

Effects of additives on the discharge behaviour of positive electrodes in lead/acid batteries

Suqin Wang, Baojia Xia, Geping Yin, Pengfei Shi

Department of Applied Chemistry, Harbin Institute of Technology, Harbin 150001, China

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Abstract

The effects of expanded graphite, carbon fibre, needle coke and polyacene, when used as positive electrode additives, on the PbO_2 electrode behaviour of lead/acid batteries are studied. It is found that, during the initial stage of charge/discharge cycling, all of the additives are able to raise appreciably the coefficient of utilization of the positive active material. By contrast, they cause, to differing degrees, a reduction in service life when a certain nitrogenous heterocyclic compound (AS) is added to the positive active material. The coefficient of utilization of the latter is increased greatly during deep cycles. The addition of the graphite–AS composite additive improves the coefficient during the total period of cycling and reduces the consumption of lead powder in the PbO_2 electrode by 14%. It is also found that the addition of 1 wt.% of Li^+ to the electrolyte has a beneficial effect on the discharge capacity of the positive electrode. When lithium sulfate is added to the lead paste, together with the graphite–AS composite additive, the results show that not only the superiority of the positive electrode can be maintained, but also the service life is not less than that of any positive electrode with the additive of graphite, AS, or graphite–AS composite additive.

Keywords: Lead/acid batteries; Positive electrodes; Discharge behaviour; Additives

1. Introduction

The lead/acid battery has many advantages, such as low cost, readily available raw materials, high reversibility, excellent adaptability to different environments, broad load range, remarkable shelf life, etc. For many years, therefore, production and sales have held top place among all the other types of accumulators that are marketed throughout the world. Moreover, many experts predict that this superiority will be maintained for many years to come.

Nevertheless, the positive active material of the lead/acid battery has a comparatively low coefficient of utilization. Usually, for discharge with a small current density, its coefficient of use is only about 45 to 50%. For discharge with a large current density, the utilization becomes even lower [1]. This fact results in a high consumption of lead. The service life and the actual specific capacity of the battery have to drop to such a low level that its practical application is limited. Therefore, how to raise the coefficient of utilization of the positive active material has become one of the problems that arouses continuous concern among sci-

entists and engineers that are working in the field of chemical power sources.

Simonsson [2] has studied the theory of the mass-transfer process, as well as the interdependent relationships between discharge state, formation conditions of PbSO_4 , and coefficient of utilization of the positive active material. It was concluded that the low coefficient of utilization of the positive active material is due to the fact that pore blockage and the limit of pore size caused by PbSO_4 both hinder diffusion in the pores and leads to a lack of electrolyte. Dietz [3] studied the effects of acetylene black, silica gel, carboxymethyl cellulose and fibre on the positive electrode, and found that these additives affect the initial capacity or the number of charge/discharge cycles by improving the crystallization process of the active material and its water-holding capability, conductivity, and stability. The research work of Tokunaka [4] showed that when a certain amount of anisotropic graphite was added to the positive lead paste, the capacity of the positive electrode was increased markedly, together with the number of charge/discharge cycles. In other studies, scientists have studied the effects of certain metal ions

on the behaviour of positive electrodes. They have concluded that the addition of inorganic positive ions, such as Al^{3+} , Mg^{2+} , Ca^{2+} and traces of Cd^{2+} , can improve the electrode behaviour and, consequently, the service life of lead/acid batteries [5]. Nevertheless, due to various factors, the above-mentioned additives have not yet been put into practical use.

In view of the present fact, the authors have attempted to develop a new type of practicable additive for positive electrodes that will raise the coefficient of utilization of the positive active material and reduce the consumption of lead. This is to be achieved under the prerequisite condition that specifications for all the manufacturing parameters should remain unchanged so as to attain the dual aim of raising the specific capacity of the battery and reducing its cost.

