

## Effects of carbon in negative plates on cycle-life performance of valve-regulated lead/acid batteries

Masaaki Shiomi, Takayuki Funato, Kenji Nakamura, Katsuhiko Takahashi, Masaharu Tsubota

*Lead-Acid Battery Laboratory, Japan Storage Battery Co., Ltd., Nishinosho, Kisshoin, Minami-ku, Kyoto 601, Japan*

### Abstract

Increasing amounts of carbon in the negative plates of valve-regulated lead/acid batteries reduced the  $\text{PbSO}_4$  accumulation and extended the life performance in the simulated cycle-life test using the operational pattern of hybrid electric vehicles and photovoltaic power systems. It improved also the rechargeability of large batteries and cycle-life performance when operated in the condition of a small overcharge. Carbon formed a conductive network on  $\text{PbSO}_4$  particles of the discharged negative plates.

*Keywords:* Lead/acid batteries; Negative plates; Carbon; Cycle performance

### 1. Introduction

The discharge performance of valve-regulated lead/acid (VRLA) batteries decreases with  $\text{PbSO}_4$  accumulation in the negative plates when used in hybrid electric vehicles (HEV) [1] or photovoltaic power systems [2]. It is also well known that  $\text{PbSO}_4$  accumulates in the negative plates during the operation of flooded batteries [3–5].

The charging efficiency of negative plates is usually better than that of positive plates due to its high hydrogen overpotential [6]. However, once negative plates are left in the discharged condition without proper charge, it is very difficult to change  $\text{PbSO}_4$  into Pb, especially in VRLA batteries [7], because the overcharge current is utilized for the oxygen reduction on charged Pb, and not for the reduction of  $\text{PbSO}_4$  into Pb. The accumulation of  $\text{PbSO}_4$  on negative plates may be caused by:

(i) a very large particle size of negative active material, which is furthermore enlarged by the recrystallization during operation or long time standing, enlarged  $\text{PbSO}_4$  being very difficult to be reduced because of its small specific surface area;

(ii) the adsorption of organic additives [8] hindering the charge acceptance of negative plates, and

(iii) the low local conductivity of localized  $\text{PbSO}_4$  which is often observed in negative plates (usually called ‘sulfation’) when left standing for a long time at a high temperature.

In order to improve the rechargeability of the negative plates, the effect of additives in the negative active material of VRLA batteries has been studied. In this paper, we intro-

duce the positive effect of reducing the accumulation of  $\text{PbSO}_4$  by optimizing the amount of carbon (C) in the negative plates.

### 2. Effects of carbon on the cycle-life performance of VRLA batteries

#### 2.1. Hybrid electric vehicles

The batteries are charged and discharged with a relatively high current in a short period; they are usually operated under the discharged condition when used in HEVs. The simulated cycle-life test using the operational pattern of the HEV batteries was carried out. The batteries were 65 Ah (3hR) 12 V starved-type VRLA ones with negative plates containing either a conventional amount (A%) or 10A% C.

The batteries are tested according to the following conditions: (i) discharge: 150 A  $\times$  8 s, (ii) charge: 150 A/14.8 V  $\times$  8.4 s, and (iii) temperature: 30 °C.

The voltage changes at the end of the discharge process during the above cycle-life test are shown in Fig. 1. For batteries with negative plates containing A% C the discharge voltage decreased earlier than for those with negative plates containing 10A% C. However, in the negative plates containing 10A% C, the decrease was not significant until cycle no. 240 000.

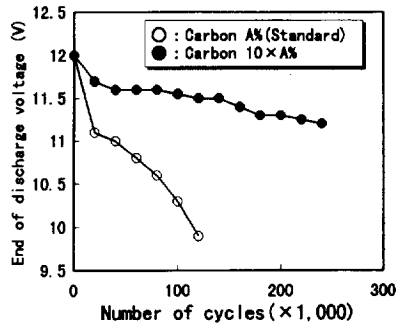


Fig. 1. Changes of the end of discharge voltage of 65 Ah (3 h R) VRLA batteries during simulated cycle-life test using operational pattern of hybrid EVs.

