

The Plate Materials of the Lead-Acid Cell

Part 2 - Anodic Oxidation of PbSO_4 , Pb_3SO_4 , $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$, and Orthorhombic PbO

JEANNE BURBANK

*Electrochemistry Branch
Chemistry Division*

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NAVAL RESEARCH LABORATORY
Washington, D.C.

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Previous Report in This Series

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ABSTRACT

Four compounds commonly present in the active material pastes of the lead-acid cell (PbSO_4 , Pb_3O_4 , $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$, and orthorhombic PbO) were individually oxidized anodically in dilute sulfuric acid. X-ray diffraction showed that each transformed to βPbO_2 . The anodic products were examined in the electron microscope directly and by means of carbon replicas. Lead sulfate and $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ formed primarily complex dendritic crystals of PbO_2 ; Pb_3O_4 gave rise to clusters of prismatic tabular crystals and nondescript nodules; and orthorhombic PbO was transformed to agglomerates of nondescript particles showing no evidence of prismatic dendritic crystallization.

These forms of crystallization are compared with those observed in commercial battery plates including lead-calcium cells giving satisfactory and unsatisfactory float performance.

The morphologies of the PbO_2 particles resulting from the electrochemical transformations depended upon the source material, and their probable growth mechanisms are discussed.

PROBLEM STATUS

This report concludes one phase of the problem; work on other phases is continuing

AUTHORIZATION

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THE PLATE MATERIALS OF THE LEAD-ACID CELL

PART 2 - ANODIC OXIDATION OF PbSO_4 , Pb_3O_4 , $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$, AND ORTHORHOMBIC PbO

INTRODUCTION

Among battery systems, the lead-acid battery is universally recognized as a reliable power source of outstanding durability, particularly when the grid is a lead-antimony alloy. Since the conversion to nuclear power in recent years, submarine cells have been fabricated with grids composed of a lead-calcium alloy owing to the health hazards introduced by possible stibine liberation during long submergences. As a result of changing to lead-calcium grids, difficulties developed with the positive active material. Investigations of the problem showed that the individual particles of PbO_2 in the active material possessed radically different morphologies in the antimonial and calcium alloy submarine cells. The failure of the positive active material in the calcium-lead cells was attributed to a poor morphology (1-3).

In the plates of the failing cells, the active material mass became soft and mushy early in life and was unable to deliver satisfactory power. Softening of the positive mass is not a new problem in the lead battery (4), but it has not been a prominent source of failure until this rather recent difficulty encountered in the nonantimonial submarine cells.

The morphology of the PbO_2 particles associated with the softening pastes was of a nondescript granular type shown in Fig. 1. In contrast, the particles observed in the active material from other satisfactory cells with either antimonial or calcium alloy grids were complex prismatic dendritic crystals, examples of which are shown in Figs. 2 and 3.

The intricacies of fabrication of active material pastes for the lead cell rest with the individual manufacturers, and their processes are known only in general terms. In an effort to determine possible sources of the prismatic dendritic crystals of PbO_2 in the satisfactory cells, a systematic examination of the morphologies developed from compounds present in raw unformed pastes was undertaken. In reality these studies are an extension of work begun much earlier at NRL by Lander (5), who established x-ray diffraction reference patterns for the basic lead sulfates. These materials, together with the compounds included in this report, comprise the major phases present in cured battery pastes prior to their "formation" to PbO_2 in the finished plates (6,7). In addition to these compounds, metallic lead and tetragonal PbO are important, but have been left for future investigations.

Three basic lead sulfates have already been studied from this morphological standpoint (8). This report describes the results obtained from anodic oxidation of PbSO_4 , Pb_3O_4 , $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ and orthorhombic PbO (massicot), designated PbO-M .

EXPERIMENTAL METHODS

Small trays (7.5 x 2.5 x 0.2 cm) were fashioned from pure lead with one end extended so that it could serve as an electrical connection above the electrolyte of the cells.

