

Discussions on the Lead/Acid Battery. No. 1

The Role of Tetrabasic Lead Sulphate in the Lead/Acid Positive Plate

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Summary

Tetrabasic lead sulphate (4BS) is only formed in battery pastes that see temperatures in excess of 70 °C. Although it is difficult to oxidise anodically, when converted to PbO₂ it forms the alpha-polymorph which gives the positive plate a long cycle life. This statement is a summary of what appear to be currently held beliefs. In this discussion, the relevant literature is reviewed showing that this view is wrong.

Introduction

The occurrence of tetrabasic lead sulphate, 4PbO·PbSO₄ (4BS), in battery paste processed at temperatures exceeding 70 °C has been known for half a century [1] and is now part of battery lore. Its presence had always been considered undesirable because of the difficulty in electroformation to PbO₂, but in the 1970s Bell Laboratories developed the use of 4BS exclusively for the active material of their standby batteries [2] and overcame the formation problem [3]. Since then, 4BS has continued in use as the active material for this product. Despite such use in commercial products, the effects of 4BS in the positive plate are unclear from the literature and several myths have been established which appear to have little basis in factual evidence. It is the object of this discussion to critically review the literature and attempt to establish the basis of the occurrence of 4BS and its effects in the positive electrode.

Preparation of tetrabasic lead sulphate

It is conventionally believed that 4BS is only formed at temperatures in excess of 70 °C by reaction of orthorhombic PbO with H₂SO₄ [4]. Cer-

tainly, Biagetti and Weeks identify PbO(o) and $80\text{ }^\circ\text{C}$ as the best conditions for the preparation of 4BS as "a uniform and reproducible product", but they also say that at lower temperatures, and using PbO(t) , the product is a mixture of reduced crystal size [2]. The formation of 4BS in battery pastes at room temperature was reported in 1942 by Mrgudich [1] who obtained 4BS contents of up to 60% on pastes that had been allowed to stand for up to 150 days at room temperature. If the paste was dried prior to storage no conversion took place.

More recent work by Chang and Wright has reinforced the above findings [4]. A range of commercial lead oxides of differing $\text{PbO(o)}:\text{PbO(t)}$ ratios was mixed with water and sulphuric acid and stored at temperatures between room and $80\text{ }^\circ\text{C}$ in both slurry and paste form. Most compositions produced 4BS if stored for long enough periods (up to 28 days). The general conclusions were that PbO(o) was more reactive than PbO(t) and that the reaction was accelerated by increasing the temperature, but 4BS could be produced at room temperature.

Other workers examined the paste composition over shorter time periods. Pavlov and Papazov [5] reported that 4BS is formed in pastes at $80\text{ }^\circ\text{C}$ but not at $35\text{ }^\circ\text{C}$. It is presumed that the phase composition was determined shortly after paste mixing. At $80\text{ }^\circ\text{C}$, the basic sulphate formed is dependent on the $\text{PbO}/\text{H}_2\text{SO}_4$ ratio; as more H_2SO_4 is added the predominant basic sulphate changes in the sequence: $4\text{PbO}\cdot\text{PbSO}_4$, $3\text{PbO}\cdot\text{PbSO}_4\cdot\text{H}_2\text{O}$ (tribasic lead sulphate = 3BS), $\text{PbO}\cdot\text{PbSO}_4$ (monobasic lead sulphate = 1BS). In a further paper, Pavlov and Iliev [15] measured the kinetics of formation of 4BS in a paste at $80\text{ }^\circ\text{C}$; 25 min is required for full conversion to 4BS and the reaction appears to occur through 3BS as an intermediate, the conversion of this to 4BS being the rate-determining step.

Varma and Fleischmann [6] carried out similar experiments and found 4BS in pastes subjected to $80 - 85\text{ }^\circ\text{C}$ for 3 h but not at temperatures between 25 and $55\text{ }^\circ\text{C}$. They also found that dibasic lead sulphate, $2\text{PbO}\cdot\text{PbSO}_4$ (2BS), formed in some instances: an observation that has not been repeated in the literature. Sekido and Yokoh [7] also report 4BS in paste and cured plates, although it is difficult to draw conclusions from this as the full thermal history is not given.

