Lead-Acid Battery:

Tetrabasic Lead Sulfate as a Paste Material for Positive Plates

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We present a reproducible method of synthesizing tetrabasic lead sulfate (4PbO·PbSO₄) which produces discrete elongated crystals approximately 22 microns long. Tetrabasic lead sulfate undergoes anodic conversion to PbO₂ while maintaining the characteristic morphology of the 4PbO·PbSO₄ crystals. This results in lead-acid battery positive plates having performance characteristics superior to those fabricated from conventional paste formulations.

We furnish data showing the performance of $4PbO \cdot PbSO_4$ positive plates as a function of plate porosity and present stress cycling data, comparing it with the behavior of typical conventional positive plates.

I. INTRODUCTION

There are two major causes of positive plate capacity degradation in float service lead-acid batteries: (i) corrosion and growth of the lead or lead alloy grid, and (ii) softening and disintegration of the PbO₂ matrix. The latter has been extensively discussed by J. Burbank.

In order to improve the stability of the PbO₂ matrix, it would be invaluable to have answers to questions concerning the nature of the grid/PbO₂ interface, the nature of the inter-particle bonding in the PbO₂ matrix and the mechanisms of the charge and discharge reactions. It is paradoxical that, although the lead-acid battery has been in use for over a century, answers to these and other fundamental questions are unknown. This is in large part attributable to the complexity of the lead-acid system which in turn is partly the result of extensive variability of materials and processes used in lead-acid battery fabrication.

In conventional positive plate fabrication, the starting material is usually a mixture of some or all of the following species: Pb, PbO (orthorhombic and tetragonal), and Pb₃O₄. The powder is mixed with

water and sulfuric acid during which many complex chemical reactions occur. The reaction product is a paste generally composed of Pb, PbO, PbSO₄, Pb₃O₄, PbO·PbSO₄, 3PbO·PbSO₄ · nH₂O and 4PbO·PbSO₄. The exact products and their relative concentrations depend upon numerous variables including: starting materials, ratio of water and acid addition, acid concentration, rate of mixing, uniformity of mixing and temperature. The resulting paste is then applied to lead or lead alloy grids and the plates are cured.

During the curing operation, additional chemical reactions take place. The products remain essentially the same as those obtained in the mixing operation but their relative concentrations may change significantly depending upon temperature and relative humidity during the curing operation. The cured plates are immersed in H₂SO₄ and the paste material is anodized to PbO₂. The modification of PbO₂ (α or β) and the microstructure of the PbO₂ matrix will reflect the particular forming conditions—current density, time, acid concentration—as well as all the process and material variables mentioned before. Such variations in plate properties are well-documented in the technical literature.3-5 It is clear, then, that efforts directed toward improvements in battery performance must also be directed to development of materials and processes that can be defined and controlled. A study of the positive plate active material (PbO2) was undertaken with the objective of arriving at a simple, direct technique whereby a reproducible and definable lead dioxide mass might be obtained which would yield improved performance characteristics.

It has been established that mechanical stability of the PbO₂ structure in a lead-acid battery positive plate is enhanced by the presence of large prismatic needles of PbO₂. ^{2,3} Burbank demonstrated that tetrabasic lead sulfate (4PbO·PbSO₄), which crystallized as large elongated prisms, underwent anodic conversion to PbO₂ while maintaining a crystal form similar to the original 4PbO·PbSO₄ crystals. It was suggested that this particular PbO₂ morphology might impart mechanical strength to the PbO₂ mass by a mechanism involving interlocking of these elongated PbO₂ crystals. It was also suggested that 4PbO·PbSO₄ might be the precursor to prismatic needles of PbO₂ which were found

to be present in satisfactory positive plates.

The apparent potential benefits to be derived from the presence of 4PbO·PbSO₄ in unformed positive plates suggested that positive plates fabricated entirely from 4PbO·PbSO₄ might have improved performance characteristics. To evaluate the applicability of tetrabasic lead sulfate

to positive plate fabrication, we studied the synthesis of 4PbO·PbSO₄ and the performance of positive plates fabricated from this material.

