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The Plate Materials of the Lead-Acid Cell

Part 1 - Anodic Oxidation of the Basic Sulfates of Lead

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ABSTRACT

The basic lead sulfates $\text{PbO} \cdot \text{PbSO}_4$, $3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}$, and $4\text{PbO} \cdot \text{PbSO}_4$ were prepared by reacting PbO and dilute H_2SO_4 . The crystalline phases were identified by x-ray diffraction patterns, and electron microscope examination showed all three to be prismatic needles.

The three basic sulfates were oxidized anodically in dilute H_2SO_4 , and x-ray diffraction showed that each transformed to $\beta\text{-PbO}_2$. The pellet made from $4\text{PbO} \cdot \text{PbSO}_4$ was mechanically strong, and the transformation to PbO_2 was largely metasomatic after the original crystals of the basic sulfate. The three anodic preparations were examined in the electron microscope and showed the presence of prismatic and nodular particles of PbO_2 .

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 1 - ANODIC OXIDATION OF THE BASIC SULFATES OF LEAD

INTRODUCTION

Studies on the lead-acid battery have long been of interest to this Laboratory owing to the continued importance of this cell in submarine service. In recent years the so-called "lead-calcium" cell has replaced the conventional antimonial lead cell on the nuclear-powered ships where the batteries were installed in float service. This change in cell type focused attention on the positive plate because shortly after installation the lead-calcium cells began to fail by softening and disintegration of the positive active material. This loss of strength and electrical continuity in the positive mass was attributed to an unsuitable crystal morphology. Other simultaneous investigations revealed that mechanical strength and battery capacity were maintained when the active material paste was knit together by prismatic crystals of PbO_2 or $PbSO_4$ (1,2). Because $PbSO_4$ is a discharge product in the plates, it is thermodynamically unstable in a float installation; and in order to retain its presence in the positive plates these plates must be carried in a partially discharged condition, and continuous float becomes impossible. In addition, fully charged batteries are almost universally desired. On the other hand, it is not known how the prismatic crystals of PbO_2 are produced in certain commercial battery pastes. Studies currently under way at this Laboratory are directed toward analysis of the factors affecting the structure of the positive active materials.

Battery plates are fabricated from a mixture of lead oxides, usually containing some free metallic lead, sulfuric acid, water, and miscellaneous additives. These materials are mixed for a brief period to form a stiff paste which is pressed into a metallic battery grid. The paste first stiffens or "sets," and the plates are then ready to be "cured." Curing is a combined setting and drying process during which several chemical reactions occur. Free metallic lead which may be present in finely divided form in the paste is spontaneously oxidized with the liberation of heat, and the reaction of the oxides and H_2SO_4 is carried essentially to completion. If the paste does not initially contain significant amounts of free lead, the curing process must be carried out in an oven in the presence of water vapor. After curing, the paste is a complex mixture of unreacted lead oxides, one or more basic sulfates of lead, and perhaps basic carbonates and hydrated lead oxides (3-14). The cured plates are assembled into battery elements and electrochemically converted into the final active materials, PbO_2 at the positive and Pb at the negative plate.

Three basic sulfates are often encountered in the cured paste: $3PbO \cdot PbSO_4 \cdot H_2O$, $PbO \cdot PbSO_4$, and $4PbO \cdot PbSO_4$. To determine whether any or all of these materials is a source of prismatic PbO_2 in the finished battery plate, each of these compounds was separately converted to PbO_2 and the morphologies of the resulting crystals examined.

EXPERIMENTAL METHOD

For this study the three commonly encountered basic sulfates of lead were prepared and anodized individually in dilute H_2SO_4 . The starting materials and final electrochemical products were identified by x-ray diffraction and examined by electron microscopy.

$\text{PbO} \cdot \text{PbSO}_4$, $3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}$, and $4\text{PbO} \cdot \text{PbSO}_4$ were synthesized from reagent grade PbO and the stoichiometric quantity of H_2SO_4 . One mole of powdered PbO was mixed in a liter of distilled water, and the required amount of 1.250 sp gr H_2SO_4 solution was added dropwise with stirring which was continued four hours after addition of the acid. The mixture for the tetrabasic sulfate was heated during the initial reaction period to approximately 80°C and then allowed to cool to room temperature. The mixtures were digested for four days at room temperature, and the solids collected on a filter and air dried. The identity of the solid phases was verified by x-ray diffraction, and the crystals were examined directly in the electron microscope.

