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Morphology of PbO_2 in the Positive Plates of Lead Acid Cells

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Several preparations of PbO_2 including positive active material from lead antimony and lead calcium cells were examined by electron microscopy. The morphology of the particles is believed to have a bearing on positive paste retention and plate performance in the lead acid cell.

The anodic coating of PbO_2 formed on pure lead sheet in H_2SO_4 was found to be prismatic when first formed, but lost its prismatic character upon prolong anodization and upon cycling.

INTRODUCTION

The primary component of the positive plate in the fully charged lead acid cell is PbO_2. This material exists in two polymorphic forms; the orthorhombic low temperature α form and the tetragonal high temperature β form (1-3), both of which have been observed in the positive plate active material of the battery and in anodic corrosion products on lead (4-7). Others have examined these corrosion products, the surfaces of battery plates, and electrodeposits of PbO_2 by electron microscopy (7-11)

Mineral deposits of PbO_2, plattnerite, do not commonly exhibit well-developed crystals, but occur in nodular masses (12). Synthetic β PbO_2 crystallized by hydrothermal treatment exhibits a morphology characteristic of its rutile structure type (13), but most synthetic PbO_2 preparations do not give crystals large enough to be described by optical methods.

The lead calcium storage battery was developed for float service in the telephone system (14, 15) and proved satisfactory in such installations. In recent years the lead calcium cell has been used on submarines in float service, but many failures were experienced in the early installations. As part of an investigation of this problem, the positive plates were examined by electron microscopy. The major difference between failing and successful cells was found to be a startling contrast in morphology of the particles of PbO_2 in the positives (16-19).

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It is generally agreed that the strength of particulate conglomerates is imparted by the morphology of the several species present. For example, Sliepcevich, Gildart, and Katz (20) discussing portland cement state that "...the strength of the concrete is attributable to an abundance of crystals in the form of splines, needles and films matted together and bonded together by the amorphous mass." In agreement with this picturization, positive battery plates that contained mostly nondescript pebble-like nodular PbO_2 particles were found to soften and fail. On the other hand, plates made up of PbO_2 particles that were prismatic needles with many branches, possibly twinned, maintained capacity and retained a firm texture.

Astakhov, Kiseleva, and Kabanov (11) examined electrolytic deposits of the two polymorphs of PbO_2 by electron microscopy, and indicated that there was a relation between mechanical strength and morphology of the crystals in the electrode, and further suggested that the same considerations would apply to the stability of battery plates.

For this investigation, commercial battery plates from several manufacturers of both lead antimony and lead calcium cells were examined by electron microscopy and considerable variation was found in their particle morphology.

EXPERIMENTAL

Carbon replicas (21) were prepared of the specimens of PbO_2, and, after removal of the PbO_2 by solution in dilute HNO_3 containing H_2O_2, the replicas were examined in an RCA EMU-2B electron microscope.

Particulate specimens of PbO_2 were dispersed by floating on water in a crystallizing dish, and picked up on parlodion films supported on specimen screens of the electron microscope. The carbon replicas were deposited by vacuum evaporation. After replication, the parlodion supporting film was dissolved in acetone by flooding the sample resting on a folded piece of filter paper from which the screens were then gently lifted with fine tweezers. The carbon replica would tend to be cemented to the screen mesh by any residual softened parlodion. The specimen was then touched to clean blotting paper and dropped onto the surface of the acid H_2O_2 solution. Following solution of the PbO_2, a matter of a minute or two, the specimen was transferred to a surface of distilled water. After rinsing, it was transferred to blotting paper or onto a peg for air drying.

TABLE 1
Preparations of PbO_2 Examined in this Study

1.	Lead sheet anodized at 1.286 v versus Hg_2SO_4/Hg electrode in 1.050 sp.gr. H_2SO_4 for 68 hours. Coating was very thin and translucent.
2.	Lead sheet anodized as above for 1464 hours. Coating was dark brown to black and spalling from the surface.
3.	Particles of PbO_2 isolated from the surface of lead sheet cycled 8 times in 1.050 sp.gr. H_2SO_4 by discharging to 0.8 v versus Hg_2SO_4 /Hg electrode once each day and recharging at constant voltage until the next discharge.
4.	Positive active material from lead calcium cells showing almost entirely prismatic crystallization.
5.	Positive active material from lead calcium cells showing predominantly nodular crystallization.
6.	Positive active material from lead antimony cell showing high degree of prismatic crystallization.
7.	Positive active material characterized by clusters of prismatic material in a matrix of fairly nondescript particles.
8.	Reagent grade PbO_2.
9.	PbO_2 obtained by extraction of Pb_3O_4 with acid.