2.2. Photovoltaic power systems

The batteries are usually operated under the partial state-of-charge (PSOC) condition. The batteries tested are the 2 Ah (10 h R) 2 V starved-type VRLA ones with the negative plates containing A%, 3A% and 10A% C, respectively. We carried out the simulated cycle-life test, using the operational pattern of the photovoltaic power systems under the following conditions: (i) discharge (1): 2 A × 0.1 h, (ii) discharge (2): 2A × 0.3 h, (iii) charge: 2A × 0.3 h, and (iv) temperature: 25 °C.

As shown in Fig. 2, a rapid decrease of the end of the discharge voltage was observed only at 400 cycles for the battery with the negative plates containing A% C. Whereas, in the negative plates containing 3A and 10A% C, the decrease was not significant until cycle nos. 920 and 1100, respectively.

Fig. 3 shows the amount of PbSO<sub>4</sub> on the negative plates in the disassembled batteries after the cycle-life test and after the supplementary charge for the same battery type, subjected to the same test for the same number of cycles. It is found that an increasing amount of carbon in the negative plates helps to suppress the PbSO<sub>4</sub> accumulation, which can be easily reduced by a supplementary charge for the negative plates with much added carbon.

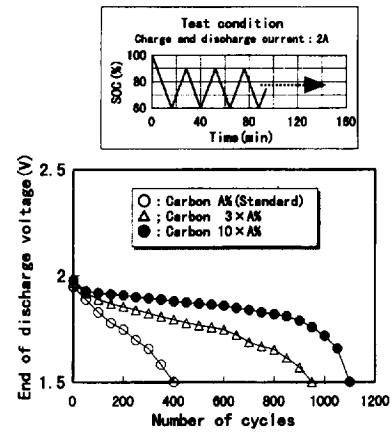


Fig. 2. Changes of the end of discharge voltage of 2 Ah (10 h R) 2 V VRLA batteries during partial state-of-charge cycling tests.

2.3. Motive power applications

The discharge capacity sometimes decreases earlier than expected when large batteries are used in forklift trucks because of the stratification of electrolyte and the accumulation of PbSO<sub>4</sub> at the bottom of the negative plates. We manufactured large (500 mm height) 260 Ah (5 h R) granular silica batteries with two types of negative plate containing different amounts C (A and 10A%) and examined the effect of increasing amount of carbon on the cycle-life performance.

The test conditions are: (i) discharge: 100 A × 1.4 h, (ii) charge: constant current (amount of charge: 115%), and (iii) temperature: 50 °C.

The discharge capacity maintained about 90% of its initial value for the battery with 10A% C even after 900 cycles, whereas, the battery with standard negative plates containing A% C sustained only about 40% of its initial capacity as illustrated in Fig. 4. The substantial decrease in capacity observed in the battery with standard negative plates is caused by the accumulation of a large amount of PbSO<sub>4</sub> at the bottom of the negative plates. However, such a phenomenon does not take place in batteries containing 10A% C.

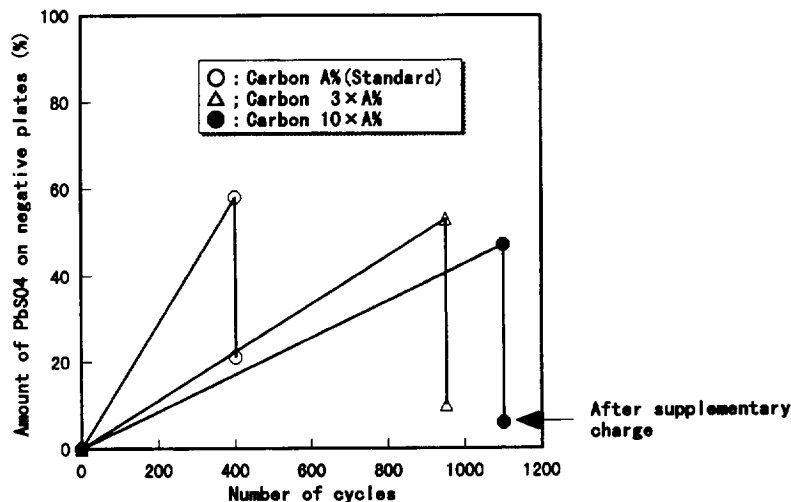


Fig. 3. Changes of the amount of PbSO<sub>4</sub> on the negative plates during partial state-of-charge cycling tests.