II. SYNTHESIS OF TETRABASIC LEAD SULFATE

Tetrabasic lead sulfate was synthesized by reacting a stirred suspension of orthorhombic PbO in water with 8-12N H₂SO₄ in a 5:1 molar ratio.

- (i) The stochiometric quantities of PbO and H₂SO₄ were premeasured.
- (ii) Water (approximately 0.85 liters per mole PbO) was preheated to 80°C and acidified to pH2 by addition of a small amount of the premeasured quantity of H₂SO₄.
- (iii) The PbO was then added to the acidified water and the mixture stirred so as to keep all the PbO in suspension.
- (iv) While maintaining the temperature at 80° C to 85° C, the remaining H_2SO_4 was slowly added to the stirred suspension over a one-hour period.
- (v) Following acid addition, heating and stirring were continued for 15 minutes after which the heat source was shut off and stirring continued for an additional 1.5 hours.
- (vi) The product was allowed to digest for 12 hours, isolated, and dried at 100°C.
- (vii) The identity of the material was verified by X-ray diffraction⁷ and the composition checked by lead analyses.⁸ The product was also examined with an optical microscope.

Synthesis of 4PbO·PbSO₄ under the above conditions results in a uniform and reproducible pale yellow material which is composed of well-defined elongated prisms as shown in Fig. 1. This crystal morphology is very similar to that reported previously for 4PbO·PbSO₄ prepared under similar conditions.⁶

The use of the orthorhombic modification of PbO in the synthesis is essential. When tetragonal PbO is used in identical reaction conditions, the reaction is not uniform and the product is a poorly defined mixture of materials. The preacidification of the water prior to addition of the oxide is also critical. When orthorhombic PbO is added to neutral water, the material converts to the tetragonal modification probably by a mechanism involving dissolution and reprecipitation of PbO. The extent of conversion depends upon the dwell time in the reaction vessel

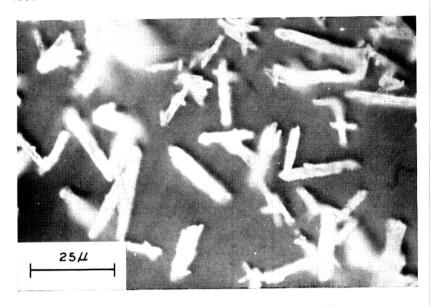


Fig. 1—Photomicrograph of 4PbO·PbSO₄ (500X).

prior to H₂SO₄ addition. When conversion occurs, the H₂SO₄ preferentially reacts with the orthorhombic PbO giving unreacted tetragonal PbO and a product having a sulfate content larger than demanded by the stochiometry of 4PbO·PbSO₄. The conversion to tetragonal PbO occurs at pH's down to 3.5 although the extent of conversion is less at this lower pH value. At pH2, no conversion is observed and a uniform, reproducible product is obtained.

Control of the temperature to a minimum of 80°C is also essential if one is to obtain a uniform and reproducible product. Below 80°C, a material having a reduced crystal size begins to appear and X-ray diffraction shows the product to be a mixture of compounds. The product prepared at 90°C is identical to that prepared at 80°C and there are no apparent reasons why even higher temperatures could not be used.

Uniformity of the reaction also requires that all the PbO be maintained in suspension. This is a very real problem because of the high density of PbO. Lead oxide which settles in the reaction vessel will not react sufficiently with the added H₂SO₄ and a mixture of products will result.

The 12-hour digestion period does not appear to be essential. Recent experiments indicate that reaction and crystal growth are essentially complete after acid addition is finished and that the product after this period is identical to that isolated after 12-hour digestion.

Finally, the other variables such as PbO/water ratio and acid addition time should be flexible within reasonable limits which will be related to the efficiency of the mixing operation.

