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Development of a long life 35 Ah capacity VRLA battery for load-leveling applications

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Abstract

A load-leveling (LL) system is needed for the effective use of electric power to preserve the environment in Japan. Although the valve regulated lead-acid (VRLA) battery is considered to be one of the suitable candidates, high requirements of long cycle life such as 2000 cycles or a calendar life of 7 years needed to be solved. We are currently developing a new VRLA battery for this application, and have succeeded in achieving over 2000 cycles with a 35 Ah class VRLA battery. It was confirmed by the detailed investigation after a cycling test of the battery that this cycle performance was achieved by improving the charge acceptance of the negative plate, avoiding the grid corrosion by applying an optimized charge condition.

Keywords: Battery; Cycle life; Load-leveling; Lead-acid; Valve regulated

1. Introduction

Development of load-leveling (LL) system to level the demand on electricity during daytime and night time has been undertaken mainly by electric power companies and by each organization. Lead-acid batteries and new types of battery such as Na–S, Li-ion and so forth have been proposed for the energy storage means for this system, and the development for this practical use has been in progress. It is especially believed that despite the lead-acid battery's advantage of low manufacturing cost it can only be applied successfully if the life performance improves. Previous valve regulated lead-acid (VRLA) batteries were usually behind compared with other new type batteries as they only performed 500 cycles with 80% depth of discharge (DOD).

In recent years, developing VRLA battery for electric vehicles (EVs) has accelerated the improvements of several performances of the lead-acid battery such as high power density, high energy density, long life, and charge acceptance. So, we have undertaken the development of long life VRLA battery for LL use based on the technology of the EV use.

Cost saving is the most required target for LL use batteries. The cost mainly consists of a battery price (initial cost) and a running cost of the system. The lead-acid battery is more suitable for LL use than any other new types of battery as its cost per Wh is incomparably low. On the other hand, concerning running costs, lifetime, maintenance cost, and the energy loss during charge and discharge are the major factors.

Firstly, short life produces a high cost system and spoils the advantage of its initial cost even if the battery price is low. Therefore, improvement in life performance is highly required to the lead-acid battery for LL use. Secondly, maintenance cost is not a problem as VRLA batteries frees you from water filling that the conventional type of battery needs. Finally, regarding energy loss during charge and discharge, general lead-acid batteries for cycle use used to perform the discharge capacity (Watt-hour efficiency) of 70–75% against charge capacity and were not superior to other new type batteries. This is attributable to the characteristic of the lead-acid batteries requiring the charge capacity of 110–120% against discharge capacity (Ah). Thus, improvement in this Watt-hour efficiency is also necessary.

Therefore, the following methods were applied into an improved 35 Ah class (5HR) VRLA battery to extend the cycle life and to achieve higher energy efficiency for LL application [1]:

(1) Add conductive carbon fiber in the active materials of negative plate to improve charge acceptance performance [2].

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(2) Maintain uniformity of the electrolyte concentration by arranging the direction of the plates like horizontal pancakes.
(3) Restrain the grid corrosion of positive plates by minimizing the over charge capacity.

In addition to those methods, we report in this paper about the relationship between charging patterns with additional interval charge and life performance for LL use VRLA batteries.

2. Experimental

The VRLA battery is 2 V single cell (35 Ah/5 h rate (HR)) [1]. To accelerate the cycle life test, it was discharged at 29 Ah/3HR (about 80% DOD against 20HR capacity) during the life performance test and discharged at 20HR during the capacity test. Three steps of constant current charge were applied to the battery during the cycle test, in order to charge the discharged battery efficiently within 8 h. The test method details are indicated in the Table 1.

Note that the test conditions are based on the case of small LL system in which 12 V batteries with 35 Ah/5HR class are used, discharged in 16 h during operation and charged within 8 h by utilizing night time electric power.