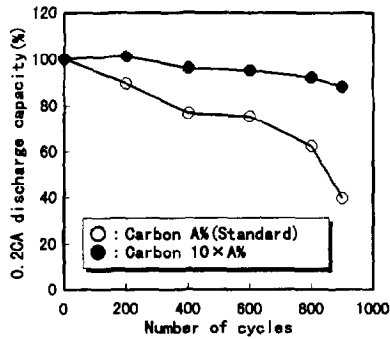


Fig. 4. Changes of the discharge capacity of 260 Ah (5 h R) granular silica batteries (500 mm height) during cycle-life tests.

2.4. Amount of overcharge

It is well known that a small amount of overcharge in the cycling test may cause an accumulation of  $PbSO_4$  on the negative plates and thus, leads to an early capacity loss. In order to ascertain the effect of increasing amount of added carbon on the performance of the cycle-life test with a small amount of overcharge, we manufactured 25 Ah (5 h R) granular silica batteries with the negative plates containing A and 10A% C. The batteries were tested under the following conditions: (i) discharge: 10 A  $\times$  1.75, (ii) charge: constant current (amount of charge: 103%, 105% and 108%), and (iii) temperature: 50 °C.

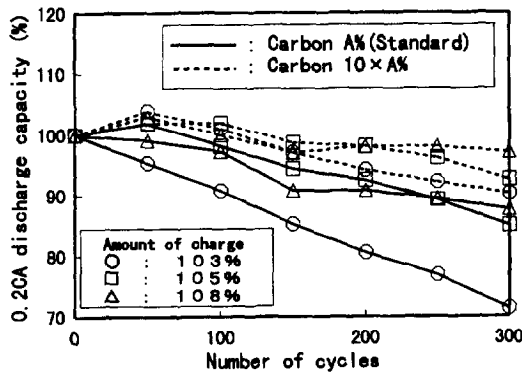


Fig. 5. Changes of 0.2C A discharge capacity of 25 Ah (5 h R) granular silica batteries during cycle-life tests.

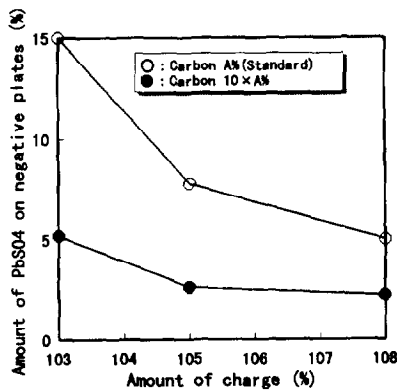


Fig. 6. Relationship between the amount of charge and the amount of  $PbSO_4$  on negative plates after 300 cycles.

The changes in discharge capacity during the cycle-life test are shown in Fig. 5. When the amount of charge decreased, the decrease in discharge capacity became greater. An initial sharp decline in discharge capacity was observed for batteries with standard negative plates including A% C, subjected to 103% charge. For the negative plates containing 10A% C, however, the discharge capacity did not decrease very much even when subjected to 103% charge. After 300 cycles, we examined the amount of  $PbSO_4$  accumulated on the negative plates. Fig. 6 shows that the amount of  $PbSO_4$  accumulation increased as the amount of charge decreased, especially for the standard negative plates with A% C. For the negative plates with 10A% C, a very small amount of  $PbSO_4$  is accumulated regardless of the amount of charge.

3. Effect of carbon on the cycle-life performance of VRLA batteries

In order to elucidate why the cycle-life performance of VRLA batteries was improved by adding more carbon to the negative plates, we carried out some tests concerning the following three factors: (i) crystallinity of  $PbSO_4$ ; (ii) particle size of  $PbSO_4$ , and (iii) conductivity of the negative plates.

3.1. Crystallinity of  $PbSO_4$

X-ray (XRD) analysis was performed to examine the crystallinity of  $PbSO_4$  for the discharged negative active materials including A% and 10A% C, subjected to cycle-life test (Section 2.2) for 300 cycles. Fig. 7 shows the XRD patterns of both of the negative active materials. No differences were observed in the crystallinity of the  $PbSO_4$  crystals.