For the electrochemical formation, a thick paste of each basic sulfate and distilled water was pressed into a pellet in a frame cut from pure lead sheet 0.625 mm thick. Bibulous paper was applied to both sides of the pellet during fabrication and allowed to remain in place until the mass had dried in air at room temperature. These plates were then wrapped with filter paper held in position with rubber bands, and sheet lead electrodes of the same size were placed on both sides of each plate. These small elements were connected in series and the pellets were anodized for 72 hours in 1.050 sp gr H_2SO_4 solution at a current density of 2.66 ma/cm² using the lead sheets as the counter electrodes.

Following anodization, the cells were opened and the pellets blotted dry. The formed material was analyzed by x-ray diffraction, examined in the optical microscope, and then extracted with saturated $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ solution. The residual particles of PbO_2 were again examined by x-ray diffraction and the optical microscope, and in addition they were studied with the electron microscope both directly and by means of carbon replicas (15).

RESULTS AND DISCUSSION

The three basic sulfates prepared for this study were all prismatic crystalline materials, and typical electron micrographs are shown in Fig. 1. The tetrabasic lead sulfate (Fig. 1(a)) crystallized in rather large prisms with a pale yellow color. The other two basic sulfates were colorless, and their prismatic forms are shown clearly in the electron micrographs (Figs. 1(b) and 1(c)). All three were readily and completely soluble in saturated $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ solution.

After anodization, the pellet fabricated from $3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}$ had oxidized around the edges near the metal frame, but the center had not been converted to PbO_2 , apparently owing to shrinkage accompanying the transformation, which caused the center to lose contact with the edges. Upon extraction with $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ solution, the formed part of the pellet disintegrated readily, leaving a powder of PbO_2 . Examination in the electron microscope showed that this was a mixture of nodular and prismatic crystals (Fig. 2).

The anodized pellet made from $\text{PbO} \cdot \text{PbSO}_4$ had also formed around the edges near the metal frame, and shrinkage had left an even larger central area unformed than in the case of $3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}$. The formed mass was readily disintegrated into small particles upon extraction with saturated $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ solution. Examination in the electron microscope again showed the presence of nodular and small prismatic crystals of PbO_2 (Fig. 3).

The pellet fabricated from $4\text{PbO} \cdot \text{PbSO}_4$ appeared visually to be totally converted to PbO_2 by the anodic oxidation and was hard, mechanically strong, and well bonded to the metallic lead frame. Optical examination showed that the original crystal shapes of the basic sulfate had been retained intact during the oxidation. This pellet was extracted for several weeks with saturated $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ solution and some fine particles were released from the mass, but the major portion of the pellet, comprising the distinct crystal forms



(a) Crystals of $4\text{PbO} \cdot \text{PbSO}_4$. These crystals were rather large for examination in the electron microscope but are shown here for comparison with the other basic sulfates of lead. The surfaces of these crystals appear irregular and somewhat flaky at this magnification.