The literature is thus consistent in that 4BS is formed in slurries or pastes when the correct $\text{PbO}/\text{H}_2\text{SO}_4$ ratio is achieved. It is formed slowly at room temperature, rapidly at temperatures of $70\text{ }^\circ\text{C}$ and above, and PbO(o) is more reactive than PbO(t) . In practical terms this means that for the usual paste manufacture/pasting/curing time-scale of a few days for a battery plant, 4BS is not formed unless high temperatures are reached. However, if paste is prepared and stored for extended periods it would seem possible that 4BS could be formed by reaction of the 3BS and PbO present in a typical paste.

If 4BS is to be used exclusively for the active material, care has to be exercised to enable paste adhesion and strength to develop. As a water paste is used, the usual paste-setting reactions, which have been likened to cement

setting [8], cannot occur. This can be overcome by using a CO_2 atmosphere which is thought to convert the surface of the 4BS crystals to carbonate, giving the paste strength from carbonate bridges [9]. Both tribasic and tetrabasic lead sulphates are subject to CO_2 pick up in damp conditions, with the replacement of SO_4^{2-} by CO_3^{2-} to give mixed basic sulphate/carbonates [10], and these appear to be a suitable substitute for the normal sulphate-forming reactions involved in the setting of a conventional oxide/ H_2O / H_2SO_4 paste. 4BS has also been used as a binder for a 'precharged' plate of PbO_2 but its mode of action is unclear [11].

Tetrabasic lead sulphate in the positive plate

The work at Bell Laboratories [2, 22] showed that plates based on 4BS gave approximately twice the cycle life of conventional leady-oxide-based plates. Other work agrees with these findings [12] but, in both cases, the cycling was carried out in such a large excess of acid that the concentration did not change significantly during cycling. This is obviously not representative of battery conditions. Although very little seems to have been published on this aspect, some unpublished work at Chloride in which 4BS was used as the active material for an automotive battery design largely substantiates the claims of the Bell Laboratories. The test results on these batteries showed the low rate (20 h), reserve capacity (25 A), and high rate (-18°C to 7.2 V/cell) to be similar to conventional paste, but the 1 h/5 h life-cycle test (BS 3911) gave 50% more cycles for the 4BS plates.

The reasons for the superior performance of 4BS-based plates is not clear. The two main theories are: (i) the large crystals of PbO_2 produced metasomatically from 4BS give a mechanically strong plate resistant to shedding [13]; (ii) 4BS is the source of $\alpha\text{-PbO}_2$ [14].

The concept of the large crystals producing a more resilient active material is an attractive one; 4BS has been found by many workers to convert metasomatically to PbO_2 [2, 3, 11 - 13], but little has been published on the length of time that this structure is maintained during cycling [22]. It is to be expected that as the discharge product, PbSO_4 , is not produced metasomatically with the original PbO_2 , the original 4BS structure will quickly revert to a normal plate structure and influence on cycle life will be minimal. Ikari *et al.*, however, found that PbSO_4 formed from 4BS had abnormal growth in the (211) and (210) planes and that this did not occur with the other basic sulphates [16]. Perhaps this type of growth mechanism could help maintain the large crystallites of PbO_2 (formed from 4BS) through many $\text{PbSO}_4/\text{PbO}_2$ cycles.

The alternative view on the reason for the extended life of 4BS-based plates is that 4BS is converted to $\alpha\text{-PbO}_2$ on formation and that the latter, being mechanically stronger and having a lower utilisation than $\beta\text{-PbO}_2$ [14], forms a 3-D network structure in the plate giving improved mechanical support and reduced shedding [17, 18]. This view is also open to question.