3.2. Particle size of  $PbSO_4$

After the cycle-life test (Section 2.2), we disassembled the batteries and examined the accumulated  $PbSO_4$  particles by scanning electron microscopy (SEM), Fig. 8.  $PbSO_4$  particles in the negative plates with 10A% C after 1100 cycles were larger than those with A% C after 400 cycles. Although  $PbSO_4$  particles are very large in the case of negative plates

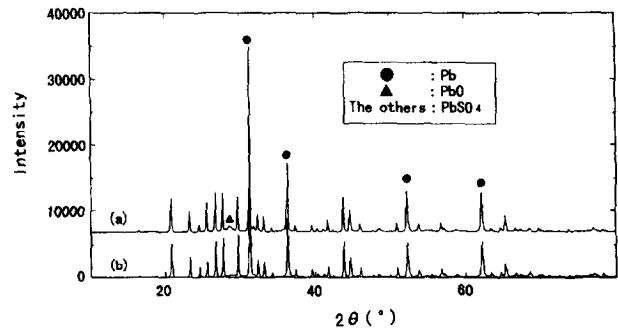
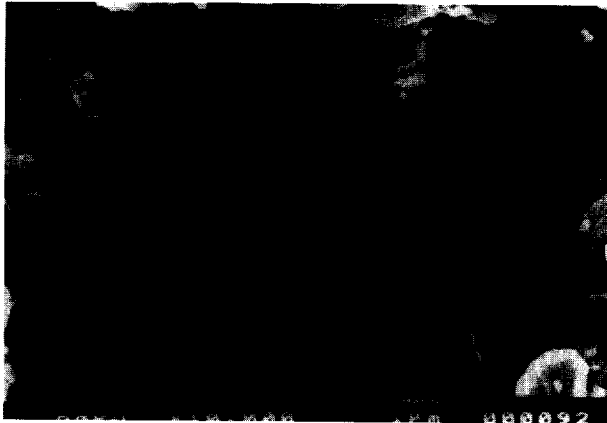


Fig. 7. XRD patterns of discharged negative active materials after 300 partial state-of-charge cycles: (a) 10A% C, and (b) A% C.

(1) Carbon: A% (Standard) -after 400 cycles-



(2) Carbon: 10 x A% -after 1100 cycles-



Fig. 8. SEM of discharged negative active materials with (1) 1A% C, and (2) with 10A% C after partial state-of-charge cycling tests.

with 10A% C, the reduction of PbSO<sub>4</sub> was found to be much easier as illustrated in Fig. 3. Therefore, the accumulation of PbSO<sub>4</sub> in the negative plates could not to be related to the size of the PbSO<sub>4</sub> particles.

### 3.3. Conductivity of negative plates

In the negative plates with a higher amount of added carbon, carbon was observed on and between the PbSO<sub>4</sub> particles, which are closely gathered, as shown by SEM in Fig. 8. An increasing amount of carbon might form a conductive network on the PbSO<sub>4</sub> localized areas and help improving the rechargeability of PbSO<sub>4</sub> in the negative plates. Thus, we manufactured the negative plates made up of PbSO<sub>4</sub> and carbon, and carried out the formation test and examined the effect of carbon in the PbSO<sub>4</sub> negative material on the formation process.

We first manufactured a special paste mixing PbSO<sub>4</sub> (Nakalai Tesque), carbon (0, 1, 3A%) and water. The paste was filled into the thin grid (40 mm x 54 mm x 0.9 mm, L x W x T) and the plates were subjected to formation in sulfuric acid (sp. gr. 1.30, 20 °C). The residual amount of PbSO<sub>4</sub> obtained during formation was analysed.

Changes of the PbSO<sub>4</sub> amounts in the negative plates during formation and plates conditions are given in Fig. 9 and Table 1, respectively. For the negative plates consisting of PbSO<sub>4</sub> without carbon, the reduction rate of PbSO<sub>4</sub> to Pb was very slow, and only 35% of PbSO<sub>4</sub> could be reduced to Pb even after 400% formation charge relative to the theoretical capacity. As shown in Table 1, this reduction proceeded only around the grid. It was found that the PbSO<sub>4</sub> active material without carbon, which is in direct contact with the conductive grid, can only be charged. By contrast, in the negative plates with A% C, the reduction rate during formation increased and some parts of the PbSO<sub>4</sub> far from the grid are also charged. They seemed to be charged along the line of carbon. The negative plates including 3A% C were charged uniformly almost all over the plates and the reduction rate is very fast. Almost all PbSO<sub>4</sub> particles could be charged by only 120% formation charge.