The first studies were directed towards the effects of some substances such as graphite and carbon-containing materials on the behaviour of the positive electrode. It was found that the effects of a certain expanded graphite were remarkable, and especially with respect to the initial charge/discharge cycles of the battery. In addition, its expansion ratio was of significance. Next, the research work was focused on the influence of some organic additives. It was also observed that a certain nitrogenous heterocyclic compound (denoted as AS) was able to improve the electrode behaviour remarkably, but its benefits declined during deep-discharge cycling. The addition of both expanded graphite and the organic composite additive to the lead paste resulted in an improvement in electrode behaviour for the whole process of charge/discharge cycling. Further work revealed that the addition of a certain amount of lithium sulfate to the electrolyte also produces a beneficial effect on electrode capacity and battery service life.

It is predicted that when the lithium sulfate is used together with the above-mentioned organic composite additive in the lead paste, the research work might attain its expected aims.

2. Experimental

For laboratory studies, a low-antimony alloy grid was adopted and had dimensions of 6.3 cm × 2.6 cm × 0.3 cm. The plate was pasted manually. The H_2SO_4 used in the paste mixing had a sp. gr. of 1.22. The pasted plate was cured for 24 h at $35 \pm 2^\circ\text{C}$ and a relative humidity of 100%. Then, it was dried at room temperature for 24 h. A constant d.c. electrochemical formation method was adopted. The formation process was continued until the bath voltage had become constant for 3 h. A test cell was made up of the formed plates. The cell contained a large amount of electrolyte with a sp. gr. of 1.28. Finally, the effects of each additive on the capacity, coefficient of utilization and service

Table 1
Additives used for positive plates

Series No.	Additive	Quantity (wt.%)	Added to the
1	Expanded graphite	0.5	Lead paste
2	Carbon fibre	0.5	Lead paste
3	Needle coke	0.5	Lead paste
4	Polyacene	0.5	Lead paste
5	AS	0.5	Lead paste
6	Expanded graphite + AS (1:1)	1	Lead paste
7	Li_2SO_4	1	Electrolyte
8	Expanded graphite + AS/ Li_2SO_4	1/1	Lead paste/ electrolyte

life of the positive electrode were examined by means of constant d.c. charge/discharge cycling. The discharge current was 280 mA, the discharging time was about 3 to 4 h, and the final potential of the discharge positive electrode versus a lead electrode was about 1.65 V.

The types (including compounding forms), quantities, and method of introduction of the additives used in the experiments are given in Table 1.

3. Results and discussion

3.1. Effects of graphite and carbon-containing materials on the behaviour of positive electrodes

Graphite and some carbon-containing materials are characterized by their excellent conductivity and water-holding capability, and are likely to produce beneficial effects on the electrode behaviour. Polyacene is a substance that has the structure similar to that of graphite. Therefore, the influence of the relevant materials mentioned above (Nos. 1 to 4 in Table 1) were observed when used as positive electrode additives. They were put, in a given certain proportion, into a lead paste and made into positive plates. The plates were then used in charge/discharge experiments. The calculation from the discharge capacity, the variation in the coefficient of utilization of the active materials with the number of cycles is shown in Fig. 1.

As can be seen from the data, all the four additives in the lead paste increase the coefficient of utilization of the positive active material during the initial cycles. Take the fifth discharge for example, the coefficient is raised by 8 to 10% when graphite, carbon fibre and needle coke are added. Polyacene exerts the greatest effect, it raises the coefficient by about 20% with the further cycling, however, the effect on capacity is diminished to different degrees, as follows. When polyacene is added, the electrode capacity is lower than

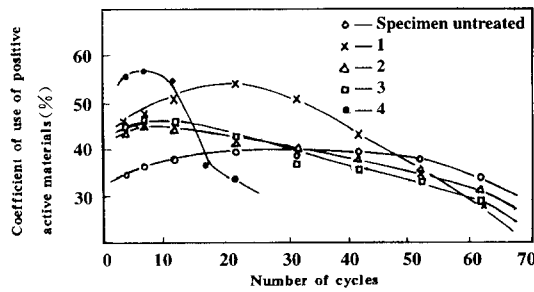


Fig. 1. Effects of the positive electrode additives on the coefficient of utilization and service life of the active material. Numbers refer to additives listed in Table 1.