Fig. 1 - Electron micrographs of basic lead sulfate crystals

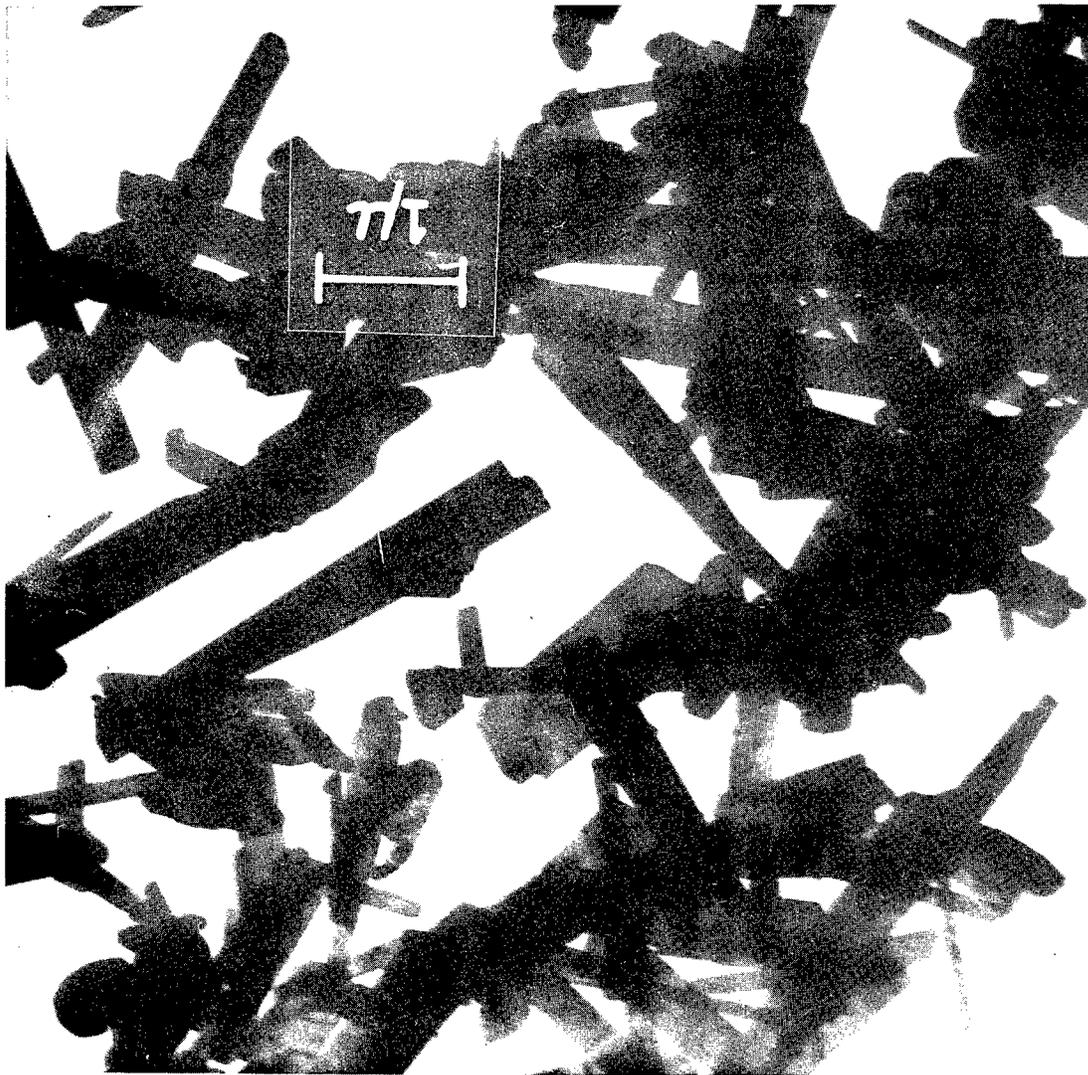


(b) Crystals of $3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}$. The wide variation in size of these slender needles is apparent in this photograph. The surfaces of these crystals are covered with protrusions which may be incipient or vestigial dendritic arms.

Fig. 1 (cont'd) - Electron micrographs of basic lead sulfate crystals

related to the original $4\text{PbO} \cdot \text{PbSO}_4$ crystals, remained intact. Electron microscope examination of crystals obtained from this pellet showed that the fine particles were a mixture of nodular and prismatic forms and that the surfaces of the large particles were very rough and irregular (Fig. 4).

X-ray diffraction analysis showed that all three basic sulfates had been converted to $\beta\text{-PbO}_2$ by the electrolytic oxidation, in agreement with the earlier findings of Ikari, Yoshizawa, and Okada (10). As reported by these authors, it was also observed in this study that the pellet formed from $4\text{PbO} \cdot \text{PbSO}_4$ contained some residual unreacted material even though it appeared to be totally formed. This residue was readily extracted

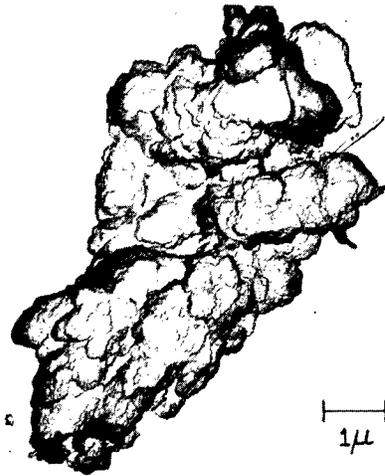


(c) Crystals of $\text{PbO} \cdot \text{PbSO}_4$. These appear to be rather thin blunted needles and were the smallest in average size of the basic sulfates prepared for this study.