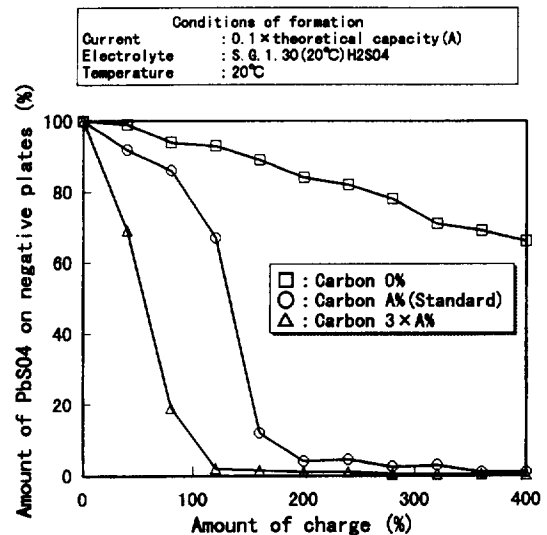


Fig. 9. Changes of the amount of PbSO<sub>4</sub> on the negative plates during formation; thickness of the positive plates: 0.9 mm.

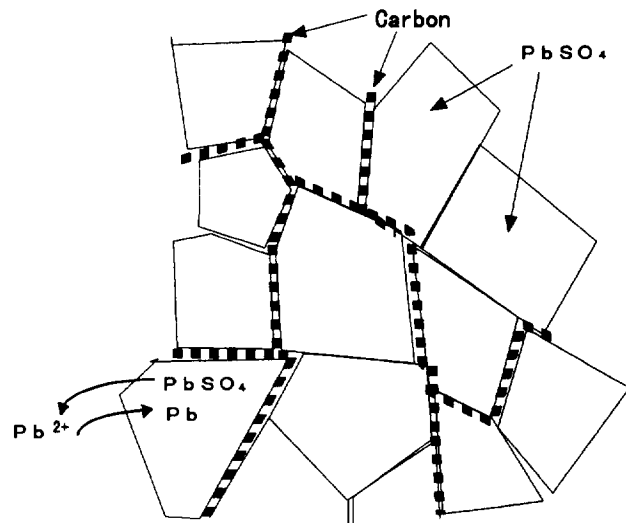
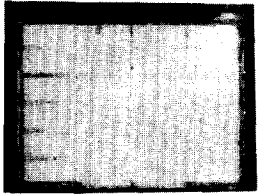
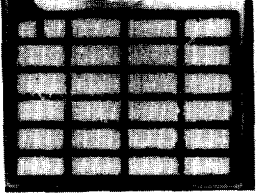
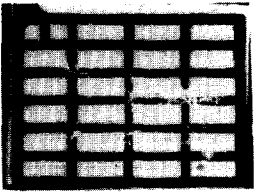

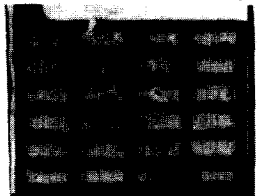
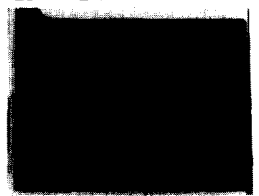
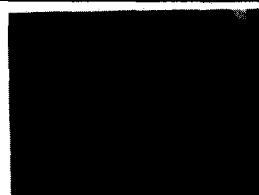
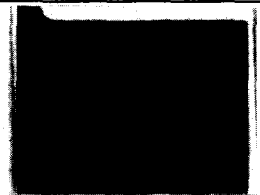



Fig. 10. Carbon conductive network formed on the discharged negative plates.

Table 1  
Negative plates during formation

Amount of carbon	Amount of charge		
	0%	120%	200%
0%			
A%			
3 x A%			

From the above valuable experiments, the effect of carbon could be explained by the conductive network theory as shown in Fig. 10. The effect of carbon added in the negative plates depends on the volumetric connection of carbon particles which form a conductive path (network) on PbSO<sub>4</sub>, thus leading to the improvement of the rechargeability of the negative plates.