The active material from the battery plates was extracted with saturated ammonium acetate solution in order to obtain dispersion into discrete particles. Pb_3O_4 was extracted with acid to give a residue of PbO_2. PbO_2 from a cycled speciman of lead sheet was removed by extraction with saturated ammonium acetate solution. The extracted material was dispersed by placing a drop of the slurry on the surface of distilled water in a crystallizing dish where the particles would float out across the surface, and these were then mounted for replication as described above.

Anodized lead sheet was replicated directly after blotting dry. The surface was scored into small squares and the sample was gently lowered into dilute acetic acid containing H_2O_2. The carbon films floated free on the surface and were transferred to distilled water for rinsing. The films were then picked up on specimen screens of the electron microscope and air dried.

Table 1 lists the several preparations examined in this study.

RESULTS AND DISCUSSION

Anodic Corrosion Product on Pure Lead

Earlier studies by electron diffraction (22) showed that the initial deposition of PbO_2 on pure lead by anodization in H_2SO_4 was preferentially oriented, and upon further anodization the deposit had random orientation. The initial deposit appears to be entirely prismatic (Fig. 1) and clusters of crystallites of similar orientation are clearly discernible. This is the kind of deposit that is too thin to give x-ray diffraction patterns but strong electron diffraction patterns are registered. The areas of similarly oriented crystallites confirm the electron diffraction observations of preferred orientation reported in the earlier studies. When the deposit was thickened by prolonged anodization, the coating began to spall from the surface. The electron micrograph (Fig. 2) of the anodic sample at this stage suggests that there is a total loss in prismatic character, and also shows the flaky nature of the coating. A coating of this type gives a polycrystalline diffraction pattern. As the speciman was cycled,

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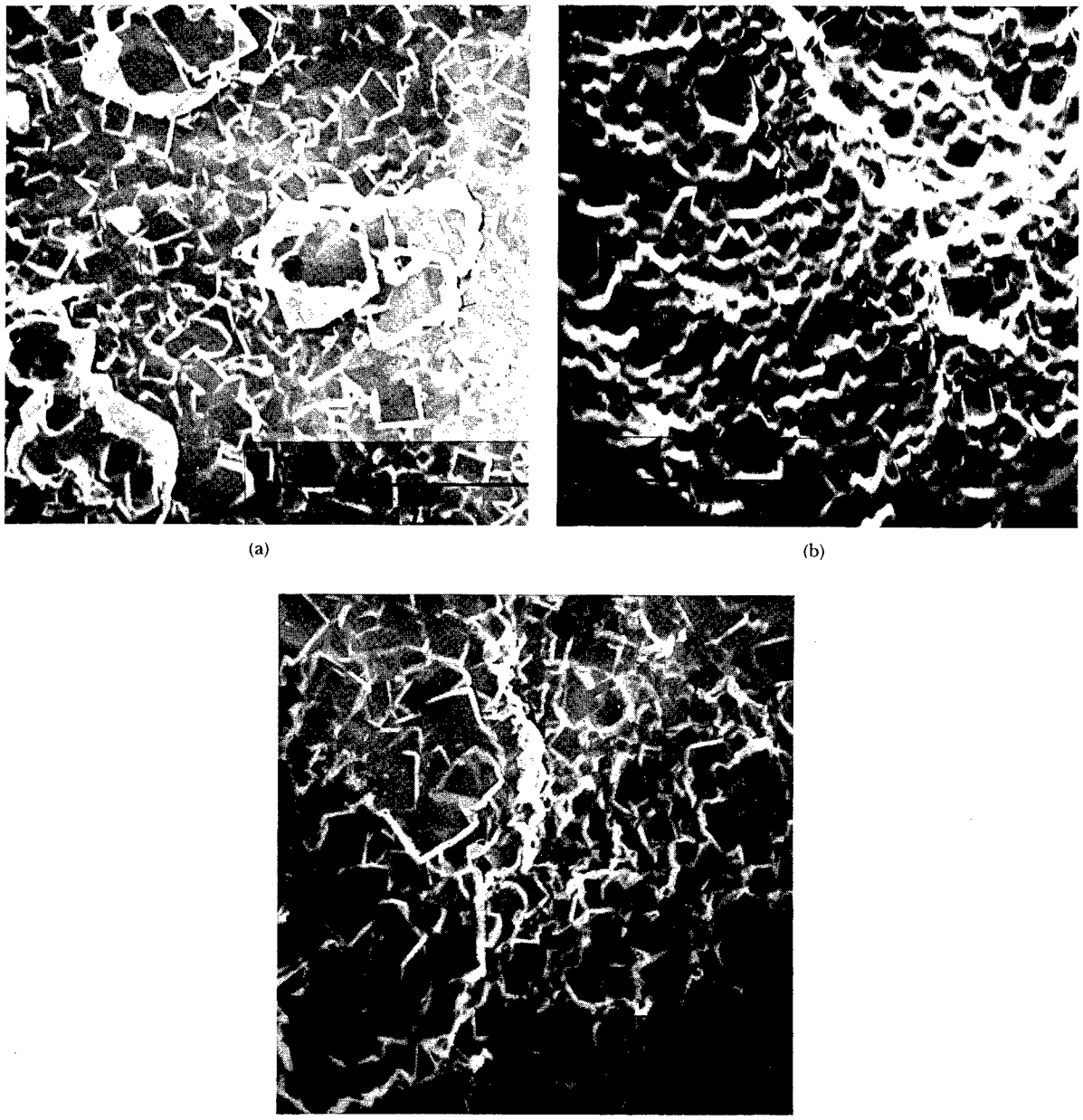