Fig. 1 (cont'd) - Electron micrographs of basic lead sulfate crystals

with saturated $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ solution, so that subsequent x-ray diffraction patterns taken from the pellet showed the presence of only $\beta\text{-PbO}_2$. It is considered that the retention of the crystal forms and pellet strength after extraction of all $4\text{PbO} \cdot \text{PbSO}_4$ detectable by x-ray diffraction shows that the prismatic forms of the large crystals of the basic sulfate are in fact retained by the PbO_2 and are not artifacts produced by a shallow conversion on the surface of the original basic sulfate crystals.

The conversion of one material into another by simultaneous addition and subtraction of matter, but without change in external form, is called metasomatism or replacement by geologists (16-18). Petrified wood is one familiar and interesting example of metasomatism, in which the wood structure is replaced by inorganic crystalline rock which



(a) Nondescript nodular forms

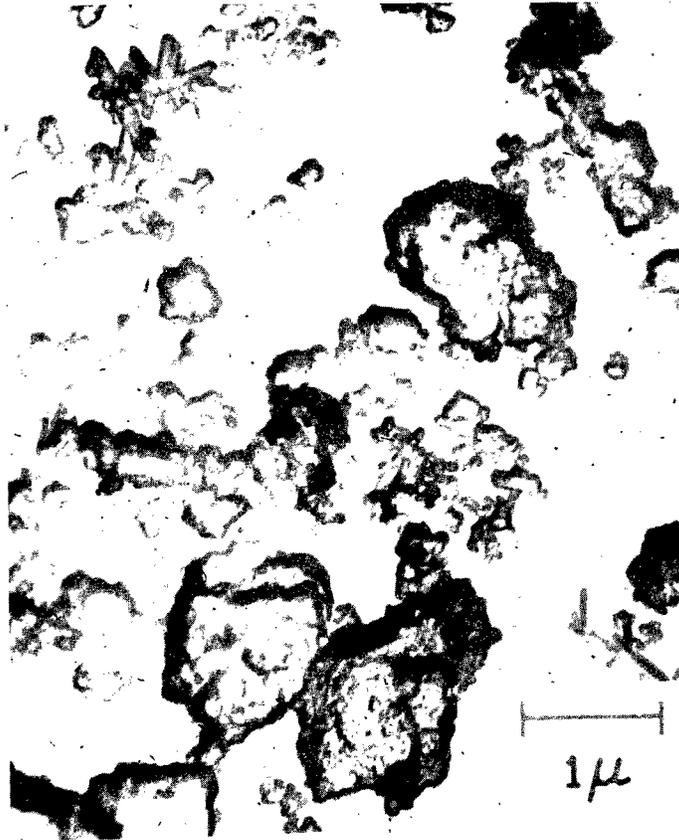


(b) Prismatic dendritic crystal

Fig. 2 - Electron micrographs of carbon replicas of PbO_2 particles formed by anodization of $3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}$

retains the external form of the original tree trunk. The term metasomatism is used in this discussion because it so aptly describes the processes of charging battery pastes to form PbO_2 in situ within the original volume of the paste, and particularly the conversion of $4\text{PbO} \cdot \text{PbSO}_4$ to PbO_2 . Electrochemical action has been thought to play a part in the formation of some geological deposits and in certain metasomatic transformations in the earth's crust, particularly when high temperatures and pressures were not active during a metamorphosis (19-22).

There is usually only a minimal volume change between host and metasome, and Table 1 lists the volume changes expected during formation of $\beta\text{-PbO}_2$ from certain compounds likely to be present in the unformed active material of the lead-acid cell. It is seen that free lead and PbO would be expected to give rise to a larger volume of PbO_2 than they themselves occupy, while the normal and basic sulfates of lead and Pb_3O_4 could

