

THE ROLE OF BARIUM SULFATE IN THE NEGATIVE PLATE OF THE LEAD STORAGE BATTERY

Ya. B. Kasparov, É. G. Yampol'skaya, and B. N. Kabanov

Translated from *Zhurnal Prikladnoi Khimii*, Vol. 37, No. 9,
pp. 1936-1941, September, 1964

Original article submitted June 20, 1962

Increase of the specific capacity* of the negative (lead) plate is a matter of great practical importance. It is known that unless the paste used for the plates contains expanders a high capacity cannot be ensured, especially at the low temperatures and high current densities of starter operation. Expanders usually consist of mixtures of certain organic substances with barium sulfate. However, the mechanism of expander action has proved to be very complex, and there have been numerous investigations of the subject in recent years [1-6]. The capacity may be raised either by increase of the true plate area due to an increase of porosity, or by deeper penetration of the action into the plate material.

It has been shown [1] that the action of the organic components in expanders depends on adsorption. We believe that the main effect of expanders is to ensure action of the plate material to a greater depth; i.e., that they make the structure of the PbSO_4 layer less compact and reduce passivation of the lead. The increase of the plate capacity was formerly [5] attributed to the isomorphism of BaSO_4 and PbSO_4 crystals. However, the literature contains no data providing conclusive proof of independent "expanding" action of BaSO_4 . We suggested in a preliminary communication [6] that the role of BaSO_4 is to retain and gradually yield organic expanders. In the present investigation additional experiments were carried out to clarify this matter. The effect of BaSO_4 on the negative plates was investigated both in presence and in total absence of organic substances.

Figure 1 shows variations of the capacity of storage cells during cycling at high current densities under starter conditions. Each cell consisted of one negative and two positive plates in excess electrolyte carefully freed from organic impurities. The discharge time at starter current density until the voltage of the cell showed a drop is plotted against the number of cycles.

Figure 2 shows variations of the starter discharge time with the number of cycles for 3-St-70 batteries with alderwood separators. The negative plates were either free from expanders, or contained BaSO_4 and an organic expander. The expander was peat† previously treated with sulfuric acid, washed with water, and dried at 50-70°.

Curve 1 in Figs. 1 and 2 refers to plates made from the usual materials without any additives. The relatively high capacity during the early cycles falls rapidly to a low value which is maintained during subsequent cycling. Plates containing only commercial BaSO_4 (curve 2) or only the organic expander (curve 3) as additives to the paste have high capacity during the early cycles; the capacity falls somewhat more slowly than in the case of plates without additives and approaches the value for the latter. On the other hand, plates containing both BaSO_4 and the organic expander in the paste (curve 4) retain a high capacity during prolonged cycling.

The high starter capacity during prolonged cycling obtained with BaSO_4 and the organic material in the paste cannot be attributed to a mere addition of the equal effects of barium sulfate and the organic expander on the capacity, because at the start of the cycling the influence of the combined expander (BaSO_4 and the organic material) is almost the same as that of either one separately, but a very large difference develops in the course of cycling. Moreover, a twofold or even threefold decrease or increase of the content of either component has little effect on the capacity or its variation with the number of cycles. If the amount of organic expander is decreased to only a small fraction rather than by a factor of two or three, a plate containing this expander even with the normal amount of barium sulfate retains its high capacity only during the early cycles.

*This article is concerned with the total plate capacity; the capacity of the double layer may be neglected by comparison with it.

†This product contains 45-60% of humic acids.

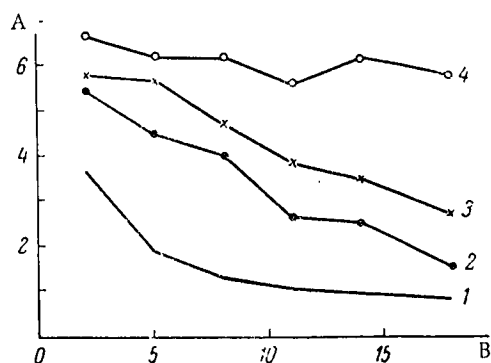


Fig. 1. Variations of the duration of full starter discharge at 30° with the number of cycles (plates in excess electrolyte). A) Time (min); B) cycles; the same in Figs. 2 and 3. 1) Without additives; 2) 0.3% BaSO₄; 3) 1% treated peat; 4) 0.3% BaSO₄ and 1% treated peat.

without added BaSO₄ (curve 1). The starter capacity of these plates was the same; it was very low and remained at that level during prolonged cycling. This confirms the hypothesis that BaSO₄ has no independent effect on the capacity of the negative plate. Cells with negative plates made with uncalcined litharge without additives (curve 3) had fairly high capacity during the early cycles, but the capacity fell sharply and by the 8th cycle became the same as that of plates made with calcined materials. The high capacity during the early cycles is therefore attributable to the presence of organic impurities present in the oxides, which gradually pass into the electrolyte and are oxidized at the positive plate.

