

Performance characteristics of lead oxides in pasted lead/acid battery electrodes

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Abstract

The performance characteristics of lead oxides used for the pasted type of lead/acid battery plate have been investigated. The α - and β -PbO polymorphs have been prepared carefully and used for pasting model electrodes. The factors that may affect the electrical capacity of such electrodes have been studied. These are: the type of oxide; percentage of free lead; additives such as carboxymethyl cellulose, zeolite and graphite. Lead hydroxide has also been studied with special attention. Photomicrographs have been taken to examine the crystal forms that develop on the electrode surface. Finally, some industrial samples have been investigated.

Introduction

The paste used to fill the grids of lead/acid battery plates consists mainly of grey oxide and sulfuric acid. The grey oxide contains both polymorphs of PbO (the tetragonal or α -modification, and the orthorhombic or β -type) in addition to traces of Pb₃O₄ and 20–35 wt.% of unreacted lead (so-called 'free lead'). The performance characteristics of the battery plates depend on the type and ratio of both types of oxide [1], the paste composition as regards the acid/oxide ratio [2], and the temperature experienced during paste preparation. These factors determine the phase composition that develops in the paste during the curing and formation process [2, 3]. The relationship between these factors and the capacity and cycle life of the battery has been investigated by many authors. Nevertheless, a systematic study of the effects of the starting PbO modification and the free-lead content have been largely ignored.

In the present investigation, model pasted plates were prepared from either or both PbO polymorphs, in addition to different percentages of free-lead powder and minor addition agents. Lead hydroxide was also added to some pastes. The effect of these elements on the electrical capacity and the morphology of the plates was investigated during the early stages of cycle life.

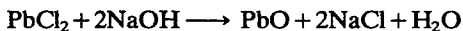
Experimental

Acids

For the preparation of pastes, 0.9 M H₂SO₄ was used, to which a 2% solution of carboxymethyl cellulose was added in some cases. The electrodes were cycled in 4.67 M H₂SO₄ (sp. gr. 1.26) at 28 °C.

Oxides

α -PbO was chemically prepared according to the procedure given in ref. 4, i.e.:

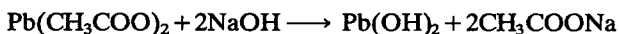


The oxide was washed, filtered and dried at 80 °C for 3 h. The product showed a well-defined X-ray diffraction pattern (XRD) for α -PbO.

Pure β -PbO was obtained by heating a sample of PbO (Carlo Erba) at 590–600 °C for 3 h [5]. The resulting yellow powder exhibited the XRD pattern of β -PbO.

Lead hydroxide

The preparation procedure [6] for $\text{Pb}(\text{OH})_2$ had to be followed strictly, as any variation in procedure yielded lead hydroxide with a different shade of colour, from white to pale green. The method involved reacting lead acetate with sodium hydroxide, i.e.:



The consistency of the product was monitored by XRD.

Industrial samples

Three samples of grey oxide were obtained from local manufacturers. They were chosen according to their method of preparation. The percentage of unreacted lead was determined for each [7] by chemical analysis.

Grids

Antimonial lead grids, Pb–3.65 wt.% Sb–0.14 wt.% Sn, were used and had dimensions of: 2.5 cm \times 2 cm \times 0.13 cm.

Pastes

The pastes were composed of α -PbO, β -PbO or mixtures of both, free-lead powder and equal volumes of distilled water and 0.9 M (5%) H_2SO_4 . To some pastes, a 2% solution of carboxymethyl cellulose solution was added, or addition ingredients were mixed with the pastes in appropriate quantities.

Minor additions

These included:

- carboxymethyl cellulose, used either alone or as a binder together with graphite or zeolite
- zeolite, an anion exchanger, grain size 106 μm
- natural graphite, average grain size 10–50 μm
- lead hydroxide, chemically prepared $\text{Pb}(\text{OH})_2$ was added to β -PbO in some cases

Pasting and curing

The grids were weighted before pasting. The paste was applied and the plates were cured for 24 h at room temperature under weight, and then for 48 h in air. The plates were reweighed to calculate the amount of paste; about 3 g was held on the grid.