(a) (b) (c)

Fig. 1 — Three specimens of pure lead sheet anodized in H_2SO_4 for 68 hrs. This thin coating of PbO_2 is prismatic and appears to exhibit definite areas of preferred orientation of the crystallites.

the coating continued to shed, and it has been shown by Feitknecht and Gaumann (7, 8) that the surface becomes covered with nodular concretions of PbO_2. The individual particles are submicron in size and appear to be spheriodal. Figure 3 shows a carbon replica of such particles isolated from the surface of the cycled specimen. These particles are rather uniform in size and appear to be approximately 0.1μ in diameter. This is in the same range observed by Feitknecht and Gaumann (8) and Burbank (23), but on the basis of x-ray line broadening, Feitknecht (7) estimated

Fig. 2 — Pure lead sheet anodized in H_2SO_4 for 1464 hrs. The individual crystallites of thinner films (Fig. 1) have disappeared, and the coating is flaking away from the surface.

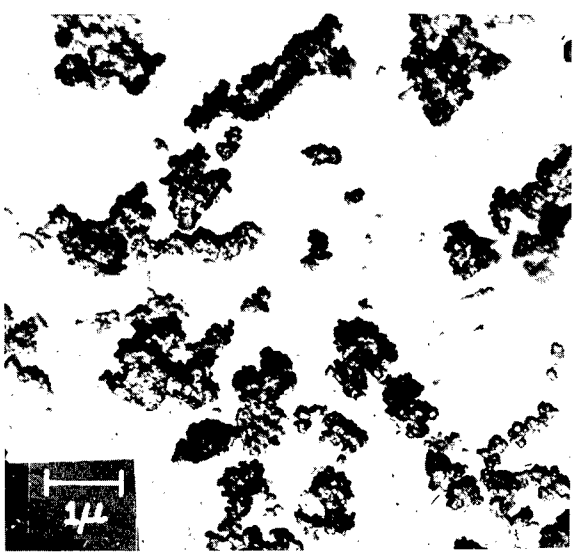

Fig. 3 — Particles of PbO_2 isolated from a sheet of pure lead cycled 8 times in H_2SO_4. The individual particles are difficult to disperse and tend to clump together, however they appear to be approximately 0.1μ in diameter, and to be spheroidal. These particles are believed to be obtained by conversion from $PbSO_4$, and unless bound by mechanical or chemical forces, readily detach themselves from the electrode surface.