To date, roughly 250 batches of 4PbO·PbSO₄ have been synthesized during this investigation. The batch sizes have ranged between 5 lbs. and 35 lbs., but most have been on the 35 lb. scale. The process has excellent reproducibility and the lead content is readily controllable within the range of 86.6 ± 0.2 percent (Theoretical: 86.60 percent Pb). It was an objective of this study to adequately control the reactants such that the lead content of the product falls within this range. Below 86.4 percent Pb, a product of reduced crystal size becomes apparent. Above 86.8 percent Pb, unreacted PbO appears in the reaction product. The synthesis process also yields a product with reproducible morphology. Detailed particle size analyses⁹ were performed on several batches which resulted in the following particle classification:

- (i) Average particle length of 22 ± 1 microns with the particle length distribution within any given batch described by a standard deviation of 10 microns.
- (ii) Average particle width of 3.5 ± 0.8 microns with the particle width distribution within any given batch described by a standard deviation of 1.7 microns.

III. PREPARATION AND CAPACITY OF TETRABASIC LEAD SULFATE POSITIVE PLATES

A paste of 4PbO·PbSO₄ suitable for application to lead or lead alloy grids requires only that the powder be mixed with water. Plates pasted with 4PbO·PbSO₄ are simply air dried, requiring no special curing operations.

The paste does not shrink or crack upon drying, thereby maintaining intimate contact with the grid members. Shrinkage and cracking of paste materials are common problems in the battery industry and a variety of specialized curing operations are often used to overcome these problems. Other studies have shown that the nonshrink property of 4PbO·PbSO₄ water pastes is attributable to the large crystal size of this material.

We demonstrated this by studying the behavior of plates which were pasted with 4PbO·PbSO₄ having roughly spherical particles of 3 microns diameter. These were obtained by mechanical grinding of the large 4PbO·PbSO₄ crystals. Upon drying, these plates showed considerable shrinkage of the material away from the grid frame. Although the

4PbO·PbSO₄ in these plates could be formed to PbO₂, the effect of shrinkage and loss of contact with the grid frame was reflected in the poor discharge characteristics of these plates. Apparently, the large crystals of 4PbO·PbSO₄ (Fig. 1) mechanically interlock to prevent movement of the individual crystals during drying which results in the nonshrink properties of the material.

We obtained detailed performance characteristics of $4 \text{PbO} \cdot \text{PbSO}_4$ positive plates in the following manner. Five water pastes of $4 \text{PbO} \cdot \text{PbSO}_4$ of varying densities were prepared by mixing the solid and water in varying proportions. These pastes were applied to preweighed commercially available lead calcium grids (c.a. 0.05 percent Ca). These grids are $2.5'' \times 3.0'' \times 0.25''$ and contain nine paste pellet frames (3 × 3). The pasted plates were air dried at room temperature for two days. The weight of dry paste in each of the five grids ranged from 91 to 110 g.

Five cells were constructed, each consisting of one 4PbO·PbSO₄ positive plate located between two comparable pasted negative plates. The 2:1 ratio of negative to positive insured that the cell capacities would be limited by the behavior of the positive plates. The separation between positive and negative plates was 0.25" and there were no separators placed between the plates. The cells were formed in 1.050 sp. gr. H₂SO₄ at 0.5 A (33 mA/in²) for 21 hours followed by 0.3 A (20 mA/in²) for 240 hours. After this treatment, there was no visual evidence of 4PbO·PbSO₄ that had not been converted to PbO₂.

The cells were transferred to jars containing 2.5 liters of 1.210 sp. gr. H₂SO₄. This large volume of H₂SO₄ was used so that there would be no significant changes in bulk concentration during discharge. The cells were then cycled at various discharge currents ranging from 0.35 A to 2.50 A until all cells gave reproducible results on two successive discharges at the same current. After the cell capacities had stabilized, cell performance data were obtained at 0.13, 0.35, 0.70, 1.00, 1.30 and 2.50 amperes. Plate potentials were measured versus mercury/mercurous sulfate reference electrodes and a positive/reference electrode potential of 0.850 V was taken to be the end of discharge. This positive plate potential (0.850 V) corresponded to a cell voltage of approximately 1.80 V.