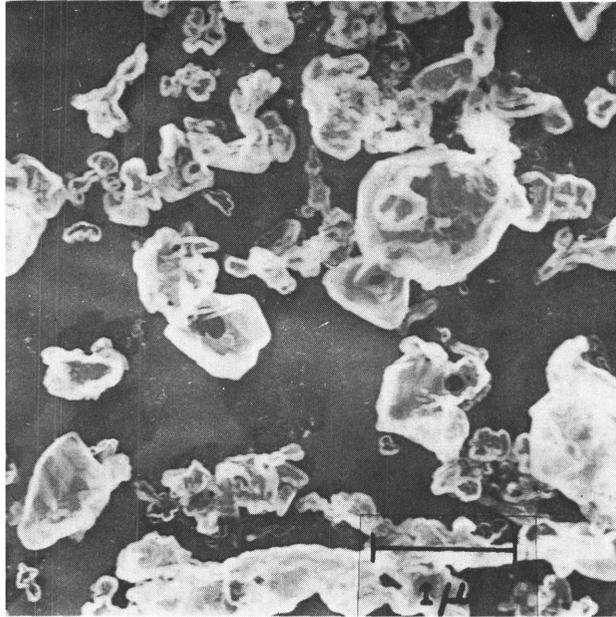


Fig. 1 - Electron micrograph of a carbon replica of particles of PbO_2 typical of the nodular formations found in the positive plates of lead-calcium submarine cells that failed in float service

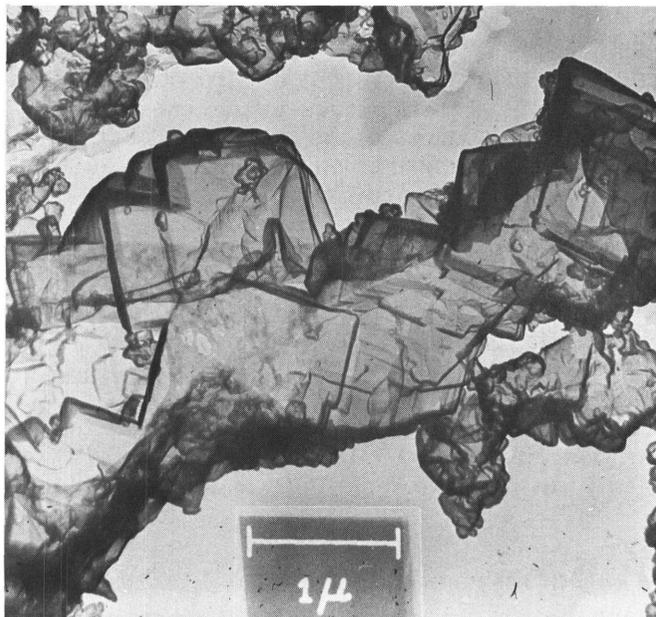


Fig. 2 - Electron micrographs of carbon replicas of PbO_2 crystals formed from the same paste as those of Fig. 1 but applied to antimonial-lead grids. These crystals are prismatic and dendritic with well-developed facets and heavy blunted stems.

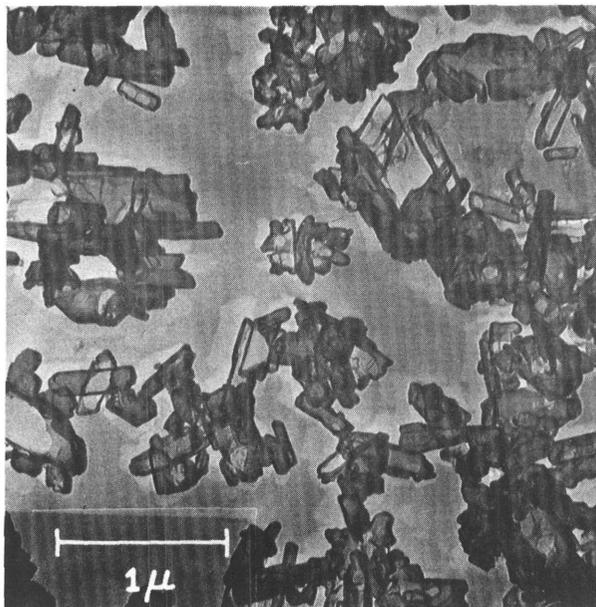


Fig. 3 - Electron micrograph of prismatic dendrites of PbO_2 found in the active material of the positive plates of small commercial lead-calcium cells that floated satisfactorily

