

Change in Specific Gravity of the Acid Electrolyte in the Lead-acid Battery Upon Repeated Charge-discharge Cycles

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Abstract

When a lead-acid battery deteriorates, the specific gravity of the acid electrolyte gradually decreases from the initial value (1.28) to 1.18-1.20. However, in our laboratory's study, the specific gravity value increased from 1.28 to 1.32-1.36 after the charge. This is very unusual. Our various results have been reported regarding this behavior. The specific gravities of batteries after discharging also gradually (but faster than the case of after charging) increased with repeating charge-discharge cycles. One of the reasons for accounting these phenomena is thought to be due to the production of fine particles of Pb and PbO₂, the recovery from the sulfation by repeating cycles of low-rate charge and high-rate discharge accompanied with the use of additives such as organic polymers.

Keywords

lead-acid battery, specific gravity, activator, organic polymer, sulfuric acid

1. INTRODUCTION

We have been investigating the prolongation of the life-time of lead-acid batteries in the view point of environmental aspects and material resources. Since 1997 [Kozawa et al., 1998], [Ikeda et al., 2000], [Kozawa et al., 2000], [Kozawa et al., 2000] and [Sugawara et al., 2003], we have been working on the activators for lead-acid batteries. When a lead-acid battery deteriorates, the specific gravity (SG) of the acid electrolyte gradually decreases from the initial value (1.28) to 1.18-2.00. When lead-acid batteries regenerated by repeating charge-discharge cycles after adding an activator, we found a curious phenomenon such as the SG of the battery gradually increased from 1.28 to 1.32-1.35 after full charge and also to a higher value after discharge. The phenomenon is also apparent in the case of an activator-free battery even though the increased amount is less than that of activator added one. The changes in the SG of batteries have been investigated on the various batteries during discharge-charge cycles to clarify the mechanism.

2. EXPERIMENTAL

2.1 Materials

Organic Polymers, P000, PN30, PNH2 and PA30, were used as activators. The deteriorated batteries (Panasonic;

85D26 and 40B19) left for more than 2 years without charging after purchase and new batteries (Green Tech Power (GTP); 80D26) were examined as shown in Table 1. In the case of activator-free GTP batteries, commercial GR grade sulfuric acid was used after dilution with distilled water.

2.2 Method

The charging of batteries was conducted by SL-3 battery charger (Daijikogyo Co., Ltd.; Meltec SL-3) mainly for 24 hours. In the case of discharge, water immersed solid wire-shaped resistors of low resistance (0.1225 Ω) were used in a series or parallel connection according to the discharge currents. The discharge currents were measured with clamp-type digital multi meters. The specific gravity was measured with a conventional float type

Table 1 Test conditions and batteries

Test	Battery	Additive
1	85D26 (Panasonic)	None
2	85D26 (Panasonic)	P000 0.25 g/cell
3	85D26 (Panasonic)	P000 0.50 g/cell
4	85D26 (Panasonic)	P000 0.75 g/cell
5	40B19 (Panasonic)	None
6	40B19 (Panasonic)	20 cycles + P000
7	40B19 (Panasonic)	P000 0.50 g/cell
8	40B19 (Panasonic)	PN30 0.25 g/cell
9	40B19 (Panasonic)	PN30 0.50 g/cell
10	40B19 (Panasonic)	PNH2
11	40B19 (Panasonic)	PA30
12	80D26 (GTP)	None (Removed)
13	80D26 (GTP)	Original, P (0.50 g/cell)

meter ranging from 1.10 to 1.30. The values above 1.30 were obtained by extrapolation.

3. RESULTS AND DISCUSSION

3.1 Deteriorated batteries

The effect of organic polymer (P000) as an activator has been added after 2 charge-discharge cycles to deteriorated batteries of Panasonic 85D26 untreated more than 2 years without charging. The third charging was conducted for three days. The discharge capacity of 85D under constant load (ca. 165 A at initial) batteries are shown in Figure 1. Discharge capacities rapidly increased after 3 days charging and showed maxima at 3rd cycle each deteriorated battery. It is found that the addition amount of activator P000 has a suitable value and surplus quantity of it decreases the performance of batteries.

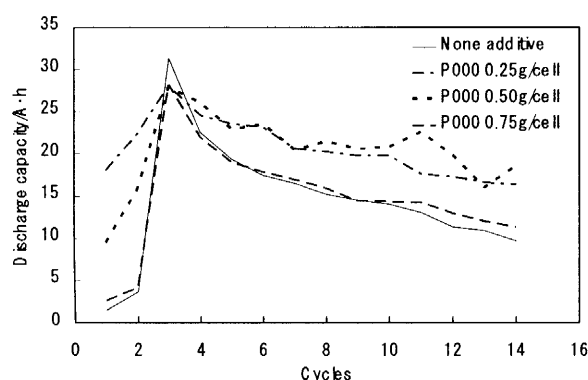


Fig. 1 Discharge capacity changes of deteriorated 85D26 batteries after adding of various additives during charge-discharge cycles. Additives were added after 2nd cycles.