Formation

For each experiment, four positive and eight negative plates were prepared. These were accommodated in four separate cell compartments. Each cell contained one

positive and two negatives. The cells were connected in series. The charging scheme was based on a nominal capacity of 0.12 Ah g^{-1} , i.e., the nominal value of the electrical capacity of the plate, C_n , was $3 \times 0.12 = 0.36 \text{ Ah}$. The applied quantity of electricity was $5 C_n \text{ Ah}$. The formation was performed by increasing the charging current in four 1-h steps; then a final high current of 500 mA was applied for 4 h.

Electrode capacity measurements

The formed electrodes were transferred to 4.67 M H_2SO_4 . Two positive and three negatives were given a primary charging at 240 mA/electrode for 1 h, then discharged through a resistance at 150 or 250 mA/electrode to a cutoff voltage of 1 V. This was repeated for five consecutive cycles. The electrical capacity of the electrode was calculated at the third cycle.

Results and discussion

The electrical capacity of positive plates C_p was determined in the absence and presence of various added constituents. The effects are presented in a systematic manner, as follows.

Free-lead content

Electrodes prepared from $\alpha\text{-PbO}$, with a free-lead content ranging between 25–35 wt.%, showed similar results for the electrode capacity at both the current densities used. A marked increase in capacity is observed at a free-lead content of 30 wt.% (Fig. 1). For electrodes prepared from $\beta\text{-PbO}$, a linear decrease in electrode capacity is observed with increase in lead content, (Fig. 2). The capacities at the lower current density are higher than those obtained at the higher current density. It is concluded that a free-lead content of 25–30 wt.% is most suited for both types and that the β -type is more suitable for use at lower current densities ($< 25 \text{ mA cm}^{-2}$).

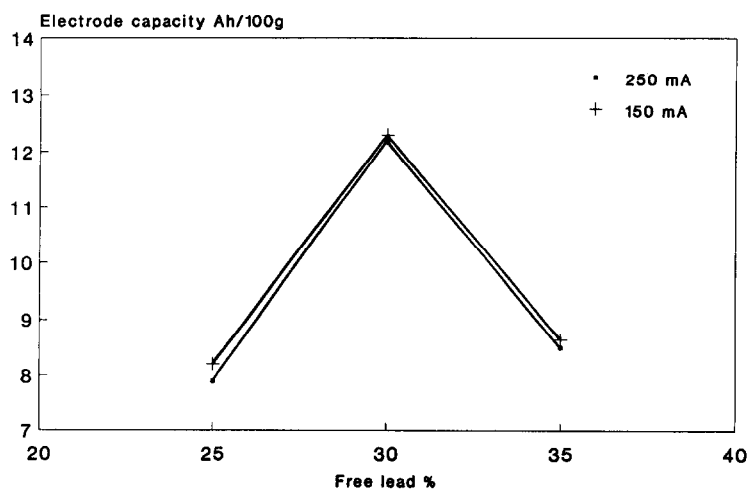


Fig. 1. Effect of free-lead content on electrode capacity; $\alpha\text{-PbO}$ precursor.

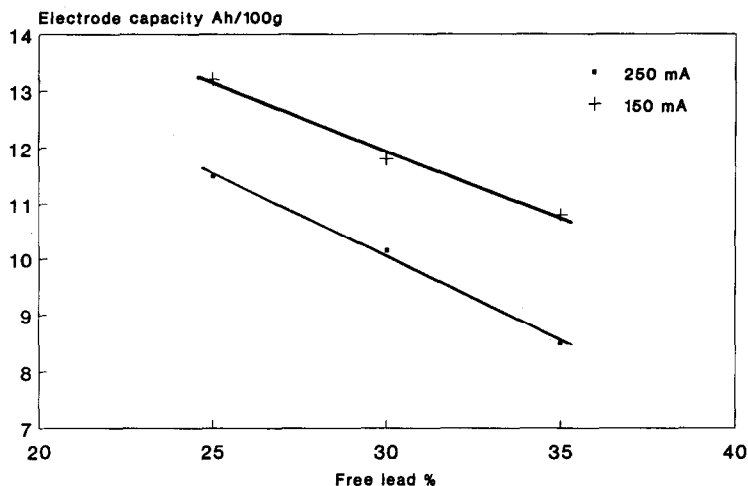


Fig. 2. Effect of free-lead content on electrode capacity; β -PbO precursor.