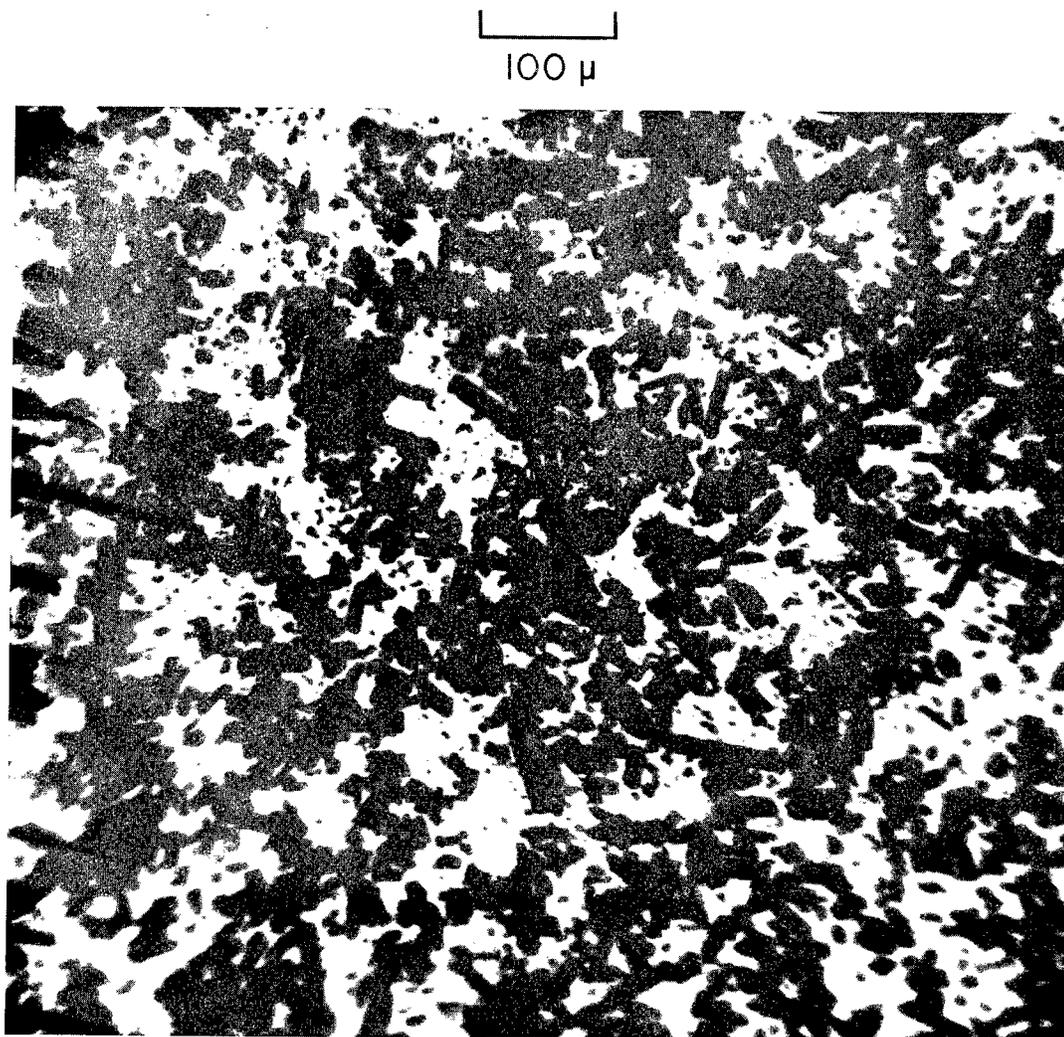


(a) A mixture of nondescript and prismatic particles



(b) A cluster of small prismatic crystals

Fig. 3 - Electron micrographs of carbon replicas of PbO_2 particles formed by anodization of $PbO \cdot PbSO_4$