In the previous work, we indicated that positive plate of a lead-acid battery requires 102% charge capacity against discharge capacity for a full charge [1]. This means that the charge capacity of 102% decreases the corrosion of the grid to its minimum. However, the same study has also proved that the 102% charge capacity is not enough for the full charge of negative plates at this stage.

Therefore, in this examination, we have attempted to investigate the best charging pattern by a method of executing additional charges every cycle in addition to every 102% charge, concentrating on the length of intervals between the additional charges. Four patterns of additional charge were made and are shown in Table 1. All patterns would uniformly have the average charge capacity of 104% throughout the cycle life test.

Table 1
Cycle life test condition of life cycle

Test battery	35 Ah/5HR VRLA (2 V cell pancake position)
Temperature	25 °C
Discharge	DOD 80% of 20HR 10.5 A (3HR) to 2.46 h
Charge	
First step	35 A to 2.35 V
Second step	8.75 A to 2.35 V
Third step	1.75 A to 102%
Additional charge	
Type 1	1.75 A to 9 h per 27 cycles
Type 2	1.75 A to 3 h per 9 cycles
Type 3	1.75 A to 1 h per 3 cycles
Type 4	1.75 A to 20 min every cycle
Capacity test	20HR (1.75 A to 1.75 V)
Charge	
First step	8.75 A to 2.35 V
Second step	1.75 A to 115%

3. Result and discussion

3.1. Result of life performance test

Capacity change of 20HR during the cycle life test is shown in Fig. 1. It indicates that even if battery specifications and average charge capacity are the same, a charging pattern changes life performance. And these charging patterns with shorter intervals between the additional charges produce longer life. It also illustrates that as to the VRLA battery used in this test has performed a long life of over 2000 cycles at the best that is three times as long as it used to perform (Type 4 in Fig. 1).

Also the battery in the test pattern Type 4 has maintained high Wh efficiency of 83–85% throughout the test. It proves that it shall maintain high Wh efficiency even considering the voltage loss of an assembled battery.

3.2. Analysis result

We have implemented the tear down analysis on the Type 3 which performed 1900 cycles (additional charge/3 cycles) and the Type 4 which performed 2100 cycles (every 104% charge) to investigate how the charging pattern affects the life performance. Figs. 2 and 3 indicate the quantitative result of lead sulfate in the negative active materials and the measuring result of electrolyte specific gravity. They also indicate the tear down analysis result of the battery in the vertical position that performed 600 cycles which compares the effect on plate structure of pancake orientation.

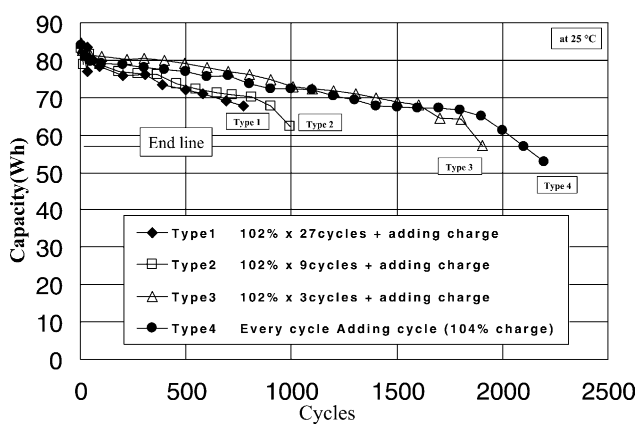

Fig. 1. Capacity change of 35 Ah cell during cycling with various additional charge conditions.

