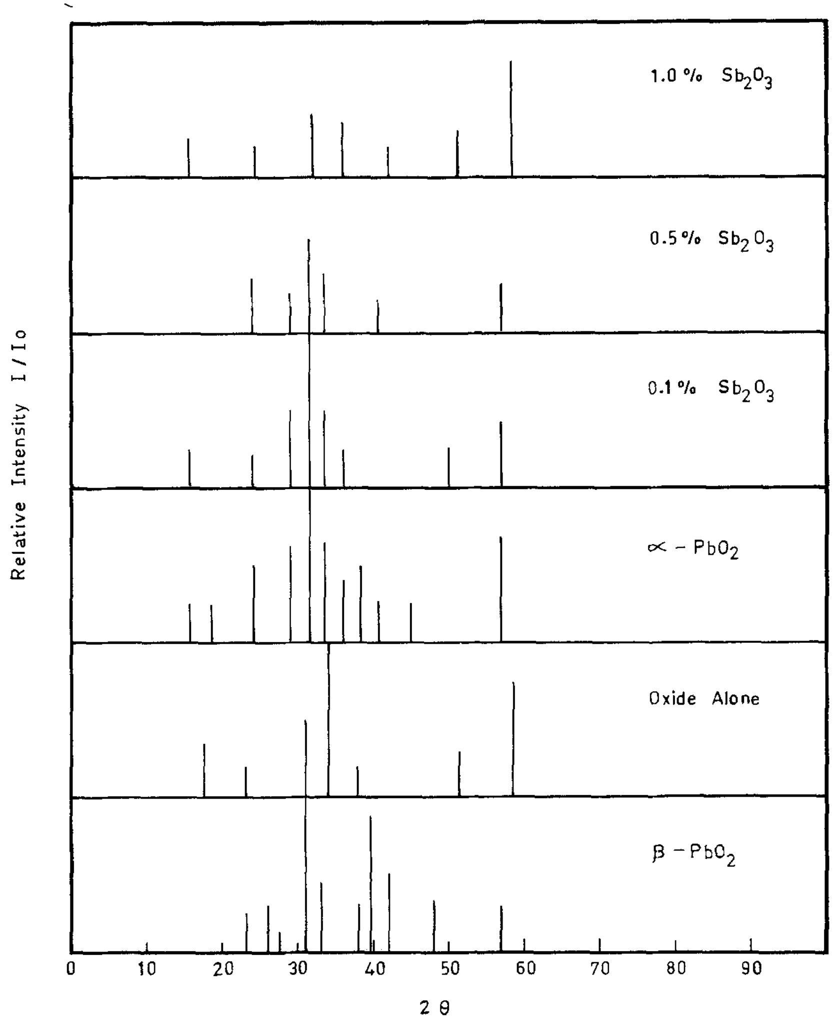

Fig. 5. X-ray diffraction patterns for different mixes.

suggested that, with cycling an inactive form of PbO_2 develops. These inactive PbO_2 particles are resistive to reduction, although fully capable of acting as nuclei for the crystallization of the active forms. Too many of these inactive nuclei will certainly result in a capacity reduction. Since these develop with cycling it is to be expected that their concentration will progressively increase resulting in the observed drop in capacity. The setting in of fluctuations after 13 cycles may be due to the partial transformation of α- to β-PbO_2.

If we assume that the inactive form arises more readily from α- rather than from β-PbO_2 the difference in behaviour between the two forms may be explained. Addition of Sb_2O_3 may compensate, though only to a very small extent, the shortage of such nucleating centres in β-PbO_2.

The behaviour of the mixture containing various amounts of Sb_2O_3 may now be explained in the light of the above discussion. Mix 1 (no additive) behaves in a similar manner to β-PbO_2. However, the absence of a maximum capacity, the low values and the early drop to zero may be ascribed plausibly to insufficient transformation of basic sulphate to the dioxide.

Fig. 2, curve (e), bears resemblances to α-PbO_2 regarding the absence of fluctuations, the high maximum capacity (double the capacity obtained in absence of Sb_2O_3) and the nearly constant mean capacity subsequent to the peak.

The difference between curves (a) and (c) in Fig. 2 cannot be solely ascribed to the action of

Sb_2O_3 on either α- or β-PbO_2 since the additive increases the maximum capacity of the two oxides only slightly. It is thus plausible to assume that the ionic species resulting from the dissolution of Sb_2O_3 in H_2SO_4 (see above) enhance the oxidation of basic sulphates to α-PbO_2 rather than to β-PbO_2. This assumption finds support in the X-ray examination of the charged mixtures.

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