When uncalcined oxides are used together with uncalcined BaSO₄ (curve 4, cycles 1-18), the same process occurs, but much more slowly, because BaSO₄ retards the transfer of impurities into the electrolyte.

After the 24th cycle (curves 1 and 2) or the 20th cycle (curves 3 and 4) the negative plates of these cells were charged, transferred to an electrolyte containing 2 g of sodium lignosulfonate (SL) per liter, and kept there for 32 hours. The purpose was to deposit an organic expander on the BaSO₄ and lead surface. After this treatment the negative plates were transferred to cells with pure electrolyte and subjected to further cycling. Figure 3 shows that after treatment of the negative plates in SL solution the capacities of all the cells rose sharply. However, in the case of cells without BaSO₄ in the negative plate the capacity fell sharply during cycling to the level for cells without organic material, whereas cells with negative plates containing BaSO₄ (calcined or uncalcined) retained a high capacity for a long time.

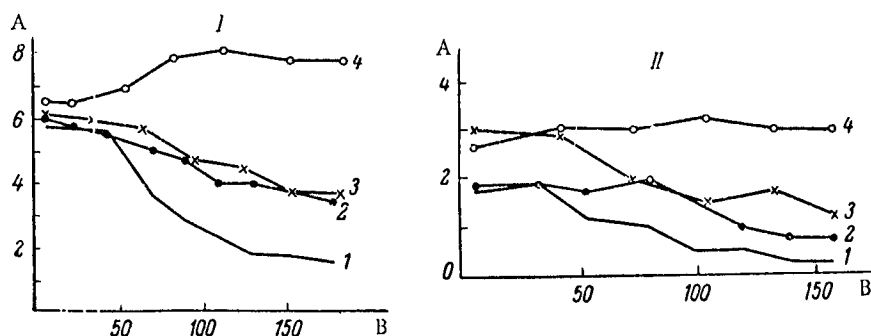


Fig. 2. Variations of the duration of full starter discharge with the number of cycles (3-St-70 batteries, alderwood separators). 1) Without additives; 2) 0.3% BaSO₄; 3) 1% treated peat; 4) 0.3% BaSO₄ and 1% treated peat. Temperature (°C): I) 30; II) 18.

It follows that the effective action of BaSO₄ and the organic expander when present together must be due to interaction of the two additives.

It was necessary to determine the nature of this interaction and to find whether BaSO₄ merely plays an auxiliary part due to its interaction with organic matter, and in particular with the organic impurities which are always present in commercial inorganic materials. Plates filled with paste quite free from organic matter were prepared. Before the paste was mixed, the lead oxides and BaSO₄ were calcined in the air at about 400° for several hours. The purpose was to remove the organic impurities which are always present in the litharge and BaSO₄, which might influence the subsequent discharge process. The electrolyte in which the plates were formed was also purified electrochemically to remove traces of organic impurities.

Figure 3 (cycles 1-24) shows the capacities of these plates (curve 2) and of plates made with calcined litharge

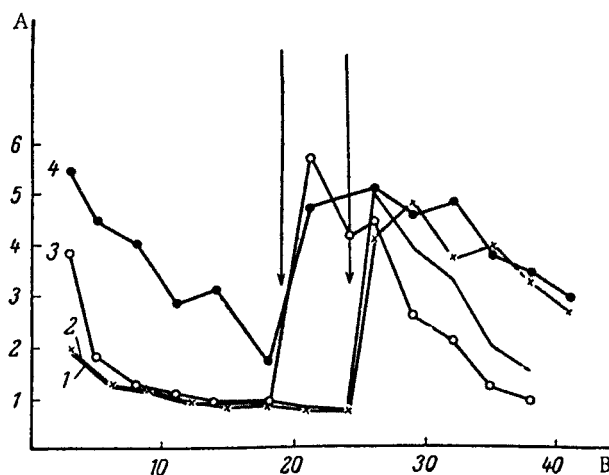


Fig. 3. Variations of cell capacity with the number of cycles under starter discharge conditions at 30°. 1) Calcined litharge; 2) calcined litharge and BaSO₄; 3) uncalcined litharge; 4) uncalcined litharge and BaSO₄; the arrows indicate treatment of the negative plates in sodium lignosulfonate solution (2 g/liter) for 32 hours after charging. The subsequent curve refers to discharge in the pure electrolyte.

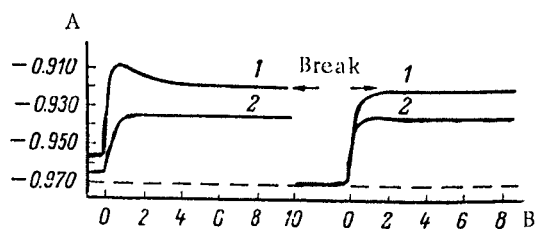


Fig. 4. Initial shift of potential during anodic polarization of a negative plate at high current density. A) φ (V); B) time (sec). 1) Without additives; 2) with BaSO₄ in paste. Dash line represents the equilibrium potential of the Pb | PbSO₄ plate in H₂SO₄ solution.