Figure 2 and Figure 3 show changes in SGs after charging and discharging of above batteries during charge-discharge cycles shown in Figure 1, respectively. Apparently, SG after charging of each battery became 1.32 after full charge and kept almost the same value during

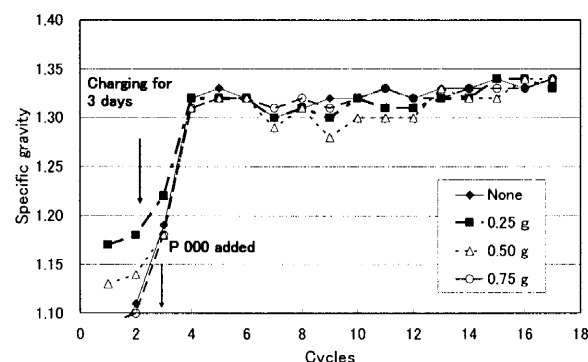


Fig. 2 Changes in SGs of batteries after charging during charge-discharge cycles. 85D26 batteries as are in Figure 1.

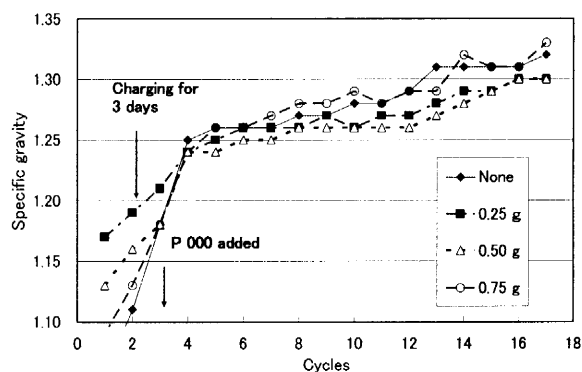


Fig. 3 Changes in SGs of batteries after discharging during charge-discharge cycles. 85D26 batteries as are in Figure 1.

the charge-discharge cycles up to 17 cycles although the discharge capacities of individual cells were different.

In the case of the change in SG after discharge, the values increased to around 1.25 from less than 1.18 at 4th cycle for all batteries. The SGs, however, gradually increased during cycles and showed different values according to the amounts of additives.

Figure 4 shows the discharge capacities of 40B19 type batteries added with various kinds of additives listed in Table 1. Except for the case of 20 cycles + P000, all batteries with and without additives kept constant discharge capacities until about 10 cycles. The battery without additives, however, showed a deterioration after 10 cycles, although the others showed constant values or higher within the experimented period except for the case of 20 cycles + P000.

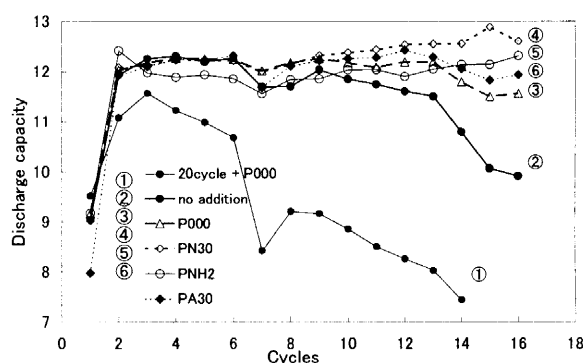


Fig. 4 Discharge capacity changes of deteriorated 40B19 batteries after adding of various additives during charge-discharge cycles.

The values of SGs after charging and discharging of deteriorated 40B19 batteries are shown in Figure 5 and Figure 6. The SG values after charging gradually increased until 8 cycles and then kept almost the constant value of 1.34.

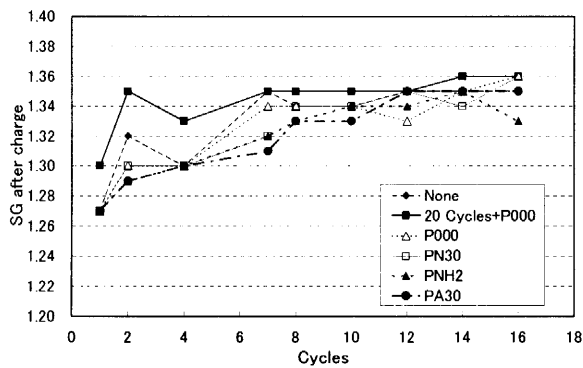


Fig. 5 Changes in SGs after charging of deteriorated 40B batteries with various additives during charge-discharge cycles.

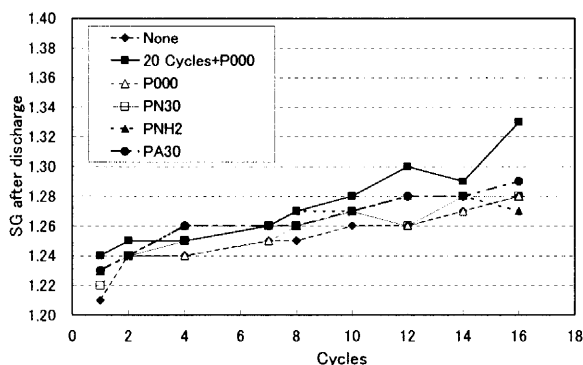


Fig. 6 Changes in SGs after discharging of deteriorated 40B batteries with various additives during charge-discharge cycles.