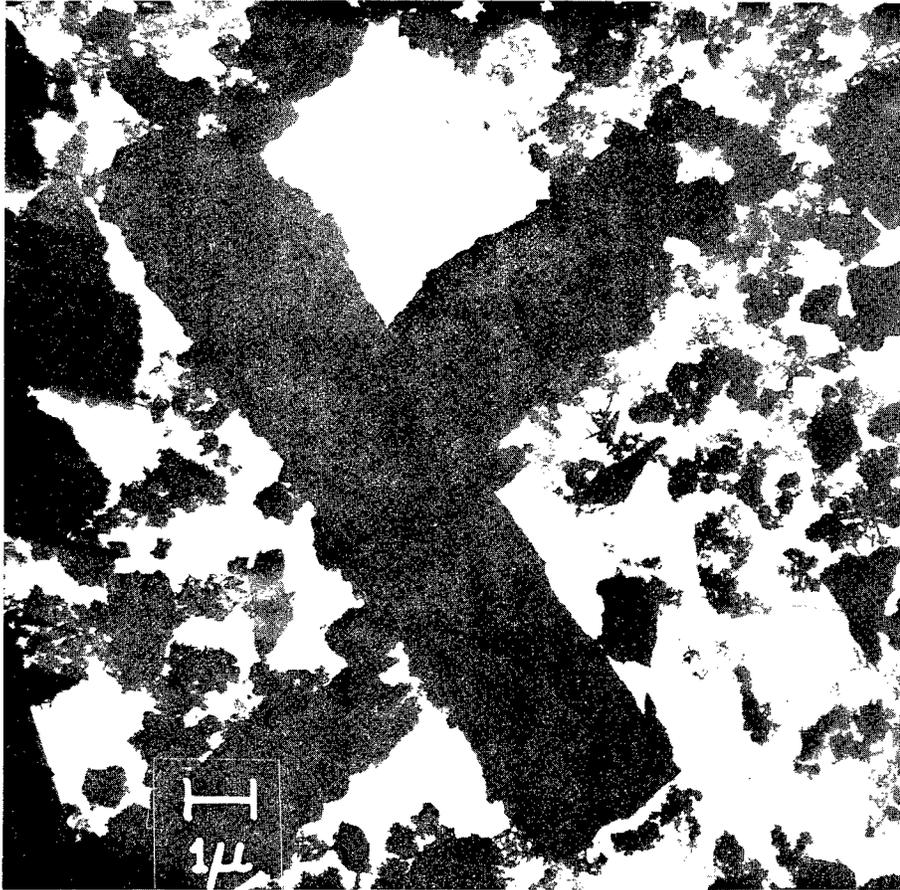


(a) Optical micrograph taken during extraction of PbO_2 with $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ solution. The large particles are metasomatic after the original basic sulfate crystals.

Fig. 4 - Micrographs of PbO_2 particles obtained by anodization of $4\text{PbO} \cdot \text{PbSO}_4$

produce shrinkage in volume. Thus a balance of these paste materials in the cured plate can result in zero change in total volume during electrochemical conversion to PbO_2 . The pore structure does vary in battery plates depending upon the relative amounts of oxide and acid used in fabrication (measured as paste density in the trade), and at least one study has shown an overall expansion of the paste on formation (8,23).

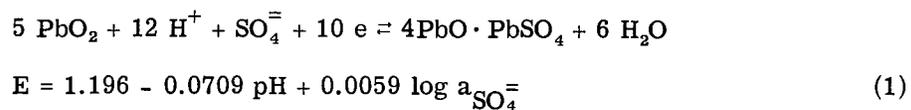
On the other hand, the large tetrabasic lead sulfate crystals have been shown in this study to transform by electrochemical metasomatic replacement, not accompanied by the expected shrinkage in volume. For every five molecules of PbO_2 formed from $4\text{PbO} \cdot \text{PbSO}_4$ only one sulfate ion need be removed from the body of the crystal with the simultaneous



(b) Electron micrograph showing a large metasomatic crystal and fine-particle material which is a mixture of prismatic and nondescript forms