that of an untreated specimen and its service life terminates on the 15th cycle. When carbon fibre or needle coke is added, the influence on capacity is similar, namely, during the initial cycles, the coefficients of utilization reached a maximum value, and the electrode capacities is almost the same as that of an untreated specimen. When expanded graphite is added, the coefficient of utilization reaches its maximum value on the 20th cycle, i.e., 15% greater than that of an untreated specimen. The capacity then declines gradually and, after about 40 cycles, the rate of degradation becomes higher than that of an untreated specimen. This leads to a shorter service life.

As far as the effects of the above-mentioned additives are concerned, the best is expanded graphite. Besides its ability to increase the conductivity, as a loose dilatant it is able to raise greatly the porosity of the active material when added to the lead paste. The latter feature facilitates the diffusion of H_2SO_4 solution into the interior of the electrodes and, thereby, reduces the concentration polarization. This fact makes both the surface structure and the inner structure of the active material take part in the chemical reaction in a homogeneous manner so that the coefficient of utilization is improved (see Fig. 2).

In addition, it is found from the preparation process of plates that graphite has the property of high absorptivity, which is also able to raise the water absorptivity of the lead paste and reduce its density without increasing its consistency. This facilitates plate pasting, especially by machinery, and also produces a beneficial effect on the pore structure of the cured plates, i.e., increase the porosity. When expandable graphite of the same kind is added, there is a significant increase in the coefficient of utilization. It follows that the effect of graphite in an expanding state is of great significance. Another advantageous result is that the addition of expanded graphite reduces appreciably (about 15%) the consumption of lead. Nevertheless, the increase in the coefficient of utilization of the active material ensures that the discharge capacity remains unchanged (see Table 2).

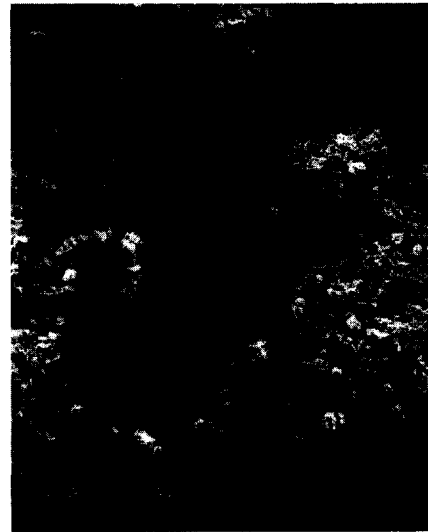


Fig. 2. Metallograph showing the porosity of the active mass.

In spite of this, the addition of graphite results in the reduction of the number of cycles. Graphite has a property of high anti-oxidation and will not be consumed by oxidation during charge/discharge cycling. From an examination of failed plates, it was discovered that there was severe softened and shedding of active materials. This implies that the reduction of the number of cycles may be attributed to the presence of graphite, which weakens the binding force of the active material. Obviously, this is an urgent problem to be solved.

A further observation showed that if the graphite content is much less than the optimum value, its effect is negligible. By contrast, if the content is in excess, the active material becomes so small that the discharge capacity is not sufficient and, moreover, the binding force is reduced so greatly that the active material becomes softened and dislodges prematurely. The most favourable graphite content is 0.5 wt.%.

3.2. Effect of a nitrogenous heterocyclic compound (AS) on the behaviour of positive electrodes

In order to capitalize on the beneficial characteristics of expanded graphite, the problem of the reduction of service life must be solved. Accordingly, an investigation was performed on the effects of some organic compounds on the coefficient of utilization and service life of the positive active material. It was found that a certain nitrogenous heterocyclic compound (AS) exerted a remarkable action on the improvement of the electrode behaviour. This phenomenon appeared after the 15th cycle, and after about the 30th cycle, the coefficient of utilization reached its maximum value (53%), an increase of 15%. Afterwards, although the capacity became attenuated, the coefficient of use was always higher than that of an untreated electrode until the service life came to an end (see Fig. 3).