These trays could be mounted directly in the specimen holder of an x-ray diffractometer by bending the extended end out of the path of the x-ray beam, and, bending it back into position, electrolysis could be resumed without disturbing the specimen following the x-ray examination. Prior to use, the trays were washed with saturated $NH_4C_2H_3O_2$ solution to remove the air-formed oxide films, and then rinsed in distilled water.

Stiff pastes made with distilled water and each of the compounds used for the study were pressed firmly into individual trays and the surface smoothed with a stainless steel spatula. Some of the packed trays were dried in air at $110^\circ C$ for one hour, and others were inserted directly into the electrolytic cells while still moist. This was necessary because changes in some of the pellets upon drying rendered them unsuitable for electrolysis.

Electrolytic cells were assembled in crystallizing dishes with the pasted trays in a horizontal position. Counter electrodes made with sheet lead directly faced the trays and had approximately the same apparent area. Direct current, 50-100 ma, was applied as soon as the cells were assembled, using the pasted trays as anodes. Electrolyte, 1.054 sp. gr. H_2SO_4 , was present in excess. In some instances filter paper, secured with rubber bands, was wrapped around the pellet, but usually this was not done, so that the conversion to PbO_2 could be observed visually. Anodization was continued for various lengths of time for the different materials.

X-ray diffraction examinations of the anodic products were all made with CuK_α radiation on a diffractometer. The materials were examined in the trays after blotting off excess electrolyte and on glass slide mounts after removal from the trays. Quartz was used as an external standard. The anodic products were examined by electron microscopy both directly and by carbon replication (9) using the same methods described in earlier work (1-3,8).

Reagent grade PbSO_4 , Pb_3O_4 , and yellow orthorhombic PbO were used; and $2\text{PbCO}_3 \cdot \text{Pb(OH)}_2$ was synthesized by passing CO_2 over a stirred water suspension of reagent grade orthorhombic PbO . The product showed the presence of the basic carbonate and the tetragonal oxide when examined by x-ray diffraction (10,11). As reported by Todd and Parry (12), it was difficult to prepare the basic carbonate in bulk, the sample being contaminated with enough tetragonal PbO to give it a pink color. If the CO_2 were bubbled through the suspension, normal carbonate resulted. It appears that formation of the basic carbonate is promoted by allowing the reaction to take place at the gas-liquid interface.

RESULTS

Some of the results obtained upon anodic oxidation of PbSO_4 , Pb_3O_4 , $2\text{PbCO}_3 \cdot \text{Pb(OH)}_2$, and orthorhombic PbO are summarized in Table 1. The compounds all gave rise to βPbO_2 , identified by x-ray diffraction. In all cases except for Pb_3O_4 , the metal of the tray first became covered with a thin layer of PbO_2 and started to gas oxygen visibly before the pellet began to show signs of conversion. Differences in the behavior of these materials became apparent upon pasting the trays.

Table 1
Results of Anodic Oxidation

Compound	Total Charge (Ah)	Anodic Product	Color	Remarks
PbSO_4	90.85	βPbO_2	Jet black	Complex dendritic crystals. The color of the anodic products seems to be related to the particle morphology.
Pb_3O_4	6.95	βPbO_2	Very dark brown	Tabular crystals and nondescript aggregates
$2\text{PbCO}_3 \cdot \text{Pb(OH)}_2$	90.85	βPbO_2	Jet black	Complex dendritic crystals
PbO-M	90.85	βPbO_2	Dark brown	Nondescript granules