That 4BS is converted to α -PbO₂ *per se* is incorrect. Several workers observe only β -PbO₂ as the product of anodisation [10, 12, 16, 21], while Yarnell and Weeks [3] report a mixture of the α and β polymorphs. The reasons for these differences can be understood from the work of Dodson [19, 20] who evaluated the effect of various battery-related parameters on the α -PbO₂/ β -PbO₂ ratio in positive plates. He found that the factors leading to an increase in the α -PbO₂ content were: increasing paste density; decreasing formation acid gravity; increasing temperature. These findings are consistent with α -PbO₂ being formed within the plate where low acid concentration conditions prevail [16]. Yarnell and Weeks used 6 mm thick plates and formed them in very low-gravity acid (1.005 SG), which would encourage α -PbO₂ production. Their data also showed that the β -PbO₂ content is doubled as the forming acid concentration is increased from 1.005 to 1.050 SG. The workers who found β -PbO₂ only, used either more concentrated forming acid [12, 13, 16] or thinner plates [12, 13], or both. Each would encourage β -PbO₂ formation. Thus, 4BS can be converted to either α - or β -PbO₂ depending on the conditions — both transformations apparently being metasomatic.

The other part of the latter theory on 4BS is that α -PbO₂ extends the life of the paste. This idea appears to have originated with the work of Simon and Jones [17, 18] who examined microscopically a wide range of positive plates and identified a hard, reticular network of α -PbO₂ that improved both the mechanical integrity and the life of the plate. The evidence presented for this mechanism was based on optical microscopy and, consequently, is open to interpretation. For instance, although Simon equates the hard PbO₂ with the α -polymorph, in the discussion following this paper Bagshaw [18] recalls data that α -PbO₂ and β -PbO₂ have similar micro-hardness and that any differences are due to porosity. Even without a reticular structure, α -PbO₂ is generally recognised as giving plates a good cycleability. Again, the evidence for this needs careful consideration. In one of the most comprehensive studies on α -PbO₂, Dodson [19, 20] concludes that α -PbO₂ increases life on overcharge test by a factor of two, but does not affect cycle life. He attributes the increase in overcharge life not to α -PbO₂ itself, but to the fact that the potential on overcharge was lower with α -PbO₂ (lower oxygen overpotential on PbO₂), resulting in reduced grid corrosion. Other workers have correlated α -PbO₂ content with cycle life [23, 24] but any effect of α -PbO₂ is often confounded by other effects. Usually, high α -PbO₂ contents are achieved by increasing paste density, but this alone would be expected to increase life because it is a stronger material with more interparticle contacts. The effect of paste density itself is difficult to quantify as increasing this will reduce the utilisation and, hence, increase cycle life. This means that there are at least three contributory factors to increased cycle life when plate density is changed. Even measuring the α -PbO₂ content of a PbO₂ sample is not easy and it is possible that some literature results are inaccurate because of this. A good review of diffraction techniques and problems in quantitative determinations is given by Hill [25].

A further question that must be raised on the α -PbO₂/improved-life theory is how does α -PbO₂ remain in the active material for sufficiently long periods to affect life? If the α -PbO₂ is discharged during a cycle then it will recharge as β -PbO₂ through the cycle: α -PbO₂ \rightarrow PbSO₄ \rightarrow β -PbO₂ [26], and this results in a rapid decrease in the α -PbO₂ content of the plate early in life. Since results as low as 5 - 10 wt.% α -PbO₂ content have been reported after as little as 10% of total cycle life, it is hard to imagine how so little α -PbO₂ could influence the active material for the remaining 90% of its life [23, 24]. Such small quantities could not form an effective 'reticular structure' nor would they be expected to act as any form of "glue" for β -PbO₂, as they would most likely be present in the interior of crystals covered by β -PbO₂. If the original α -PbO₂ was located in the plate interior where the utilisation was very low then one could see how relatively high α -PbO₂ contents could be maintained well into the life of the plate [20]. In such instances, however, the α -PbO₂ would not be in that part of the plate which is being cycled and, hence, would have little effect on life.

A further mechanism for the destruction of α -PbO₂ is self discharge, which is reported as being higher for the α - than for the β -polymorph [20]. Hence, it would be expected that plates left on open circuit for any length of time would suffer serious losses in α -PbO₂ content. One way to counter this would be to maintain cells on float, and this could be the one application where any benefits of α -PbO₂ would be found, especially since float duties usually involve few discharges — unfortunately there appears to be little in the literature on this aspect.