Similar results are obtained if organic impurities are removed from the litharge and BaSO₄ by repeated treatment with 0.01 N KMnO₄ instead of calcination.

These experiments show that the intrinsic properties of BaSO₄ as the expander component are not destroyed by calcination or by treatment with KMnO₄ solution; neither are the intrinsic properties of litharge altered by calcination.

Thus, added BaSO₄ is effective under severe discharge conditions only in presence of an organic expander, and ensures prolonged action of the latter. The relatively high capacity usually found in plates containing only commercial BaSO₄ in the paste is attributable to the combined action of BaSO₄ and organic impurities in the paste.

The strength of the bond between the organic substances and BaSO₄ can also be assessed from the behavior of plates with and without BaSO₄ during anodic polarization until the active spongy lead is converted into lead dioxide ("polarity reversal") followed by reduction of the lead dioxide to spongy lead. It might have been expected that during discharge to lead dioxide and exposure of the plate at this high anode potential the surface-active substances would be oxidized and that after charging, the capacity of such a plate would be much less than in the preceding cycle. It was found, however, the only plates without added barium sulfate showed a sharp drop of capacity. In the case of plates containing barium sulfate the starter capacity remains almost unchanged after polarity reversal.

It is natural to suppose that the function of BaSO₄ is to retain the organic material at the plate/solution interface, i.e., where lead ions pass into solution and where lead sulfate crystallizes. The fact that BaSO₄ crystals act as an adsorbent or "store" for the organic surfactant may account for the combined action of BaSO₄ and the organic expander. The organic surfactant is adsorbed on the barium sulfate surface by specific or chemically reversible adsorption, and when the plate is discharged it is partially transferred to the forming PbSO₄ crystals by surface diffusion. It should be pointed out that an excess of expander lowers the plate capacity as the result of adsorptive block-

ing of the PbSO_4 and lead surface (known as "sulfation" of the plate [7]). It is therefore likely that BaSO_4 not only prevents loss of the organic material from the negative plate, but also restricts its access to the adsorptionally active plate surface during discharge, when the surface area is greatly diminished.

Therefore BaSO_4 , unlike the organic expander, is not a depassivator but merely retains the depassivating organic expander during prolonged cycling.

The fact that isomorphism of BaSO_4 and PbSO_4 crystals may be of some significance in the action of the storage battery is not denied by these views. An oscillographic trace of the initial portion of the discharge curve (anodic polarization curve) of a well charged negative plate showed (Fig. 4) that the presence of calcined BaSO_4 in active material made from calcined litharge prevents the initial sharp rise of potential, "whiplash", and diminishes the more prolonged rise of potential. Both these rises of potential are due mainly to supersaturation of the electrolyte with lead sulfate if PbSO_4 crystal nuclei are absent from the plate or are present in insufficient numbers [8]. The supersaturation is decreased by BaSO_4 , which is isomorphous with PbSO_4 , and the PbSO_4 concentration polarization is thereby diminished. The practical effect of the depolarizing action of BaSO_4 is to raise the discharge voltage of the lead battery. Halfway through the discharge the potential is, of course, the same without BaSO_4 as in its presence, as there are enough PbSO_4 crystals to reduce supersaturation.

SUMMARY

1. It is shown that the role of BaSO_4 in the expander is to preserve the surface-active organic component of the expander, to ensure regulated supply of this component to the reaction zone, and subsequently to adsorb it reversibly at the discharge stage when most of the organic material is desorbed from the active surface of the plate. Adsorption on BaSO_4 may protect the surface-active organic substance against anodic oxidation.

2. The isomorphism of BaSO_4 and PbSO_4 results in a decrease of polarization at the start of discharge owing to decrease of the supersaturation of the solution with lead sulfate.

LITERATURE CITED

1. B. N. Kabanov, Proceedings of Second Conference on Metal Corrosion [in Russian], Izd. AN SSSR, Moscow-Leningrad, Vol. 2, 67 (1943); Dissertation, KÉIN, Kazan' (1942); DAN SSSR, 31, 582 (1941).
2. A. K. Lorents, Report of the Storage Battery Scientific Research Institute [in Russian], Leningrad (1951).
3. E. Willinganz, Trans. Electroch. Soc., 92, 281 (1947).
4. E. Ritchie, J. Electroch. Soc., 100, 53 (1953).
5. E. A. Belitskii, Colloquium Papers, Moscow [in Russian] (1939, 1940).
6. Ya. B. Kasparov, É. G. Yampol'skaya, and B. N. Kabanov, Proceedings of the Fourth Conference of Electrochemistry [in Russian], Moscow, 744 (1959).
7. T. I. Popova and B. N. Kabanov, ZhPKh, XXXII, 326 (1959).
8. B. N. Kabanov, DAN SSSR, 31, 338 (1941).

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-to-cover English translations appears at the back of this issue.