the particles to be about 100A. It is difficult to obtain good dispersion of such fine material by the techniques used in this work, but these certainly lie within the colloidal range. It is these particles that form a reddish cloud in the electrolyte near the electrode surface if gas evolution is vigorous enough, and in turn give rise to lead trees as they circulate in the cell and come into contact with the negative electrode. As the anodic coating builds up, it tends to lose electrical contact with the lead surface and continuity between individual particles. In Planté plate formation, it is necessary to retain the PbO_2 particles in a mass on the surface to get adequate capacity from the plates. Feitknecht's electron micrographs taken during self-discharge show that prismatic sulfate crystals grow during open-circuit stand. In a study of lead calcium cells (16-19) it was shown that even in pasted plates when the active material is composed of nondescript nodular PbO_2 particles, the plates would not give satisfactory capacity until sufficient prismatic $PbSO_4$ had been formed to bind the mass together. Planté in 1887 (24) described similar behavior thus: "A singular phenomenon frequently observed with secondary lead cells: it is found that immediately after charging, the battery will not pass enough current to heat a platinum wire, but after standing on open-circuit for about 24 hours it will heat the same wire to incandescence." He attributed this to a film of gas, but it appears from the electron microscopic investigations that during the 24-hour stand sufficient sulfate crystallized to cement the particles into a conducting mass.

Battery Plates

The positive active material from commercial battery plates shows a wide variety of particle morphology varying from complex prismatic crystals to nodular forms. Some commercial plates appear to be entirely prismatic in nature while others are entirely nondescript nodular formations. Still others contain clusters of well-developed prismatic crystals in a matrix of nondescript material. These formations are illustrated in the electron micrographs shown in Figs. 4-8. It has been shown in an earlier study (16-19) that plates containing large amounts of prismatic material maintained capacity whereas plates comprised mainly of nondescript particles suffered excessive capacity loss, and failed because of softening of