PbSO_4

Lead sulfate remained a smooth pellet throughout the drying period prior to anodization. When submerged in the acid electrolyte, the cake cracked into numerous pieces and appeared to remain agglomerated in curds throughout the anodic treatment. The exposed metallic surfaces of the tray oxidized first, followed by slow conversion of the white sulfate crystals to dark PbO_2 near the metal-pellet contacts. The transformation gradually spread to other areas, but there were pieces of the pellet that did not become converted to PbO_2 apparently because they were not in electrical contact with the rest of the material. The PbO_2 formed from PbSO_4 was jet black and curdy, and electron microscopic examination of the particles showed that they were small complex dendritic crystals, examples of which are shown in Fig. 4.

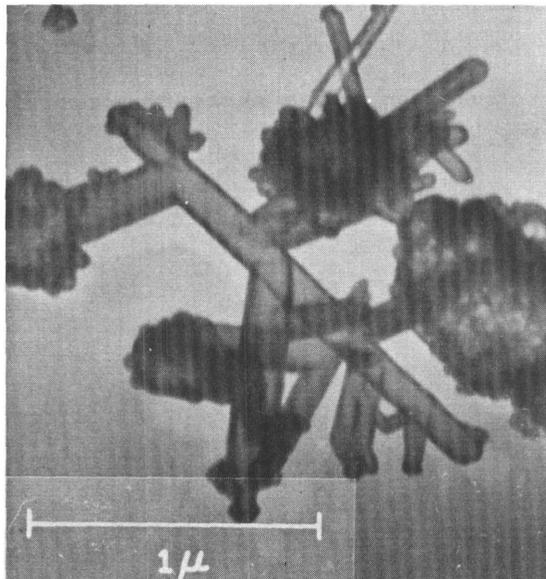


Fig. 4 - Electron micrograph of PbO_2 crystals obtained by anodic oxidation of PbSO_4

Pb_3O_4

The pellet formed from Pb_3O_4 developed three or four long thin cracks in the drying process, but essentially remained in place and did not visibly change upon insertion into the electrolyte. Conversion to PbO_2 became apparent almost immediately after anodization began, starting near the metal and along the edges of the cracks in the pellet and rimming the bright orange pieces in a band of dark brown. This conversion gradually and apparently uniformly spread to the center of each piece until the entire mass was converted. The exposed metal of the tray itself did not become coated with PbO_2 nor did it show any visible gassing until the pellet was essentially wholly converted. This suggests that the oxidation of Pb_3O_4 is kinetically easier than the oxidation of the lead itself, and the resulting PbO_2 reduced the effective current density on the metal tray to such an extent that development of a protective anodic coating was delayed. Slow or incomplete formation of the protective anodic coating on battery grids during plate formation could be a detrimental factor in using pastes containing large amounts of Pb_3O_4 . As formation of the pellet progressed, the surface of the central unconverted areas became white, probably owing to chemical reaction with the electrolyte to form normal or basic sulfates. At the end of anodization, the entire pellet was dark brown and the surface was noticeably crustier in feel than the interior. This crisp surface was probably a result of the conversion to the white material during the anodic treatment.

The particles of PbO_2 obtained from oxidation of Pb_3O_4 (Fig. 5) were mainly agglomerates of small tabular crystals and nondescript formations. The product appeared to be completely free of the dendritic type of crystallization.

$2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$

The pellet made from $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ gassed CO_2 vigorously when inserted in the electrolyte; however, enough of the pellet remained in place so that the experiment was carried through to the end. The conversion to PbO_2 took place initially on the metal