Although digressing somewhat, it is interesting to speculate on the conditions for α -PbO₂ formation. Although many suggestions have been advanced [14], the main criterion seems to be plate porosity: the lower the porosity the higher the α -PbO₂ content [16, 19]. This, coupled with the known effect of acid concentration on the α -PbO₂/ β -PbO₂ ratio [19] leads to the conclusion that the pH in the plate interior is the controlling factor [27, 28]. This is normally stated as: α -PbO₂ forms in alkaline or neutral media and β -PbO₂ in acid media. Experimental evidence suggests that reality is somewhat more complex. It is often very difficult to obtain pure α - or β -PbO₂, and many methods give mixtures of the two polymorphs. High purity α -PbO₂ is formed in acetic acid solution, pH 3.9 - 4.7 [29], and also in other acidic solutions, e.g., Pb(NO₃)₂ (pH 3.5) and HClO₄/Pb(ClO₄)₂ (pH 1) [28]; KHSO₄ (pH 0.7) [27]. If pH was the only controlling factor, then around pH 1 would appear to be the point at which the relative stabilities of the two polymorphs change — not pH 7 as is conventionally taught. An alternative explanation has been advanced in the past, however, which involves the adsorption of solution anions onto an intermediate in the Pb²⁺/Pb⁴⁺ reaction [30, 31, 36]. Although this suggestion is not currently popular, it could prove useful as a starting point for further ideas on the reason for the formation of α - and β -PbO₂. As far as the lead/acid battery is concerned, with a sulphuric acid electrolyte, acid specific gravity and paste density appear to be the main factors in determining the α -PbO₂/ β -PbO₂ ratio.

Tetrabasic lead sulphate in the corrosion layer

There have been several reports of the occurrence of basic sulphates in the corrosion products of lead and lead alloys [32 - 35]. This is possibly to be expected as it has been firmly established that the interior of the corrosion layer contains PbO [37] and, presumably, a high pH environment — conditions necessary for the formation of basic sulphates. Other workers have failed to detect basic sulphate [38 - 45] and reports of 4BS itself are very few [32, 34]. The detection of basic sulphates in the corrosion product is normally by *ex situ* diffraction techniques and, as most corrosion films are a complex mixture of compounds, unambiguous detection of 4BS or other basic sulphates, presumably in small quantities anyway, is very difficult.

Conclusions

In the review of the lead/acid battery by Burbank *et al.* [14], thirteen questions were detailed to delineate areas in which more research was needed. Of these thirteen questions, six are reproduced verbatim below as being pertinent to this discussion.

- By what mechanism does the positive plate active material soften and fail?

- Why does the X-ray diffraction pattern of α -PbO₂ show abnormally low intensity in standard mixtures of the two polymorphs? What is the source of α -PbO₂ in modern battery plates? What function, if any, does α -PbO₂ serve in determining the operational characteristics of the positive plate? Can the apparent anomalies for formation of α -PbO₂ as a corrosion product on grid alloys and in the active material be resolved?

- What is the kinetic mechanism and charge exchange reaction of the reversible PbO₂/PbSO₄ electrode? What characterises the behaviour of electrodes of α - and β -PbO₂ and mixtures of the two polymorphs?

- What factors control the geometrical morphology of PbO₂ and PbSO₄ crystals in the positive plate? Is there an intrinsic size and shape associated with plate durability?

- Can the nature of the surface change of PbO₂ electrodes with time be determined? Is this related to crystal structure, stoichiometry and physical morphology of the electrodes?

- Is oxygen liberation on α -PbO₂ kinetically easier than oxidation of PbSO₄ to β -PbO₂? Does this have a bearing on the charge acceptance rate at the positive plate? Does this control the appearance and growth of hard sulphate?

This list was compiled in 1968. How many of these questions have been answered in the twenty years since then? The evidence is that very few have. Is this because the questions are too difficult, is it due to lack of interest, or is it because we have convinced ourselves that we know the answers? Is it important that we find answers and if so, how do we go about it?

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