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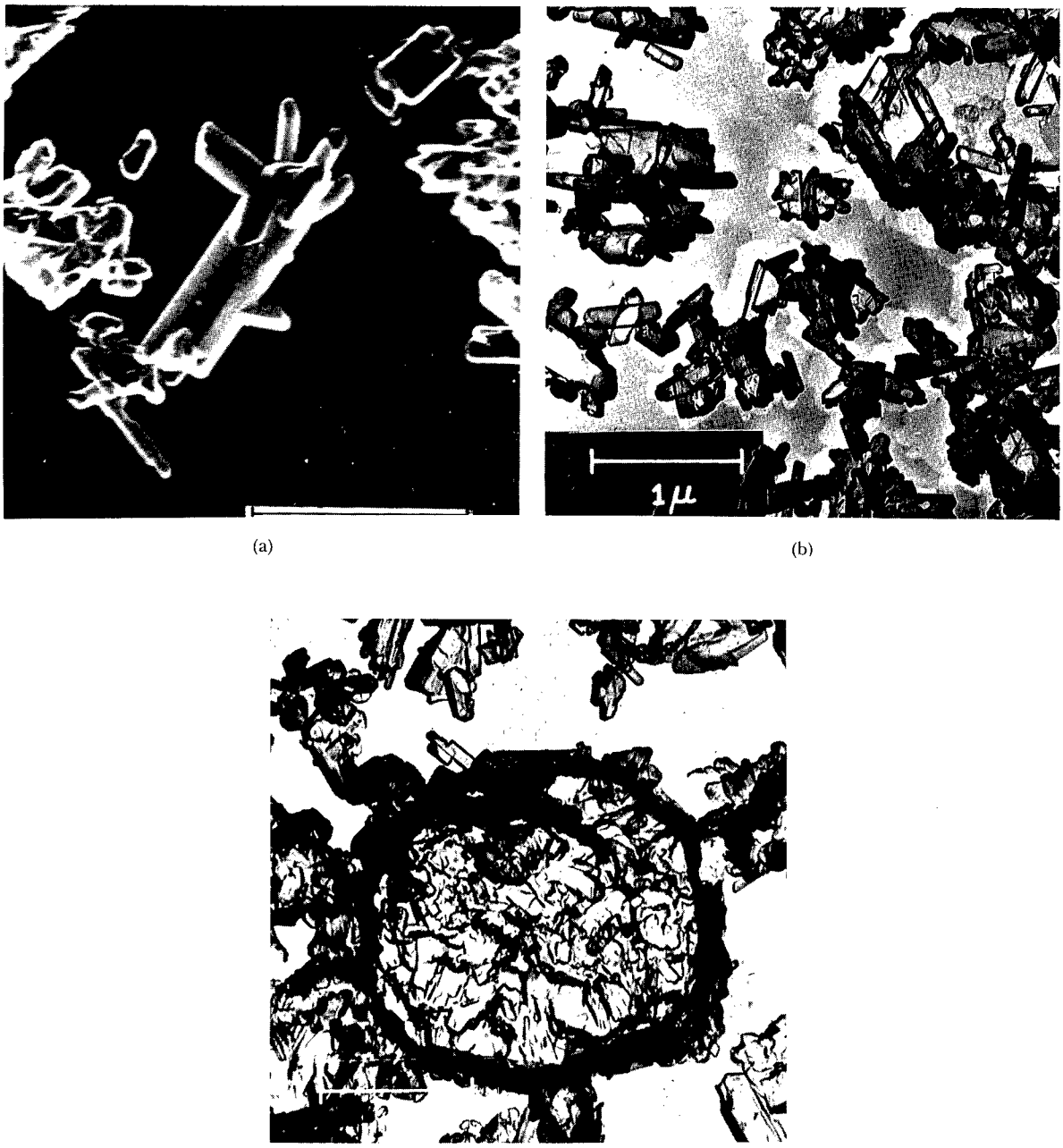
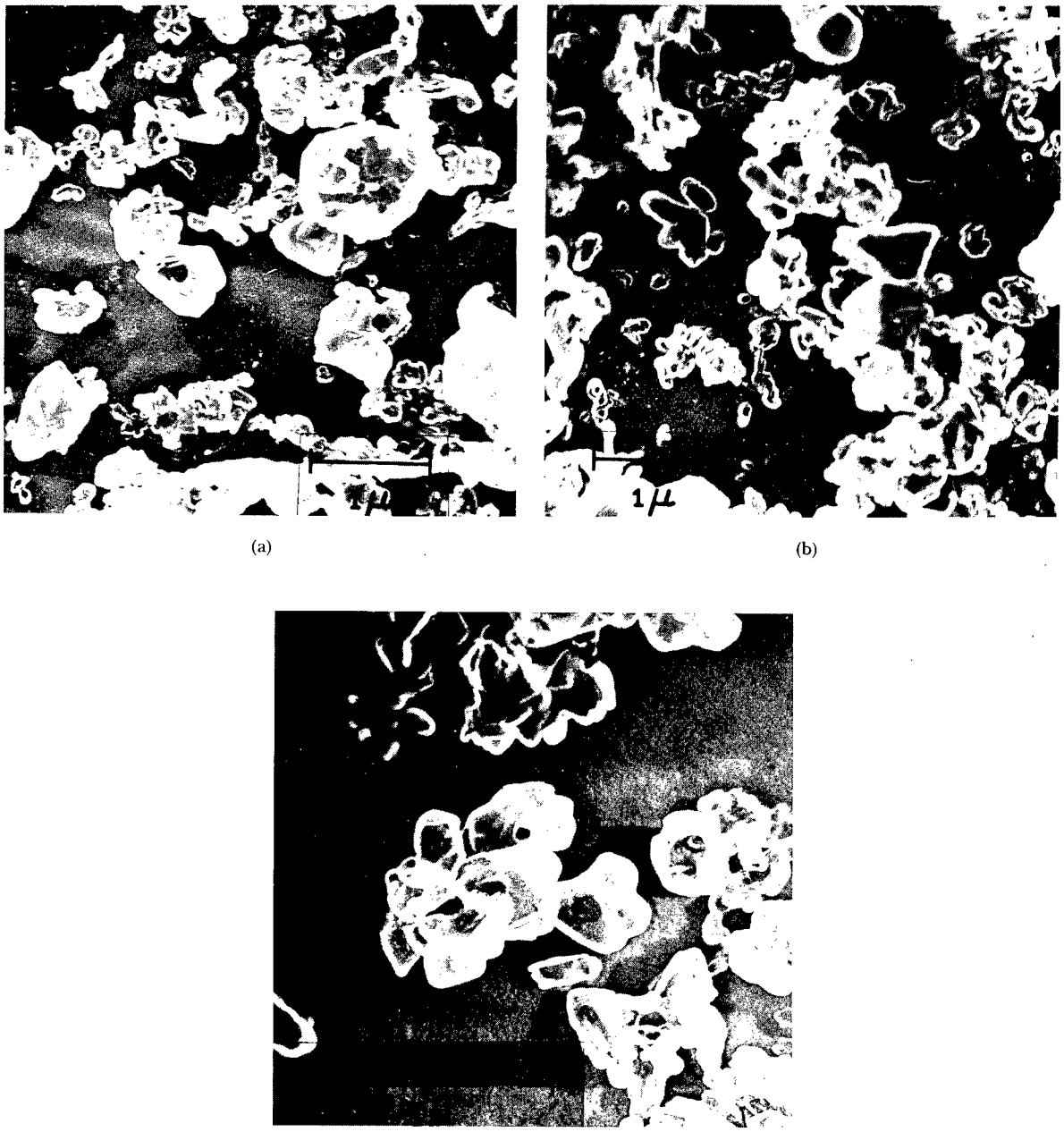