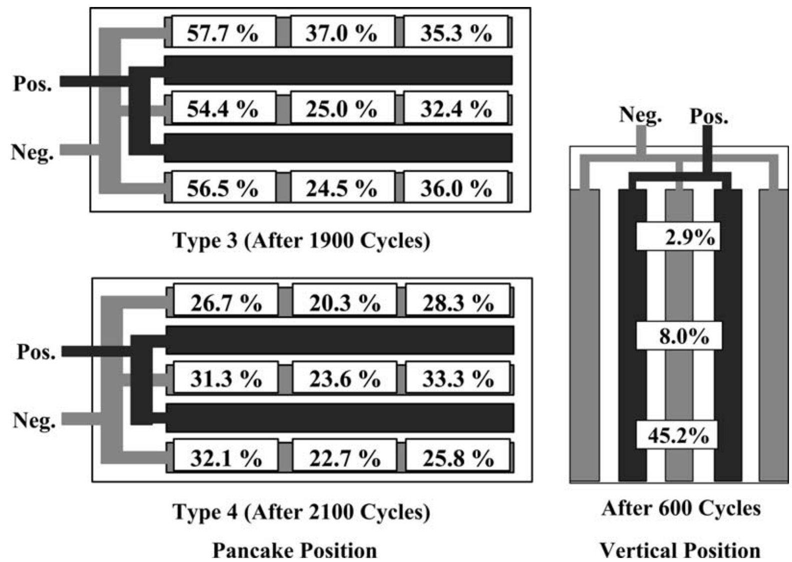

Fig. 2. Distribution of the amount of lead sulfate in the negative electrode after the cycle life test.

3.2.1. Residual lead sulfate quantity

We have investigated the distribution of lead sulfate in the active materials. Accumulated lead sulfate was left partially at the lower part of plates in the case of the vertical plate orientation because it was affected by the stratification of electrolyte. On the other hand, for pancake orientation, lead sulfate remains at either of the upper/lower part of the plates were not found. It is assumed that the stratification was suppressed in the case of the pancake position.

We have confirmed (in the comparison between the pancake positions) that the Type 3, where additional charges were made every 3 cycles, has more lead sulfate left. That shows the Type 3 is more likely to cause the sulfation to the negative plates than the Type 4 which was charged with 104% capacity every time. The reason why the lead sulfate left uncharged during the 102% charge becomes less likely to be charged during the interval to the next additional charge shall be explained later.

The Types 1 and 2 have longer intervals between the additional charges than the Type 3. Therefore, sulfation progresses more quickly in those two and their cycle lives are shortened.

3.2.2. Specific gravity of electrolyte

The maximum difference of the specific gravity in the cell of vertical position is 0.020 which makes it obvious that the electrolyte was stratified. However, the specific gravity of the Types 3 and 4 positioned horizontally were 0.005 and 0.008, respectively and were less stratified

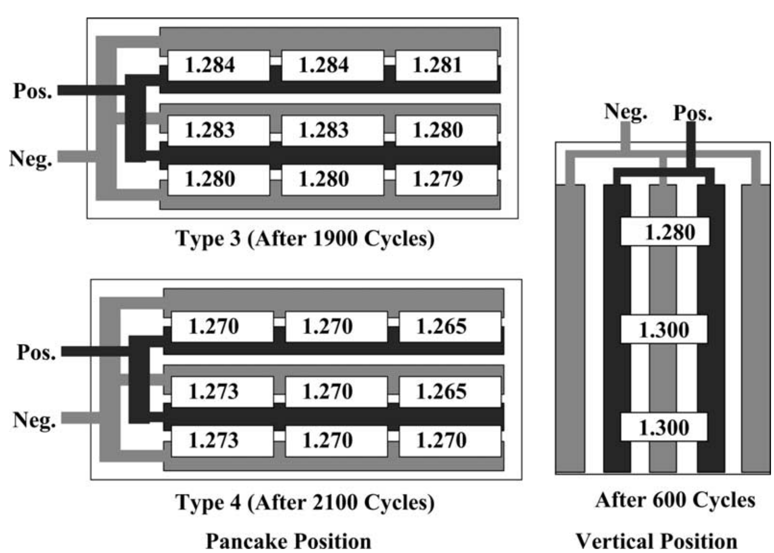

Fig. 3. Distribution of the electrolyte concentrations (specific gravity) in the cell after the cycle life test.