SGs after discharging gradually increased through out the experimented period. That for the battery added 20 cycles + P000 showed high values corresponding to the small discharge capacity shown in Figure 4. The others, however, showed high values in disagreement with the discharge capacities after several cycles.

3.2 New GTP batteries

The discharge capacity changes of new GTP batteries with and without additive are shown in Figure 7. The battery without an additive showed a lower discharge capacity than that of original one indicating the effectiveness of the additive.

Changes in SGs after charging and discharging of GTP batteries with and without additives are shown in Figure 8 and Figure 9, respectively. From these figures, it is found that the SG of GTP battery originally containing the additive shows an increase up to 1.36 after 30 cycles although that for the additive-free keeps the value near the nominal one (1.27). The SG values after discharging also the same profile for both batteries. Namely, SG for GTP increased up to 1.28 after 35 cycles, but that for the additive-free one exhibited a low value of 1.20.

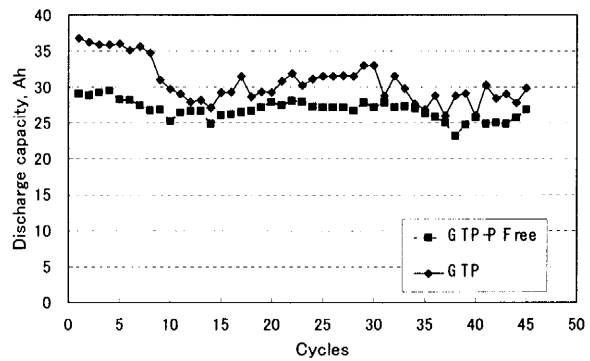


Fig. 7 Discharge capacity changes of new GTP batteries with and without additives during charge-discharge cycles.

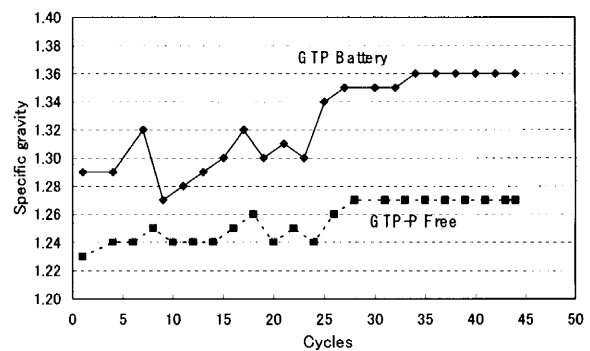


Fig. 8 Changes in SGs after charging of new GTP batteries with and without additives during charge-discharge cycles.

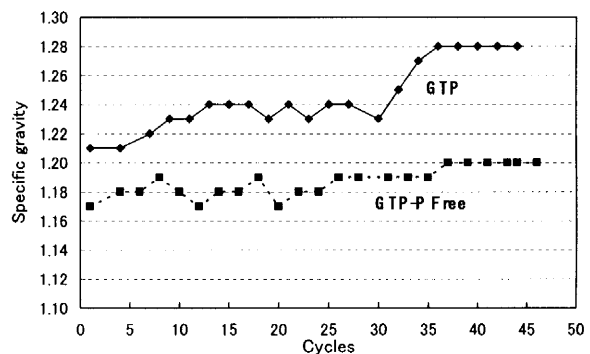


Fig. 9 Changes in SGs after discharging of new GTP batteries with and without additives during charge-discharge cycles.

These phenomena are not interpreted by vaporization of water but by some effects of additives. Namely, the discharge tests were conducted at high rate and charging was done with low rate, so the electricity was effectively used to reduce the PbSO_4 to Pb at negative electrode and also to oxidize to PbO_2 at positive electrode increased accompany with the effects of additives. Pb particles so produced would be very fine and also oxi-

dized to PbSO_4 during discharge periods with a high efficiency causing a gradual increase in specific gravity of the electrolyte of the battery accompany with the recovery of sulfation in the case of deteriorated battery. In the case of new battery, it is somewhat complicated. One of the reasons may be considered due to an additional reduction of un-formed active materials of electrodes.

4. CONCLUSION

The following phenomena have been observed when deteriorated lead-acid batteries have been regenerated by the repeating of low-rate charging and high-rate discharging cycles with additives such as organic polymers.

The specific gravities of batteries after charging gradually increased with repeating charge-discharge cycles and became almost constant values ranging 1.30-1.36, which of batteries containing additives, however, were higher values than that for non-added one and the nominal value of 1.28.

The specific gravities of batteries after discharging also gradually (but faster than the case of after charging) increased with repeating charge-discharge cycles.

One of the reasons for accounting these phenomena is thought to be due to the production of fine particles of Pb and the recovery from the sulfation by repeating cycles of low-rate charge and high-rate discharge accompanied with the use of additives such as organic polymers.

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