The cells were then disassembled. The positive plates were washed in water for 3 hours and dried at 80°C for 18 hours. The PbO₂ pellets were removed from each plate and the total amount of PbO₂ in each plate was determined by weighing. Porosity data on the PbO₂ pellets were obtained with a Numinco Model MIC 901 mercury intrusion porosimeter.

Figure 2 shows the performance of 4PbO·PbSO₄ plates as a function of porosity. Each data point represents an average of at least two and sometimes three porosity measurements. The dashed line is the 5-hour rate performance (0.90 A) interpolated from the data at the other rates. For the porosity range studied, the data at discharge rates between 2.50 A and 0.35 A show a linear increase in material utilization with increasing porosity.

Although it is generally accepted that positive plate efficiency increases as plate porosity increases, to the authors' knowledge this is the only quantitative data of this type that have been published. Since increasing porosity of the PbO_2 mass facilitates diffusion of the H_2SO_4 electrolyte into the matrix, the performance data in Fig. 2 are strong evidence for a diffusion controlled reaction.

At the low discharge rate of 0.13 A the linear porosity-utilization relationship does not hold (no curve has been drawn through these points). This is not unreasonable since one would expect that for any given plate, there should be a maximum discharge rate below which

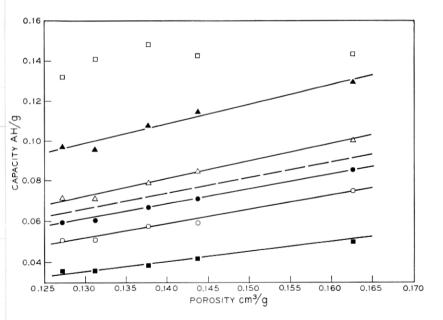


Fig. 2—Capacity (AH/g) vs Porosity (cm³/g) for 4PbO·PbSO₄ plates. \blacksquare 2.50 A \bigcirc 1.30 A \blacksquare 1.00 A \triangle 0.70 A \blacksquare 0.35 A \square 0.13 A

Dashed line is interpolated 0.90 A (5-hour rate) performance.

the diffusion of electrolyte is sufficient to satisy the demands of the discharge.

For discharge rates sufficiently low where diffusion is not limiting, material utilizations which are independent of porosity would be expected. The 0.13 A data show this to be the case. Excluding the lowest porosity data, the utilizations are reasonably independent of porosity. It may be that 0.13 A is borderline for diffusion control for the porosity range studied here which would account for the lower utilization of the plate having the least porosity.

A porosity of 0.130 cm³/g corresponds to positive plate loading densities typical of present commercial products. At 0.90 A, which is the rated 5-hour discharge current for this plate, a porosity of 0.130 cm³/g corresponds to a utilization of approximately 0.065 AH/g. This is equivalent to a utilization of 29 percent (theoretical = 0.224 AH/g) which compares quite favorably with 25–30 percent utilizations realized from commercial plates of comparable design at the 5-hour rate. In addition, data has been accumulated on approximately 2000 plates of varying designs and sizes which correspond closely to positive plate sizes in current commercial product. At tetrabasic lead sulfate loading densities of 68–70 g/in³ these plates consistently yield capacities of 30 AH/lb. at the 5-hour rate. This is equivalent to 30 percent utilization which again compares favorably with current commercial product.