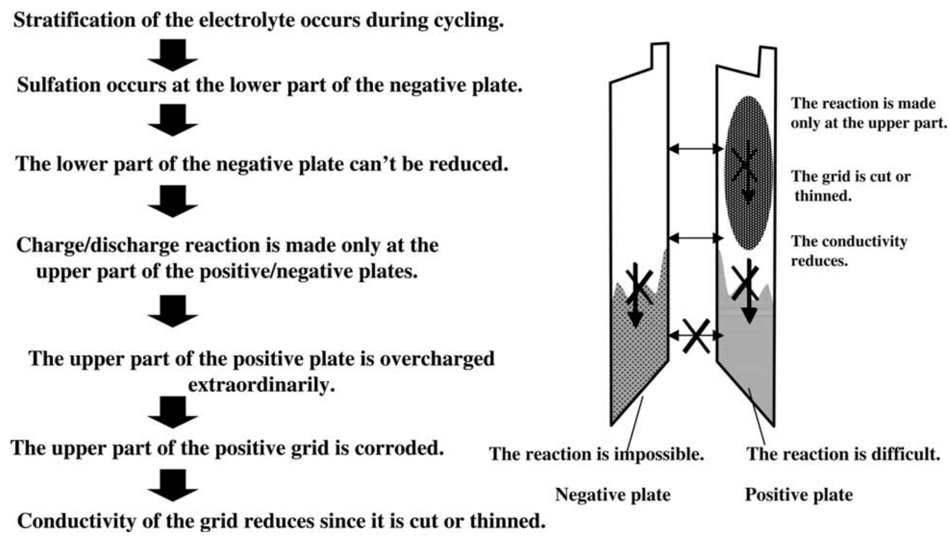

Fig. 4. The failure model of the vertical position cell.

compared with the vertical position. This proves that the pancake position enables the plates to obstruct the deposit of high density electrolyte during charging and to prevent stratification.

Also, the average values of the electrolyte specific gravity was calculated which are 1.282 in Type 3 and 1.270 in Type 4, respectively. The specific gravity of Type 3 is higher by 0.012, even though it has more lead sulfate left in the negative plates. It is assumed that this is because the actual capacity of negative plates was decreased by the sulfate and the additional charge worked as overcharge for the negative plates and accelerated the electrolyte loss. It is generally known that higher specific gravity of the electrolyte accelerates the corrosion rate of the positive grid. Therefore, the increase of the specific gravity in the Type 3 may accelerate the corrosion of its positive grid.

3.3. Battery failure model

The processes of battery failure in both cases of the vertical and pancake positions are illustrated in Figs. 4 and 5, respectively as models.

In case of the vertical position, stratification of electrolyte occurs rapidly and it causes sulfation at the lower part of negative plates. The sulfation prevents the battery from being charged and discharged in the upper parts of both its positive and negative plates. As a result, charge and discharge activity becomes concentrated only in the upper parts of the plates, which are consequently overcharged, and the corrosion of the positive grid causes a short life.

On the other hand, in the case of the pancake position where there is no stratification of electrolyte, all plates are equally charged without localized sulfation. Uniform