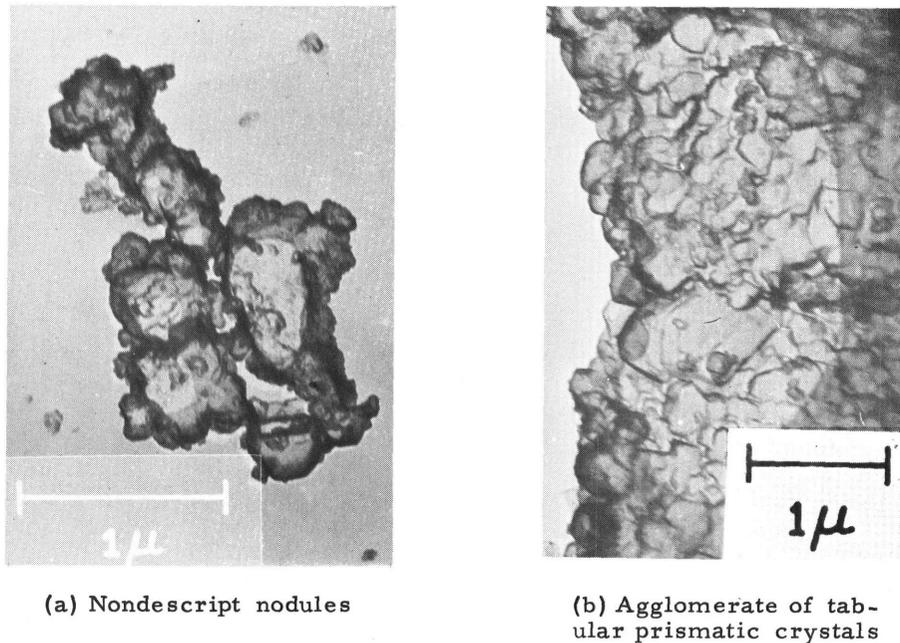


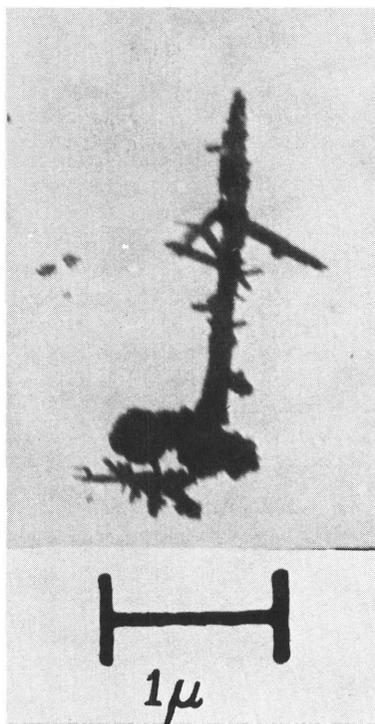
Fig. 5 - Electron micrographs of carbon replicas of PbO_2 formed by anodic oxidation of Pb_3O_4 showing two types of crystallization

surface, followed by very slow conversion of the basic carbonate pellet material in areas near the metal tray. A considerable amount of material remained untransformed at the end of the experiment, and this was a very soft white paste with a creamy consistency. The jet black particles of PbO_2 formed from this pellet were particularly delicate and complex dendritic crystals with numerous slender branches. Because of their complexity, they were especially difficult to replicate satisfactorily, and their intricate forms are best shown by direct micrographs (Fig. 6). It has been thought that the presence of basic carbonate on the surface of unformed battery plates leads to improved strength in the final plate (6). It is possible that a matted surface of intricate dendritic crystals such as observed in this preparation could indeed strengthen a plate surface.

PbO-M

The paste fabricated from PbO-M could not be dried satisfactorily because the mass in the tray shrank severely, cracking into many pieces having a slight tinge of red on the edges. These curled up away from the tray, presenting the appearance of a dried clay field. The change in volume on drying indicates that the oxide can hold a significant amount of water, but x-ray diffraction examination of paste freshly applied to a tray did not show that the wet material was crystallographically any different from the initial dry reagent: there was no detectable shift or change in shape of the diffraction peaks. The water in the paste of this material must be bonded to the particle surfaces, but the wetting process was not reversible, so the dried mass was not restored to its former plasticity by rewetting. Because of the marked shrinkage upon drying, trays of PbO-M were inserted into the electrolyte while still moist, and the pellet held together satisfactorily.