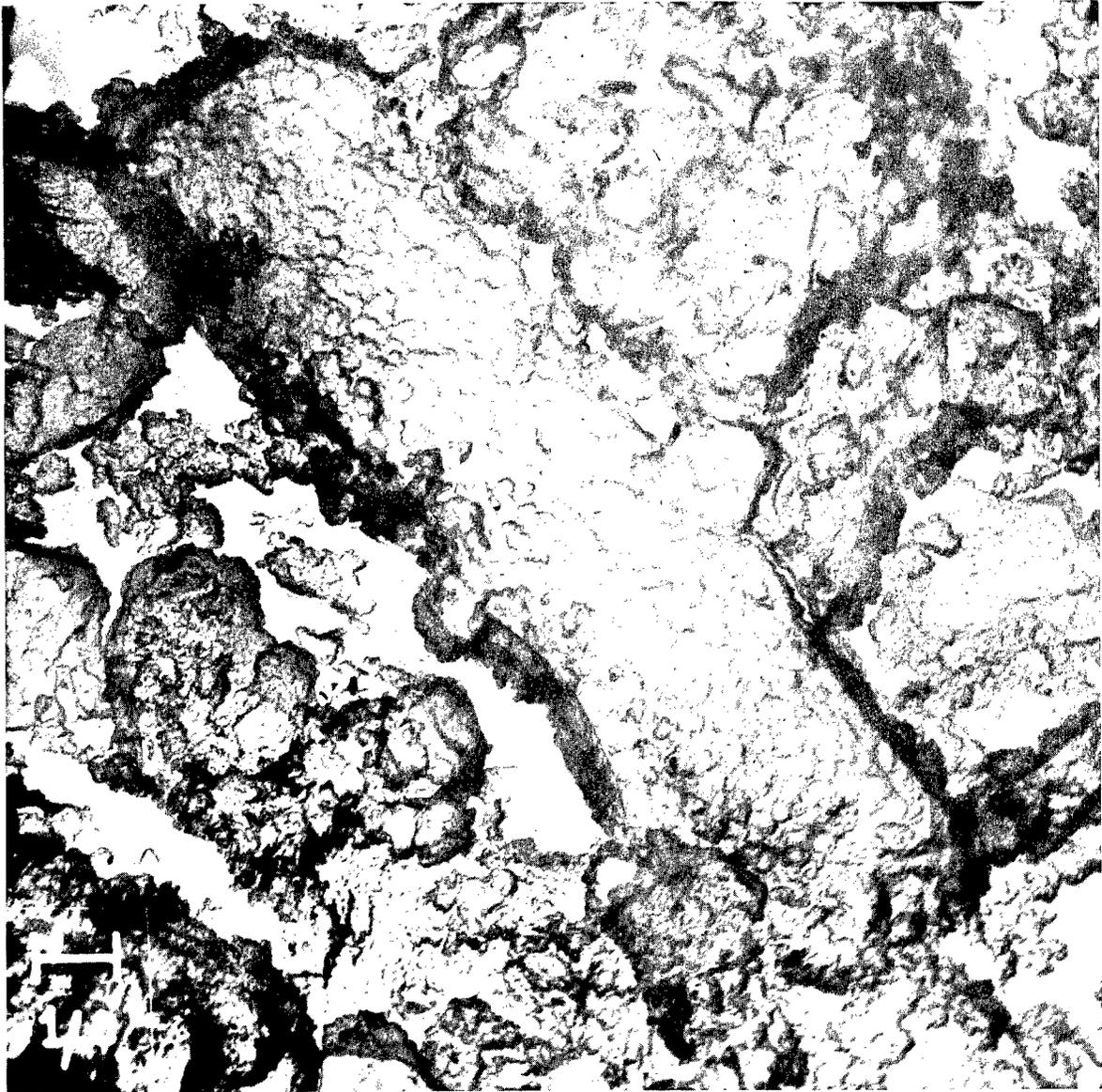
Fig. 4 (cont'd) - Micrographs of PbO_2 particles obtained by anodization of $4\text{PbO} \cdot \text{PbSO}_4$

addition of six oxygen atoms as indicated by the reaction:



where E is calculated by assuming the standard free energy of formation of $4\text{PbO} \cdot \text{PbSO}_4$ is -374.88 kcal based on the free energies of formation of PbO and PbSO_4 . As indicated in Table 1, there would be a 15% decrease in volume upon conversion of a crystal of $4\text{PbO} \cdot \text{PbSO}_4$ to an equivalent amount of PbO_2 according to Eq. (1). This replacement of one molecule of $4\text{PbO} \cdot \text{PbSO}_4$ ($\text{Pb}_5\text{O}_8\text{S}$) with 5PbO_2 (Pb_5O_{10}) would result in no change in weight and the difference in volume could cause porosity within the metasome.

On the other hand, the volume change indicated for this compound in Table 1 may be eliminated if lead ions present in the electrolyte are electrodeposited within the volume



(c) Electron micrograph of carbon replica including one of the metasomatic crystals. The surface is crenulated which may be evidence of grain structure within the metasome.

Fig. 4 (cont'd) - Micrographs of PbO_2 particles obtained by anodization of $4\text{PbO} \cdot \text{PbSO}_4$

occupied by the original crystals present in the unconverted paste mass. The initiation of the transformation may be the deposition of tetravalent lead ions at active sites on the surface of an original crystal, and the transformation may then spread readily throughout the body of the crystal from this surface initiation by a diffusion mechanism across the interphase boundary. The volume of the tetrabasic crystal could be replaced exactly by the addition of an appropriate number of lead ions from solution: approximately 9.083 from solution for every 50 lead ions in the crystal.