Figure 3 presents the capacity-porosity data in a different format. The data show that, over the range studied, the less material per unit volume, the greater the capacity per unit volume. These data show that a reduction in the material loading density per unit volume results in an increase in plate efficiency which more than compensates for the reduction in capacity to be expected from the reduced quantity of material in the grid. These unexpected results have very interesting implications. For example, if the 1.0 A data in Fig. 3 is extrapolated to lower material densities, a loading density of 55 g/in3 will correspond to a utilization of 6.1 AH/in3. This, in comparison to 4.25 AH/in3 at a "normal" density of 69 g/in³, represents a 43.5 percent increase in capacity for a 20.3 percent decrease in material. Unfortunately, there are problems associated with the use of low material densities. As will be seen later, lowering material densities results in reduced plate life. In addition, there is the practical problem of how to achieve low 4PbO PbSO₄ plate loading densities. In general, lower loading density plates are obtained by increasing the ratio of water to 4PbO PbSO4 in the preparation of the paste. However, as the ratio of water to 4PbO PbSO4 is increased, the paste becomes more fluid and a point

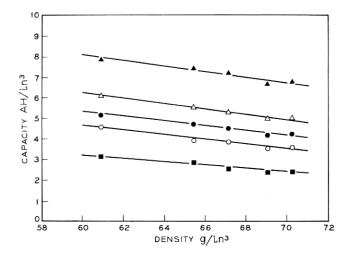


Fig. 3—Capacity (AH/in³) vs density (g/in³) for 4PbO·PbSO₄ plates. \square 2.50 A \bigcirc 1.30 A \bullet 1.00 A \triangle 0.70 A \bullet 0.35 A

is reached where the paste is too fluid for application to a grid. A paste density of 60 g/in^3 appears to be the useful low limit for water pastes of $4\text{PbO} \cdot \text{PbSO}_4$.

In the work reported here, ten days formation was required to convert the $4 \mbox{PbO} \cdot \mbox{SO}_4$ plates to \mbox{PbO}_2 . In many other experiments, which are not detailed here, 7–10 days formation in 1.050 sp. gr. $H_2 \mbox{SO}_4$ were required to achieve complete conversion of $4 \mbox{PbO} \cdot \mbox{PbSO}_4$ to \mbox{PbO}_2 . This is significantly longer than the 2–3 days required to form conventional positive paste formulations. The reduced formation efficiency is a result of the comparatively large particle size of $4 \mbox{PbO} \cdot \mbox{PbSO}_4$ and is not a property of the chemical composition of the material. This was demonstrated by studying the formation characteristics of

4PbO·PbSO₄

whose particle size was mechanically reduced. These plates converted completely to PbO₂ after only 2–3 days formation. This strongly suggests that the efficiency of the formation process is related to the material surface area.

IV. CYCLE BEHAVIOR OF TETRABASIC LEAD SULFATE POSITIVE PLATES

Continuous cycling and overcharge of lead-acid cell positive plates accelerate degradation of the PbO₂ matrix. In order to evaluate the

stability of 4PbO·PbSO₄ positive plates as compared to conventional plates, stress cycling experiments were carried out. These experiments were also designed to evaluate the effect of porosity on the stability of 4PbO·PbSO₄ positive plates. The details of the experiments are as follows. Five preweighed grids (2.5" × 3.0" × 0.25"), identical to those described previously, were pasted with water pastes of 4PbO·PbSO₄ of varying densities and air dried at room temperature for 48 hours. We obtained two other plates having identical grids from a commercial battery manufacturer and included them in this experiment for comparative purposes.

Cells were assembled as described previously and were formed in 1.050 sp. gr. H₂SO₄. The cells having the 4PbO·PbSO₄ positive plates were formed at 400 mA for 10 days whereas the two cells having the commercial positive plates were formed at 400 mA for 2 days followed by 250 mA for 2.5 days. After formation, all positive plates were washed with water, dried at 80°C for 3 hours and weighed to determine the amount of material in the grids.