Minor additions to the paste

A set of experiments was made using β -PbO, 30 wt.% Pb and some minor additions in the paste. Carboxymethyl cellulose was needed as a binder. Additions of 0.5, 1 and 2 wt.% were added. At these concentrations, the binder did not affect the electrode capacity. It was subsequently used safely, especially with graphite.

Graphite

Natural anisotropic graphite was mixed with the paste in the percentages: 1, 2.5 and 5 wt.%. In all cases, 2 wt.% of carboxymethyl cellulose was mixed with the paste. Only 1 wt.% graphite was found to be beneficial; it increased the capacity slightly. Nevertheless, marked mechanical disintegration and increased gassing was observed with higher percentages of graphite.

Zeolite

An anion exchanger was investigated in the percentages: 0.5, 3, 5 and 8 wt.%. Only the lowest percentage produced an increase in the capacity of the positive electrode. Up to 3 wt.% maintained the capacity at the original value. Thus, it may be concluded that this material may not be added by more than 2 to 3 wt.% to the pastes.

Lead hydroxide

This was most interesting, the positive electrodes tested contained 5, 10 and 15 wt.%. The maximum electrode capacity was observed in presence of 10 wt.% $\text{Pb}(\text{OH})_2$, Fig. 3. The decrease found at both lower and higher percentages is not fully understood. Higher electrode capacities were obtained at higher currents, as seen in Fig. 3. It may be postulated that lead hydroxide is transformed to α -PbO and noncrystalline oxidation products. These compounds reveal features of electrode capacity similar to those obtained for α -PbO-pasted electrodes. Recently, there has been an increasing interest in the role of OH^- and H^+ ions [8] and lead hydroxide [9] on the electrode performance.

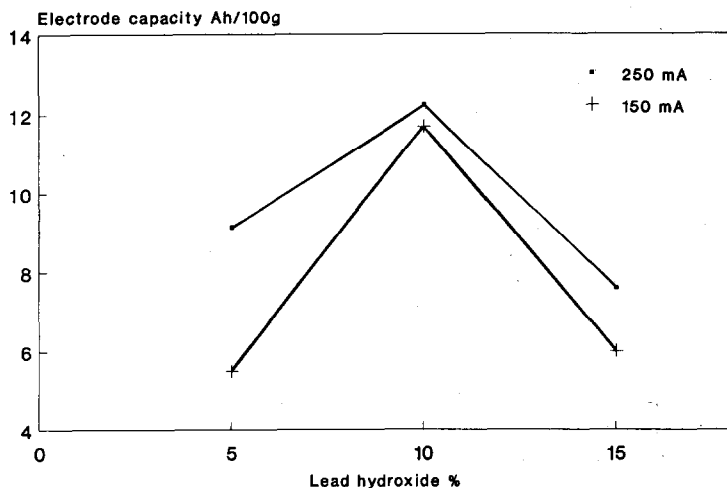


Fig. 3. Effect of lead hydroxide content on electrode capacity; β -PbO precursor.

TABLE 1

Properties of industrial samples

Sample no.	Method of preparation	Temperature of preparation (°C)	Free lead (wt.%)	Type of oxide ^a
I	Barton pot	400	36.9	Mainly β -PbO
II	Ball mill	150	25.8	α -PbO and some peaks for β -PbO
III	Rotary mill	105	11.5	Mainly α -PbO

^aAs determined by XRD phase analysis.

Industrial samples

The XRD pattern was obtained for each industrial sample. These were compared with the standard patterns for α -PbO and β -PbO, from which the prevailing type of oxide in each sample was determined qualitatively. The results are shown in Table 1.