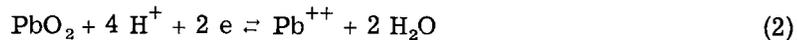
Table 1
Properties of Compounds Likely to be Present in Unformed Active Material
of the Lead-Acid Cell

Compound	Molecular Weight	Density	Gram Molecular Volume (cc)	Moles PbO ₂ Formed per Mole of Compound	Δ V* (cc)	% ΔV per Pb atom
Pb	207.21	11.341	18.28	1	6.56	35.87
PbSO ₄	303.27	6.323	47.96	1	-23.12	-48.21
PbO (orthorhombic)	223.21	9.642	23.15	1	1.69	7.30
PbO (tetragonal)	223.21	9.355	23.88	1	0.96	4.02
Pb ₃ O ₄	685.63	8.925	76.79	3	-0.76	-2.97
PbO · PbSO ₄	526.48	7.02	75.0	2	-12.66	-33.77
3PbO · PbSO ₄ · H ₂ O	990.92	6.5 †	152.	4	-13.	-34.
4PbO · PbSO ₄	1196.11	8.15	146.76	5	-4.51	-15.38
β - PbO ₂	239.21	9.63	24.84	-	-	-

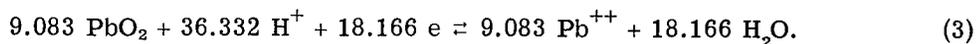
* Volume change upon conversion to β - PbO₂ per gram atom of Pb in the compound.

† A very approximate value obtained from the material synthesized for this study.

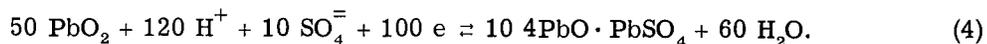
This mechanism can be represented by the following scheme:



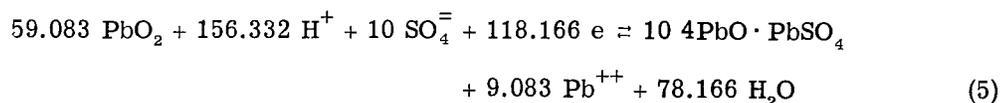
and for 9.083 lead ions,



For every 50 tetravalent lead ions formed in the crystal, Eq. (1) becomes:



By combining Eqs. (3) and (4), the reaction for the metasomatic replacement at constant volume would be written:



$$E = 1.22 - 0.078 \text{pH} + 0.005 \log a_{\text{SO}_4^{=}} - 0.0045 \log a_{\text{Pb}^{++}}.$$

Taken on the basis of either the weight or the volume remaining constant, this conversion defines a reference state for a thermodynamic system as discussed by Thompson for metasomatic processes (24). This same mechanism could metasomatically replace any of the original crystals in the paste; however, a greater mass transfer would be involved in the conversion of the others.

The fact that the pellet of PbO_2 formed from $4\text{PbO} \cdot \text{PbSO}_4$ retained its strength even after extraction with $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ solution indicates that $4\text{PbO} \cdot \text{PbSO}_4$ crystals in the unformed paste may impart strength to the finished plate, provided that their physical distribution in the active mass is suitable. Simon and Jones (25) have shown that in certain battery plates there exists a network of hard PbO_2 that is continuous throughout the paste and suggested that this originated from a network of one of the basic sulfate crystals initially present in the unformed plates. It was further suggested that this hard network might be $\alpha\text{-PbO}_2$; however, only $\beta\text{-PbO}_2$ was observed by x-ray diffraction as the anodic product from all three basic sulfates under the conditions used in this study. On the other hand, metasomes are frequently particularly hard and dense owing to their diffusional growth mechanism which somewhat resembles a zone refining process. On the basis of the results of this study, it seems likely that the network described by Simon and Jones arises from tetra-basic lead sulfate crystallized in this pattern in the unformed plate.

In earlier investigations of the active material pastes of certain lead-calcium batteries, the small particles were consistently prismatic (1). However, none of the three basic sulfates examined in this study gave rise to prismatic crystals to such an extent; the fine-particle material was a mixture of nodular and prismatic crystals in all three instances. On the other hand, the crystals of $4\text{PbO} \cdot \text{PbSO}_4$ prepared for this study were of a fairly uniform and large size, and it is possible that fine-particle prismatic PbO_2 arises from small crystals of this same material when these are present in unformed battery plates.

Other mechanisms can give rise to prismatic PbO_2 . For example, it has been shown that antimony in the grid alloy leads to prismatic growth of PbO_2 (26). Some prismatic PbO_2 appeared in the anodization of $\text{PbO} \cdot \text{PbSO}_4$ and $3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}$ in this study, and hydrothermal recrystallization also produces prismatic crystals (27). It is anticipated that future investigations of positive active materials will lead to further understanding and result in optimization of the physical structures required to give maximum plate durability, thus extending battery life.

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