Each cell was reassembled and transferred to jars containing 2.5 liters of 1.210 sp. gr. H₂SO₄. The large volume of H₂SO₄ was used for the reason stated previously. The seven cells were connected in series and given 7 discharge-charge cycles. The first four discharges were at 1.00 A and the last three at 0.90 A. All discharges were to a 1.75 V end-voltage. After each of these discharges, the series string was recharged over a period of approximately 16 hours at such a rate that 120 percent of the discharge capacity was returned to the highest capacity cell in the string. The positive plates were then removed and the three PbO₂ pellets in the top row of the grid were removed leaving six pellets in each grid. The plates were returned to the cells and the removed PbO₂ pellets were washed with water and dried at 80°C. This pellet material was examined with an optical microscope, studied by X-ray diffraction and analyzed for PbO₂ content.¹⁰

The reassembled cells were then placed on the following cycle routine. All cells in the string were given a deep discharge at 600 mA (5-hour rate) to 1.75 V once a week and a 1.0 hour discharge at 600 mA every other working day during the week. The deep discharges were followed by approximately 16 hours charge at such a rate that 120 percent of the discharge capacity was returned to the highest capacity cell in the string. The 1.0 hour discharges were followed by 100 percent overcharge over a 23-hour period. This cycle routine was continued until all cells gave less than 4 hours capacity at the 5-hour rate.

A photomicrograph of the unformed paste material from the com-

merical plates used in this experiment is shown in Fig. 4. The material is actually a mixture of white and reddish crystals of varying sizes and differs markedly in both crystal size and shape from 4PbO·PbSO₄ shown in Fig. 1. Figures 5 and 6 are photomicrographs of PbO₂ from a 4PbO·PbSO₄ and a commercial plate respectively after the initial seven cycles. X-ray diffraction showed the PbO₂ derived from both the 4PbO·PbSO₄ and commercial plates to the β-modification. X-ray diffraction analysis of many other 4PbO·PbSO₄ plates formed in 1.050 sp. gr. H₂SO₄ showed that β·PbO₂ was exclusively produced. The PbO₂ derived from 4PbO·PbSO₄ is composed of rather large prismatic crystals resembling the original 4PbO·PbSO₄ crystals. This observation confirms an earlier similar report.⁶ On the other hand, the PbO₂ obtained from the commercial plates is of a much smaller particle size and the crystal shape is not obvious at this magnification.

The results of the cycling experiments are presented in Fig. 7. The material densities were calculated from the measured weights of PbO₂ and the known pasteable volume of the grids. The initial data for the 4PbO·PbSO₄ grids show, in general, higher initial capacities for those plates having less material. This is in agreement with the quantitative observations reported earlier in Fig. 3. The 4PbO·PbSO₄ plate data

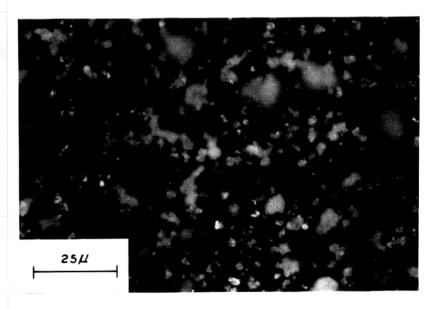


Fig. 4—Photomicrograph of commercial unformed positive paste material (500X).

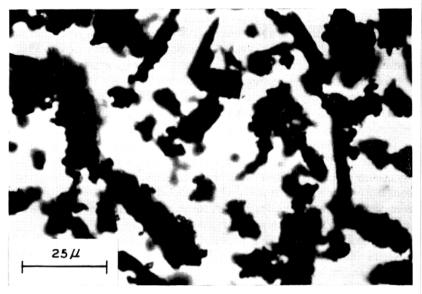


Fig. 5—Photomicrograph of βPbO_2 from $4 \text{PbO} \cdot \text{PbSO}_4$ (500X).

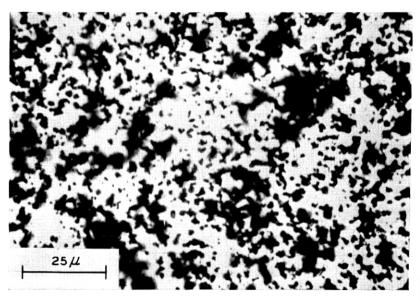


Fig. 6—Photomicrograph of βPbO_2 from commercial plates (500X).