The electrical capacity for the electrodes prepared from sample I had a value close to that for β -PbO + 35 wt.% free lead. Sample II showed an electrode capacity similar to a sample of α -PbO containing 25 wt.% free lead. It was also noticed that, at the lower current density, it gave higher electrode capacity values. This indicates the beneficial effect of β -PbO at lower current densities.

For sample III, which consists mainly of α -PbO, the electrical capacity was close to that for the α -PbO sample that contained the lowest percentage of free lead; though it exhibited a lower capacity at the lower current density.

The foregoing results suggest that the free-lead percentage in any sample controls the electrode capacity. This is despite the fact that lead was mixed as powder with the chemically prepared oxides, but was encapsulated by the oxide in the industrially prepared samples.

Electrode morphologies after discharge

After cycling cells that comprised positive and negative plates of the same composition, samples of electrodes were examined in a scanning electron microscope (SEM). The results are presented as follows.

α -PbO

The paste consisted of 70 wt.% α -PbO + 30 wt.% free lead. At a magnification of 1000, the positive plate shows a basal structure of discrete fine crystals and elongated crystals (Fig. 4(a)) that are finely ridged, as can be seen in Fig. 4(b). The negative plate shows a homogeneous crystalline structure of lead sulfate, as revealed at magnifications of 1000 and 2000 (Figs. 4(a) and (b)).

β -PbO

A paste of 70 wt.% β -PbO + 30 wt.% free lead was used. After discharge, the positive plate exhibited a more discrete basal structure. The elongated crystals are larger and different in shape compared with those in the case of the α -PbO paste. Figures 5(a) and (b) show the positive active-material morphology at magnifications of 1000 and 2000, respectively.

The morphology of the negative plate comprised a very fine grained structure topped with well-defined crystals, Fig. 5(b).

Graphite

The paste consisted of 69 wt.% β -PbO + 30 wt.% free lead + 1 wt.% graphite. The positive contained very large prismatic crystals, Fig. 6(a). This structure may be responsible for the mechanical deterioration of the plate and the decreased electrical capacity. The negative plate shows — at the same magnification — a crystalline structure with many voids (Fig. 6(b)).

Zeolite

The paste ingredients were 67 wt.% β -PbO + 30 wt.% free Pb + 3 wt.% zeolite. After the third discharge, very clear pyramidal crystals developed on the positive-plate surface, as revealed in Fig. 7(a). The surface of the negative plate had a fine-grained structure, in addition to some larger, rose-like spiral dislocations, Fig. 7(b).