(a) (b) (c)

Fig. 4 — Three specimens of positive active material from lead calcium cells showing almost entirely prismatic crystallization. Plates composed of these particles remained firm and retained capacity in shallow cycling tests.



(a) (b) (c)

Fig. 5 — Three specimens of positive active material from lead calcium cells showing predominantly nodular crystallization. Plates composed of these particles softened and failed after a few weeks of shallow cycle testing.

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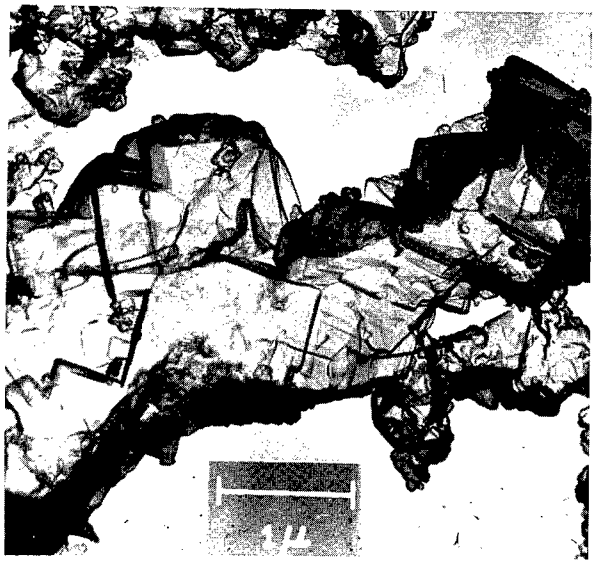


Fig. 6 — Positive active material from a lead antimony cell. Massive prismatic conglomerates were characteristic of the active material in this sample.

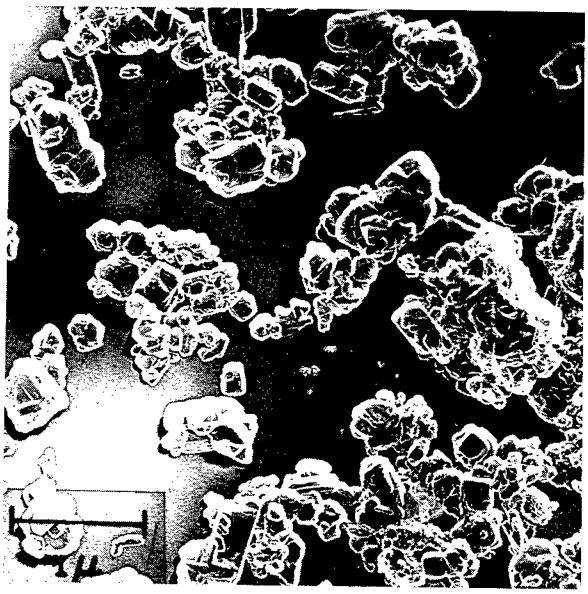


Fig. 7 — A large cluster of prismatic crystals showing many side arms illustrating the interlocking believed to be associated with morphology of this type which is believed to impart mechanical strength to the positive paste

the active mass. If the plates containing nondescript particles were operated in such a way as to retain prismatic sulfate crystals in the active