We carried out the formation test of PbSO<sub>4</sub> plates with different kinds of carbon to ascertain the importance of the

volumetric connection of carbon particles. Carbon X (fine powder), Y (standard) and Z (coarse powder) were used. The plates were manufactured by adding A, 3A and 10A% C and subjected to the formation for 80% amount of charge relative to its theoretical capacity. The amount of PbSO<sub>4</sub> examined after the formation and the cell voltage at the start of the formation are shown in Figs. 11 and 12, respectively. Carbon X was found to improve the reduction of PbSO<sub>4</sub> and lower the polarization during charge. By using carbon X, only one-third of the amount used for carbon Y was enough to charge the PbSO<sub>4</sub> plates. Fig. 13 shows the relationship between the size of the carbon and residual amount of PbSO<sub>4</sub> after the formation charge. It was found that the reduction of PbSO<sub>4</sub> proceeded with a decrease in the size of added carbon.

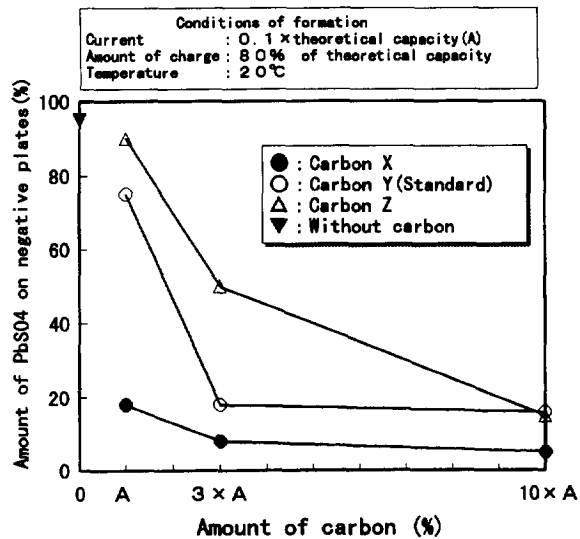


Fig. 11. Relationship between the amount of carbon and the residual amount of PbSO<sub>4</sub> on the negative plates after the formation tests.

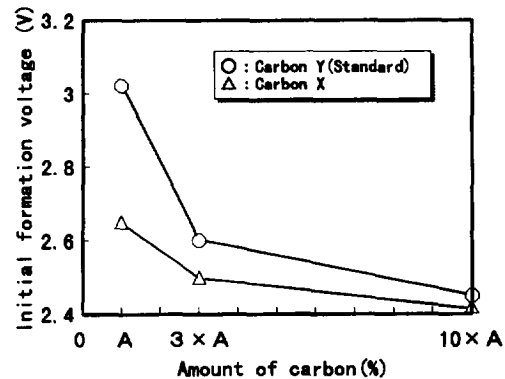


Fig. 12. Relationship between the amount of carbon and the initial formation voltage.

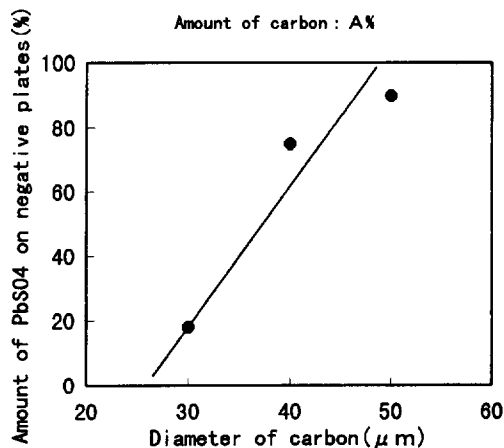


Fig. 13. Relationship between the diameter of carbon added and the residual amount of PbSO<sub>4</sub> on the negative plates after the formation test.

From the results of the improvement of rechargeability of the negative plates containing fine and bulky carbon X, we may conclude that the carbon effect mentioned above is due to the volumetric connection of the conductive carbon particles between each other on PbSO<sub>4</sub> particles.

#### 4. Conclusions

The addition of increasing amounts of carbon on the negative plates suppresses the PbSO<sub>4</sub> accumulation effectively as well as the improvement in cycle-life performance, especially for the batteries operated in partial state-of-charge conditions such as HEV or photovoltaic power system applications. These positive effects are caused by a conductive network of carbon particles formed on PbSO<sub>4</sub> particles.

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