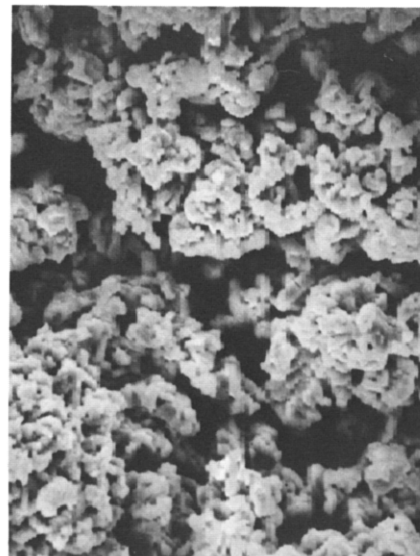
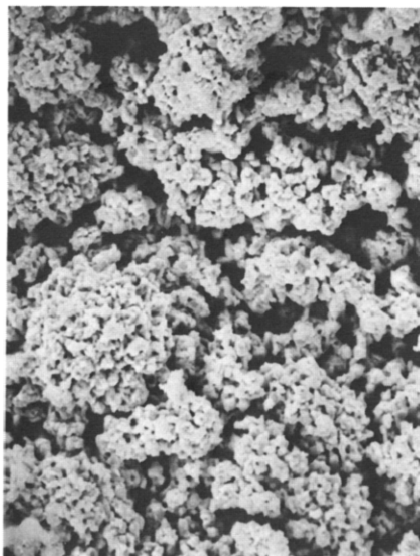
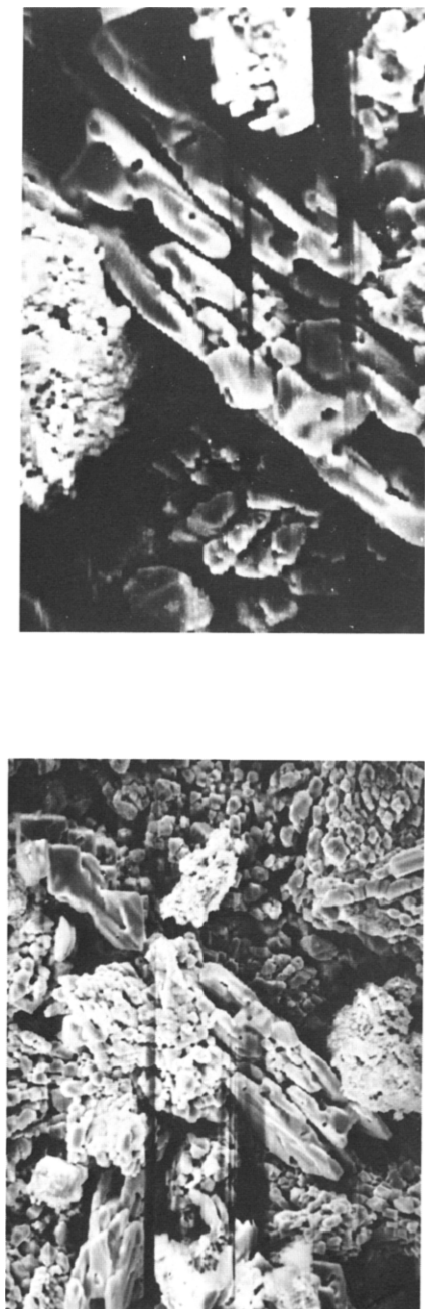
Lead hydroxide

A paste of 60 wt.% β -PbO + 30 wt.% free lead + 10 wt.% $\text{Pb}(\text{OH})_2$ was applied to the electrodes. The morphology of the positive plate at 1000 \times magnification showed a very fine-grained structure, yet not a compact one, together with some elongated crystals, Fig. 8(a). On the other hand, the negative-plate morphology was very crystalline, and rather similar to that for the paste that contained the α -PbO. This last observation supports the conclusion that $\text{Pb}(\text{OH})_2$ probably behaves like α -PbO.