Table 2
Effect of expanded graphite on the consumption of the positive active material and its discharge behaviour

Specimen	Lead powder consumption (g/plate)	Lead paste apparent density (g/ml)	Coefficient of use at $I=280$ mA (%)	Discharge capacity (Ah)
No graphite	11.9	4.2	36.2	1.05
0.5 wt.% graphite	10.1	3.7	46.6	1.15

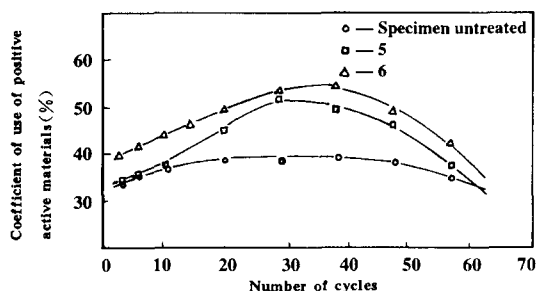


Fig. 3. Relationship between the coefficient of utilization of the positive active material and the number of cycles after addition of AS. Numbers refer to additives listed in Table 1.

In view of the above-mentioned effective action of AS on the positive electrode and the important action of graphite on the improvement of the active-material utilization during the initial cycles, as well as giving a reduction in lead consumption, it was anticipated that a combination of both additives would produce, to a certain extent, a synergistic effect. Therefore, a new composite additive was prepared by a certain method (graphite:AS=1:1) and then introduced to the lead paste. The experimental results showed that the coefficient of utilization of the electrode containing the new composite additive was much higher than that of an untreated electrode during the whole process of charge/discharge cycling. During the initial cycles, the coefficient of utilization was increased by about 7%. On the 40th cycle, the coefficient reached its maximum value (an increase of about 15.8%), and on the 60th cycle, it remained higher than that of the untreated electrode by 8% (Fig. 3). This illustrates that the addition of the graphite-AS composite has a marked synergistic effect. When AS is introduced into the positive lead paste, not only does it maintain the original superiority of graphite, but also it improves the phenomenon that its capacity attenuates faster in the final stage of cycle life.

Based on the laboratory findings, the characteristics of the graphite-AS composite additive and the practicability of its technical process were verified in the Shenyang Battery Plant, China, the Shenyang Battery Research Institute, China, and the Harbin Battery Plant, China, respectively. The test results obtained in the Shenyang Battery Plant showed that the consistency and 'sandy' nature of the lead paste was excellent and

suitable for plate pasting by machinery. The test results obtained in the Shenyang Battery Research Institute showed that when 1 wt.% of the new composite was added to the lead paste, the density of the lead paste, for a suitable hardness, was 3.6; on average, the active material of each plate (15 Ah) was 14.13% less than that of the comparison plate (without the new composite additive). Some assembled batteries were tested and inspected by the National Testing and Inspection Centre, and their indexes of technical specifications are listed in Table 3. When the new composite additive was tested in the Harbin Battery Plant under conditions of the technical process used in practical production, the test results showed that, on average, the active material of each plate (15 Ah) was 14.4% less than that of an untreated electrode. Assembled batteries with the new composite additive were also tested and inspected in the plant; the results are listed in Table 4.

As can be seen from the data given Tables 3 and 4, the indexes of technical specifications with the graphite-AS additive are similar to those of the batteries produced by the conventional process. The difference between the two types of batteries is that the number

Table 3
Test results of batteries with 1 wt.% composite additive

Battery No.	Without additive		With additive	
	1	2	3	4
Duration of first starting test for the dry-charged battery at 180 A to ≥ 1.0 V (min)	1.29	1.39	1.48	1.48
Capacity, $C_{20} \geq 100$ (%)	103.93	103.93	105.19	104.38
Duration of starting test at -18 °C and 180 A to ≥ 1.4 V (min)	1.50	1.49	1.50	1.50
Battery voltage (V) during starting test at $4C_{20}$ A and -18 °C after:				
5 s	8.26	8.02	7.88	8.19
30 s	8.05	7.81	7.68	7.98
60 s	7.78	7.54	7.38	7.68
and the duration to 6.0 V (s)	118	113	116	113
Durability in cycling (unit)	7	7	6	6