Fig. 6 - Direct electron micrograph of complex dendrites of PbO_2 obtained by anodizing $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$



Transformation of the pale yellow pellet to dark brown PbO_2 took place after the metallic tray first became covered with a layer of PbO_2 , and the conversion spread gradually from the metallic contacts into the body of the mass. Electron microscope examination of the PbO_2 formed from PbO -M showed only nondescript agglomerates and a few platelets, examples of which are shown in Fig. 7.

DISCUSSION

Battery Plates and PbO_2 Morphology

The results of this study show that PbSO_4 and $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ give rise to complex dendritic crystals of PbO_2 upon anodic oxidation under the conditions employed. A comparison of Figs. 3, 4, and 6 indicates that PbSO_4 was the most likely source of the crystals observed in the positive plates of the satisfactory lead-calcium cells described in earlier work (1). The terminations of the dendrite arms are blunted or rounded, whereas the dendritic branches observed on PbO_2 crystals electroformed from $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ were typically pointed, the crystals were more complex, and the arms were more slender (Fig. 6). When the same commercial paste that failed in the lead-calcium submarine cells was applied to antimonial grids, prismatic forms appeared, but of a still different habit (Fig. 2). These crystals had more numerous well-developed facets, less extensive branching, and thicker arms. Some prismatic dendritic crystals were observed in the products obtained from oxidation of the basic sulfates (8). These probably came from small amounts of material that converted to normal PbSO_4 or basic lead carbonate during the experiments.

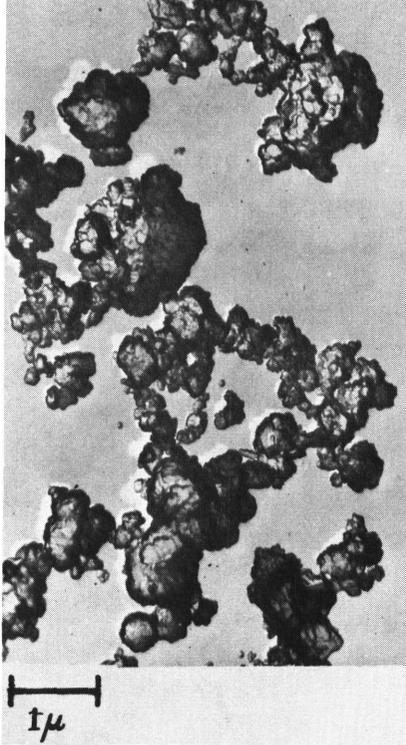


Fig. 7 - Electron micrograph of nodular particles of PbO_2 resulting from anodic treatment of orthorhombic PbO

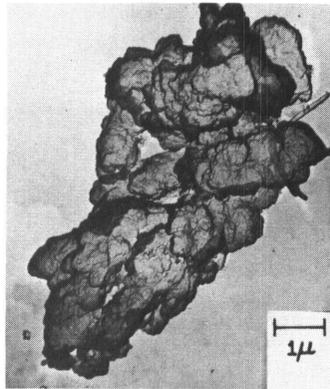
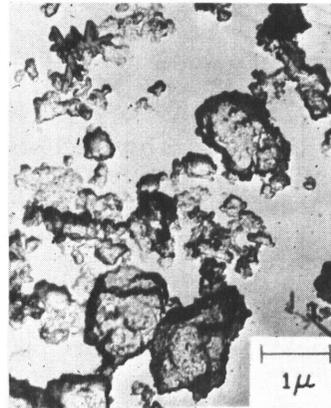
In this study, nondescript granular formations resulted from oxidation of PbO -M and Pb_3O_4 . These appear to be similar in form to the products obtained from oxidation of two of the basic sulfates (Fig. 8) and to those characteristic of the active material of the failing plates in the lead-calcium submarine batteries (1,8). A comparison of Figs. 1, 5, 7, and 8 strongly suggests that the cured paste of the failing submarine plates was composed primarily of a mixture of PbO -M, $PbO \cdot PbSO_4$, and $3PbO \cdot PbSO_4 \cdot H_2O$, with little or no basic carbonate or normal sulfate present. Because the specified capacity of these plates is moderately high, a medium or low density paste would have been used (6). This in turn would indicate that the original paste was more likely to contain large amounts of $3PbO \cdot PbSO_4 \cdot H_2O$ and $PbO \cdot PbSO_4$ rather than excess free PbO -M, which could be expected in a high density paste.