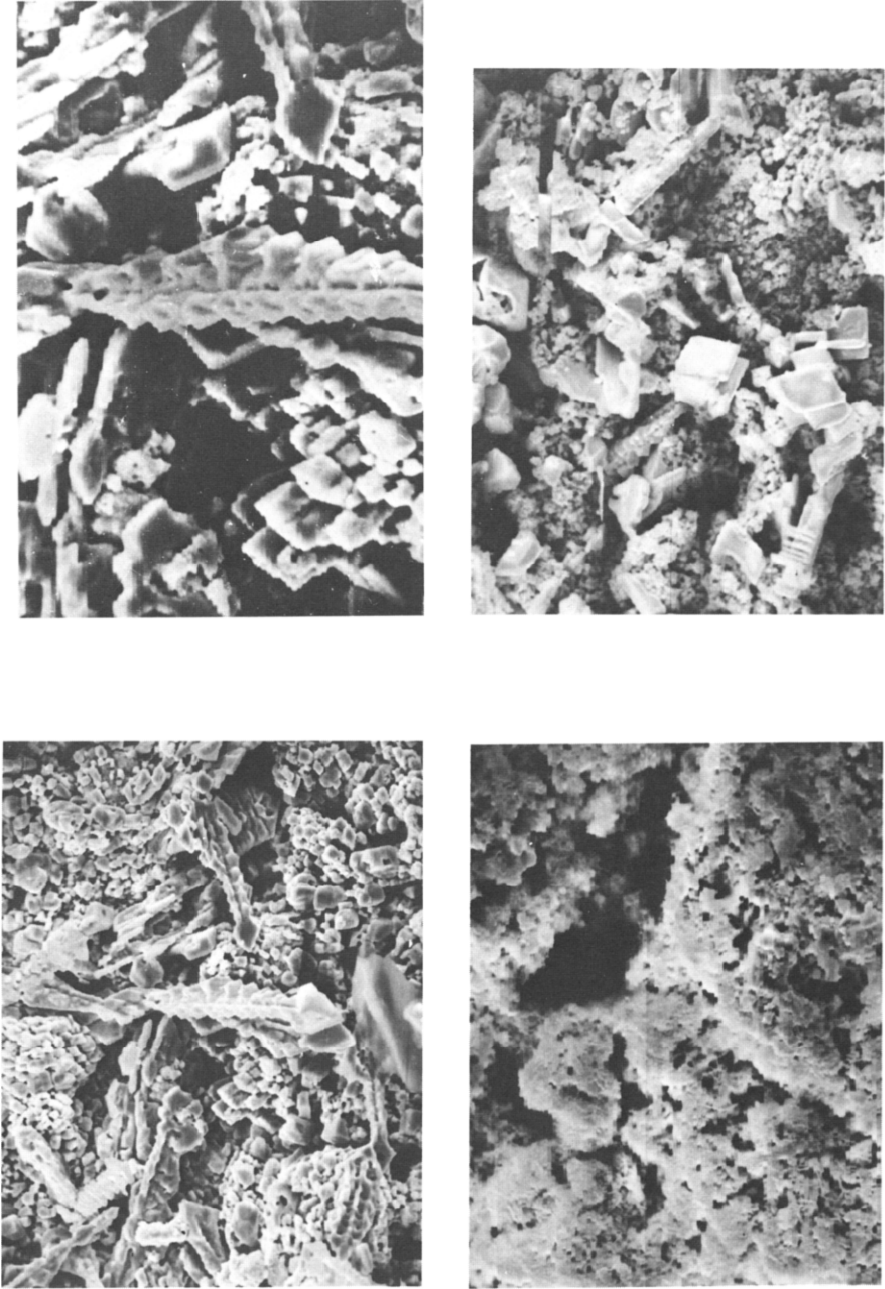
Morphology of industrial samples

Electrodes prepared of sample no. I (Barton pot), which contains mainly β -PbO, were cycled as described. The positive plate showed large prisms similar to those found in an electrode that contained graphite, see Fig. 9(a). The negative plate contained the lead sulfate crystals of varying size, Fig. 9(b).

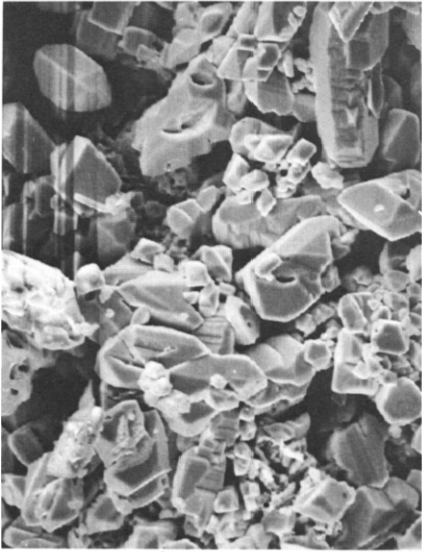
The morphology of sample II (ball mill) that contains mainly α -PbO together with some β -PbO, is presented in Fig. 10. The positive-plate morphology shows pyramidal growths, on top of which, some scattered, fine-grained material is observed (Fig. 10(a)).



(a) (b)
Fig. 4. Morphology of positive (upper) and negative (lower) plates: α -PbO + 30 wt.% free-lead precursor. (a) 1000 \times ; (b) 2000 \times .