Table 4
Test results of batteries with 1 wt.% composite additive made in the Harbin Battery Plant

Type of battery	6-QA-60*			
	Battery No.			
	1		2	
	Total voltage (V)	Cell voltage (V)	Total voltage (V)	Cell voltage (V)
Test on dry-charged battery (240 A, 150 s)	7.75	1.29	7.83	1.31
Test on starting ability (-18 ± 1 °C):				
3rd test	8.55	1.43	8.63	1.44
5th test	8.46	1.41	8.83	1.41
7th test	8.55	1.43	8.56	1.43
Storage capacity (2nd test) (min)	95		96	

* 6-QA-60=12 V 60 Ah, dry-charged SLI.

of cycles of the former is only one unit less than that of the latter.

3.3. Effect of Li^+ ion on the behaviour of positive electrodes

An examination was also made of the effects of some positive ions from metal sulfates used as additives in electrolyte on the positive electrode behaviour. It was found that a certain amount of Li^+ ions was an effective additive for improving the coefficient of utilization of the positive active material and its service life. When an electrode without the graphite-AS composite additive was used in the process of charge/discharge cycling, and Li^+ was added to the electrolyte, it was discovered that, in the initial stages, the electrode capacity and the coefficient of utilization of the active material were both improved greatly. On the fifth discharge, the coefficient was increased by about 18%, but the attenuation of the capacity was accelerated and this led to a reduction in the service life by five cycles. By contrast, when an electrode was used together with the graphite-AS additive and Li^+ was introduced into the electrolyte, not only did the coefficient of utilization of the active material display a high level at the initial stages, but also the service life of the electrode was not less than that of any untreated electrode (Fig. 4).

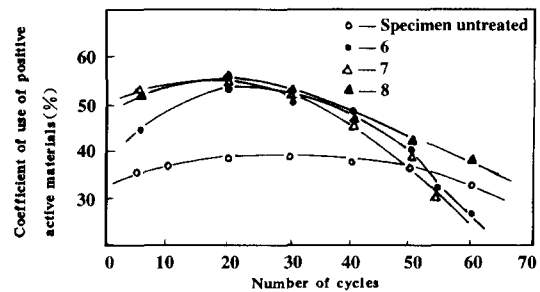


Fig. 4. Relationship between the coefficient of utilization of the positive active material and the number of cycles on the condition of the electrolyte containing Li^+ . Numbers refer to additives listed in Table 1.

In summary, it appears that when the addition of a small amount of Li^+ to the electrolyte and the graphite-AS composite additive are used jointly, there is a reduction in the consumption of lead and an improvement in the electrode behaviour under the prerequisite condition that the service life of the battery remains unchanged. In this way, the cost of the battery will be lowered and the objective of raising its energy density will be attained.

4. Conclusions

1. Addition of 0.5 wt.% expanded graphite in the lead paste of the positive plate raises the coefficient of utilization of the active material by about 15% during the initial stages of charge/discharge cycling, and reduces the consumption of lead by about 14%. In this case, the lead paste is of a 'sandy' type with excellent properties: its hardness and consistency remain unchanged, whereas the cycle life is reduced to only a small extent.

2. Addition of a certain nitrogenous heterocyclic compound (AS) in the lead paste of the plates will, at most, raise the coefficient of utilization of the positive active material by 15% during the medium and final stages. The addition of a graphite-AS composite additive will raise appreciably the coefficient of utilization of the active material during the entire period of charge/discharge cycling. Nevertheless, these little change in service life is not so imaginable as compared with that for an untreated battery.

3. The addition of Li^+ ions to the electrolyte not only maintains the improvement of the positive electrode caused by the measures taken above, but also extends the service life to some degree. The test results show that the service life is not less than that of a battery without the addition of graphite, AS, or graphite-AS composite additive.

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