Active material of the nodular type of crystallization performs in a very satisfactory manner when $PbSO_4$ cement is present to stabilize the grains in a concretion, but in float service the cement is converted to PbO_2 , causing shrinkage and loss of interparticle contact (1). As a result, the plate cannot yield its stored energy.

Growth Mechanisms

Dendritic crystals result when the growing edge is bathed in mother liquor and in the presence of concentration gradients (13). It is thus possible to conclude that during the growth of prismatic dendritic crystals, characteristic of certain battery plates, the solution penetrated the paste mass ahead of the growth front of the PbO_2 particles, simultaneously converting the initial paste material to the normal sulfate. The formation of the $PbSO_4$ must take place just ahead of the electrochemical oxidation front, otherwise the plate will be soft and very porous because of shrinkage accompanying the transformation of $PbSO_4$ to PbO_2 . Two factors come into play during such a conversion mechanism:

(a) PbO_2 particles resulting
from $\text{PbO} \cdot \text{PbSO}_4$



(b) PbO_2 particles obtained
from $3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}$

Fig. 8 - Electron micrographs of carbon replicas of the products obtained upon anodic treatment of two basic sulfates of lead

the rate of electrochemical conversion to PbO_2 must not exceed the rate of percolation of the electrolyte into the active material, but the rate of conversion must be high enough to prevent undue expansion of the paste by excessive crystallization of PbSO_4 .

Granular crystallization results from massive transformation of one solid phase into another (13). Thus the growth of nodular particles of PbO_2 may be pictured as taking place by nucleation on the surface of aggregates of the active material paste, followed by growth into the solid phase across the interphase boundary, each granule expanding until growth is stopped by interference of other adjacent grains or exhaustion of the material. In such a growth mechanism, the rate of transformation exceeds the rate of penetration of liquid into the mass: the growth front is not bathed by mother liquor.

These considerations suggest the possibility that either morphology may be attained irrespective of the starting materials per se. If the rate of conversion is chosen so that the electrochemical transformation just lags penetration of the mass by the electrolyte, prismatic crystals would be expected. Of course, the current density used in the formation process determines the rate of PbO_2 crystallization, and it would be of interest to determine how the submicroscopic morphology varies with the current density employed in the transformation. Temperature and acid concentration can also be expected to affect the crystal morphology on this scale, just as these factors have been shown to affect the optical microstructures (14).

The Presence of Antimony

When the same paste was applied to antimonial and lead-calcium alloy grids, there was a difference in both composition and morphology of the formed active material (3). As pointed out above, dendritic crystals in the antimonial paste were of a different habit from those obtained by anodization of PbSO_4 and $2\text{PbCO}_3 \cdot \text{Pb(OH)}_2$, Figs. 2, 4, and 6. The many facets on the crystals from the cells having lead-antimony alloy grids could arise from a dual function of the antimony. A soluble antimony species may be preferentially absorbed on the growing crystals of PbO_2 producing a unique morphology, promoting wetting or permeation of the paste by the electrolyte so that the crystals are bathed in liquid during their growth. The fact that antimony induces the simultaneous formation of α and β PbO_2 (3) might be a result of such preferential absorption on certain crystal faces inhibiting their development. This promotes growth in other directions, which results in the stacking of layers in the crystal in a way to produce the αPbO_2 lattice. Further work is required to define this mechanism.

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There is no limitation on the length of the abstract. However, the suggested length is from 150 to 225 words.

14. **KEY WORDS:** Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical content. The assignment of links, roles, and weights is optional.