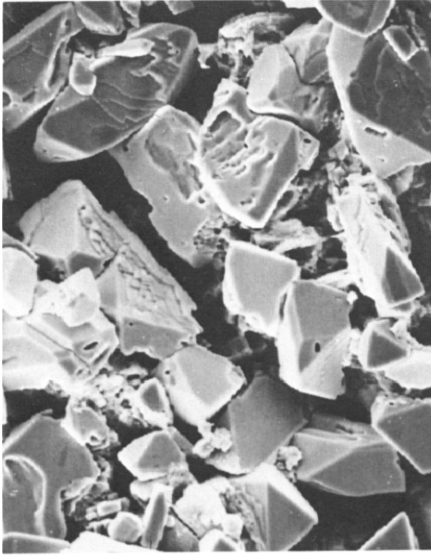
(a) (b)
Fig. 5. Morphology of positive (upper) and negative (lower) plates: β -PbO + 30 wt.% free-lead precursor. (a) 1000 \times ; (b) 2000 \times .



(a)

(b)

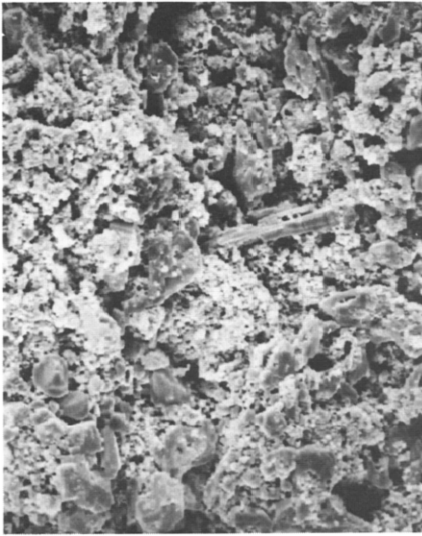
Fig. 6. Electron micrographs of plates made from 69 wt. % β -PbO + 1 wt. % graphite + 30 wt. % free lead; 1000 \times . (a) positive plate; (b) negative plate.



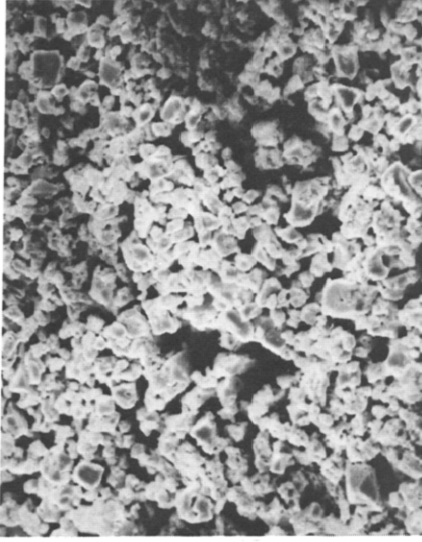
(a)

(b)

Fig. 7. Electron micrographs of plates made from 67 wt. % β -PbO + 3 wt. % zeolite + 30 wt. % free lead; 1000 \times . (a) positive plate; (b) negative plate.



(a)



(b)

Fig. 8. Electron micrographs of plates made from 60 wt. % β -PbO + 10 wt. % Pb(OH)₂ + 30 wt. % free lead; 1000 \times . (a) positive plate; (b) negative plate.



(a)



(b)

Fig. 9. Electron micrographs of plates from sample I; 1000 \times . (a) positive plate; (b) negative plate.



(a)



(b)

Fig. 10. Electron micrograph of plates made from sample II; 1000 \times . (a) positive plate; (b) negative plate.

The negative plate has a fine-grained basal structure that contains some screw dislocation structure, Fig. 10(b). These structures resemble those obtained in presence of zeolite (Fig. 7(b)). It has been stated previously that the negative plate undergoes a dissolution/precipitation reaction, during charge/discharge cycles, that results in formation of lead sulfate crystals. Organic additives control the nucleation and growth of such crystals [3]. These organic 'expanders' are also known to be adsorbed on lead and lead sulfate crystals [10–12]; the additives control the migration of Pb^{2+} ions formed during cycling of the plates. Eventually, the expanders cause an increase in the active surface area of the electrode and also enhance the formation of well-defined crystals.

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