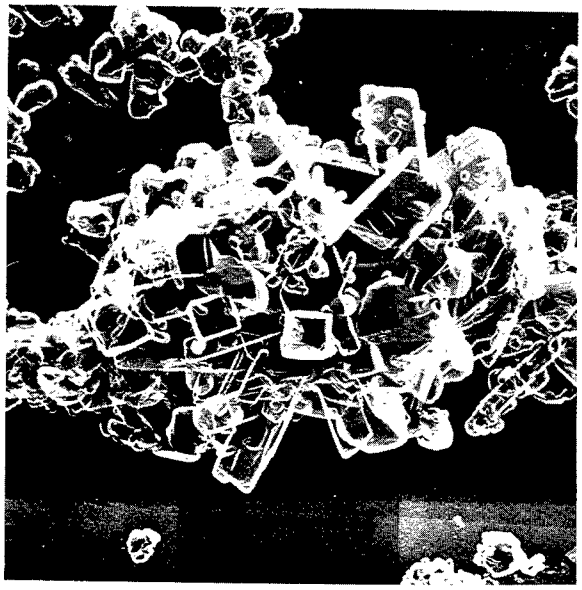


Fig. 8 — Particles of positive active material showing an intermediate development of prismatic character. These particles retain some prismatic form but are not characterized by intricate branching and would not be expected to impart mechanical strength to the active mass.

material, satisfactory performance could be obtained from them. It is apparent that morphology of the particles plays a significant role in the retention of the positive active material in the lead acid cell.

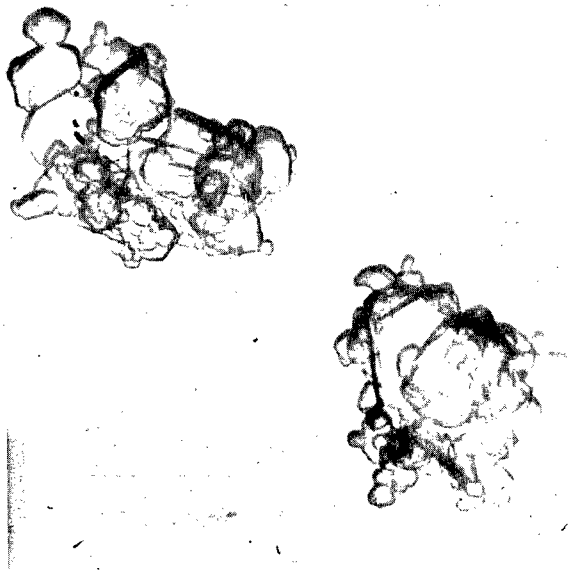
Miscellaneous Preparations

Reagent grade PbO_2 was also examined as a matter of curiosity, and the sample available at this Laboratory showed a mixture of prismatic and nondescript particles (Fig. 9). The growth habit of the prismatic crystals was different from that exhibited by the prismatic battery samples.

If Pb_3O_4 is extracted with acids that react with the divalent lead, PbO_2 is deposited. The lattice of Pb_3O_4 contains both divalent and tetravalent lead and the residue of PbO_2 is formed by deposition from solution. This material is not contained as such in the Pb_3O_4 lattice. Fig. 10 is an electron micrograph of the PbO_2 residue obtained from extracting Pb_3O_4, and shows a lack of well developed crystals. The individual particles are very small and no prismatic forms were observed.

It is concluded that the morphology of battery active materials may be correlated with the performance of the plates at least under certain

(a) Prismatic crystals showing a growth habit different from those contained in the active material of the cells illustrated in Figs. 4, 6, and 7



(b) Mixture of nodular and prismatic forms. This type of material formed the bulk of the sample.

Fig. 9 — Particles of reagent grade PbO_2

Fig. 10 — PbO_2 obtained by extraction of Pb_3O_4. The smallest individuals appear to be spheroidal, and the large particles may be conglomerates of those small units. There appears to be no tendency toward prismatic development.

conditions. Optical microscopic examination of the active materials (25) has also shown variations in structure of a different order of magnitude. These studies suggest that improvements in battery performance may be expected to result from such examinations of structures and physical mechanisms of operation. It is hoped that this study will serve to stimulate further investigations of paste morphology and its relation to electrochemical and mechanical properties of battery active materials.

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