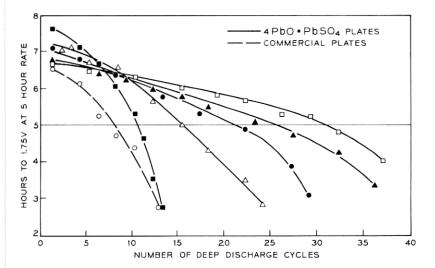


Fig. 7—Time to 1.75 V vs number of deep discharge cycles at the 5 hour rate (600~mA) for 4PbO. PbSO_4 and commercial plates.

show a general correlation between material density and cycle life. Cycling of positive plates induces stresses in the PbO₂ matrix since the conversion of βPbO₂ to PbSO₄ is associated with a 57 percent increase in volume. The molar volumes are 27.9 cm³/mole for PbO₂ and 43.8 cm³/mole for PbSO₄. Regardless of whether the stability of the PbO₂ matrix is attributable to mechanical interlocking of the PbO₂ crystals or chemical bonding between PbO₂ particles (it is probably a combination of both), the matrix stability would be related to the extent of interparticle contact. Consequently, plates with higher material densities would be expected to exhibit longer cycle life than low density plates and, as Fig. 7 shows, this is indeed the case. In all cases the 4PbO·PbSO₄ plates, regardless of material density, gave better cycle lives than the commercial plates. The data for the two commercial plates are not differentiated since both plates behaved identically.

Capacity failure of all plates was caused by shedding of PbO₂ and the rates of capacity degradation reflect the rates of PbO₂ shedding for these plates. In a comparison of the 4PbO·PbSO₄ and commercial plates based solely upon material density, the cycle life of the commercial plates would be expected to be in the 20–25 cycle region whereas only 8 cycles were obtained. This demonstrates that particle morphology

plays an important role in determining the PbO₂ matrix stability.

There is an apparent inconsistency in the 4PbO·PbSO₄ plate data in that the 64.2 g/in³ plate gave better cycle performance than the 66.8 g/in³ plate. The densities were calculated from the known grid pasteable volume. Although care was taken to minimize overpasting or underpasting of the grids, slight variations would result in errors in the calculated densities which may account for the above discrepancy.

Pellet samples from all cells were analyzed for PbO₂ to determine if there was any correlation between material density and PbO₂ contents of the 4PbO·PbSO₄ plates and also to determine if there were any significant analytical differences between the commercial plates and the 4PbO·PbSO₄ plates. The PbO₂ contents of the seven plates ranged between 90.2 percent and 94.3 percent but they were not significant in relation to the cycle test results.

Although these results involve a comparison with only two plates from the same manufacturer, they are consistent with results reported for similar experiments on lead calcium grids. It is reasonable to conclude that the superior performance of the tetrabasic lead sulfate positive plates can be attributed to the characteristic size and shape of the PbO_2 particles obtained from $4PbO\cdot PbSO_4$.

V. CONCLUSIONS

Tetrabasic lead sulfate, having definable and reproducible chemical and physical properties, can be synthesized providing that the reaction parameters are properly controlled. The use of the material in positive plate fabrication is simple and straightforward. Water is the only liquid used in paste preparation and no special plate curing conditions are required. Since water is used, the definability and reproducibility of the 4PbO·PbSO₄ material enables one to accurately define and control the properties of the resulting paste which allows control of plate performance.

The formed tetrabasic lead sulfate plates yield initial capacities which compare very favorably to current commercial product. A drawback is the additional formation time required. Various methods of reducing the formation time are being investigated. Some of these have been very successful and the effects of these on plate performance are presently being evaluated.

The use of 4PbO·PbSO₄ results in a significant improvement in the cycle behavior of lead-acid positive plates. Although the cycle data cannot be directly extrapolated to actual float service life, it is clear

that we have realized a substantial improvement in the mechanical stability of the $Pb0_2$ structure. This is consistent with the objective of improving float service life of lead-acid cells used in telephone service.

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