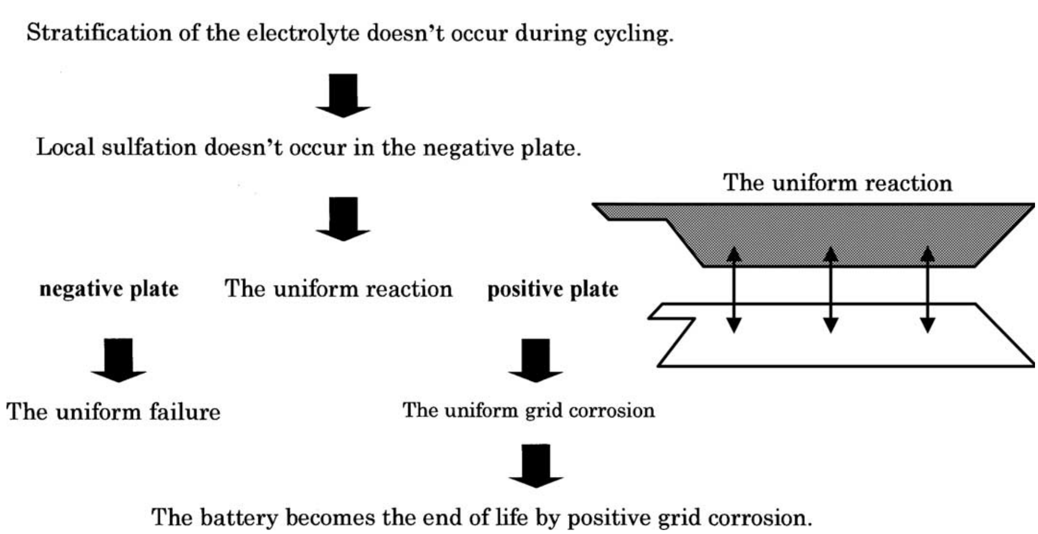

Fig. 5. The failure model of the pancake position cell.

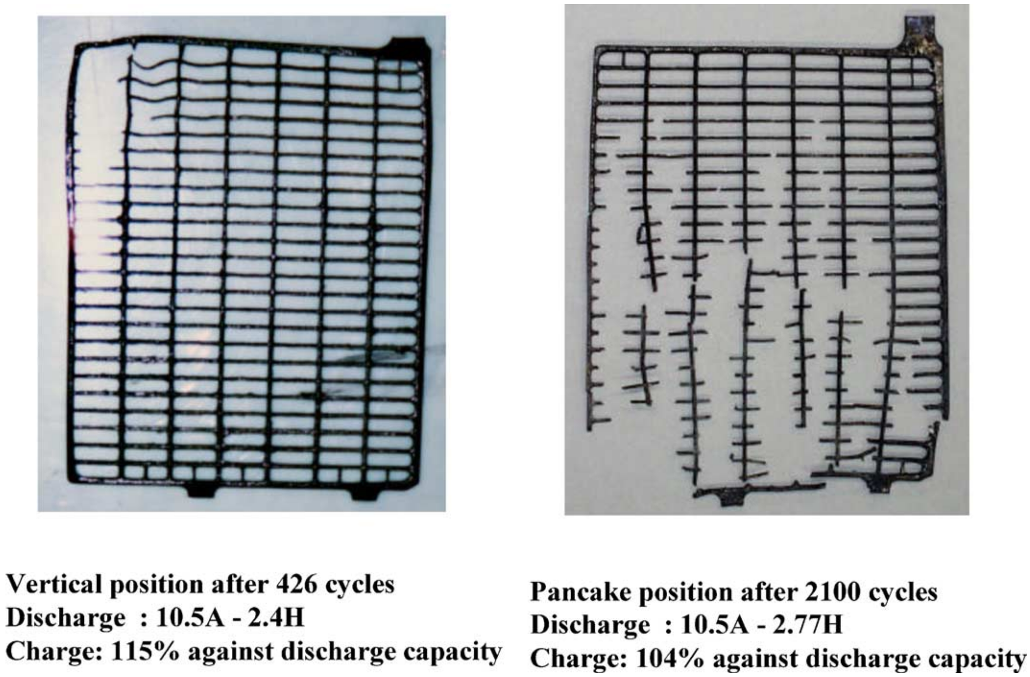

Fig. 6. Appearance of the positive grid after the life cycle test.

deterioration of the active material of negative plates as well as the equal grids corrosion of positive plates occurs. The battery life is ended by the grids corrosion of positive plates after all.

These models demonstrate that positive grids are partially corroded at the upper part in the vertical position and are equally corroded in the pancake position at the end of battery life. The positive grids' appearance for the vertical position

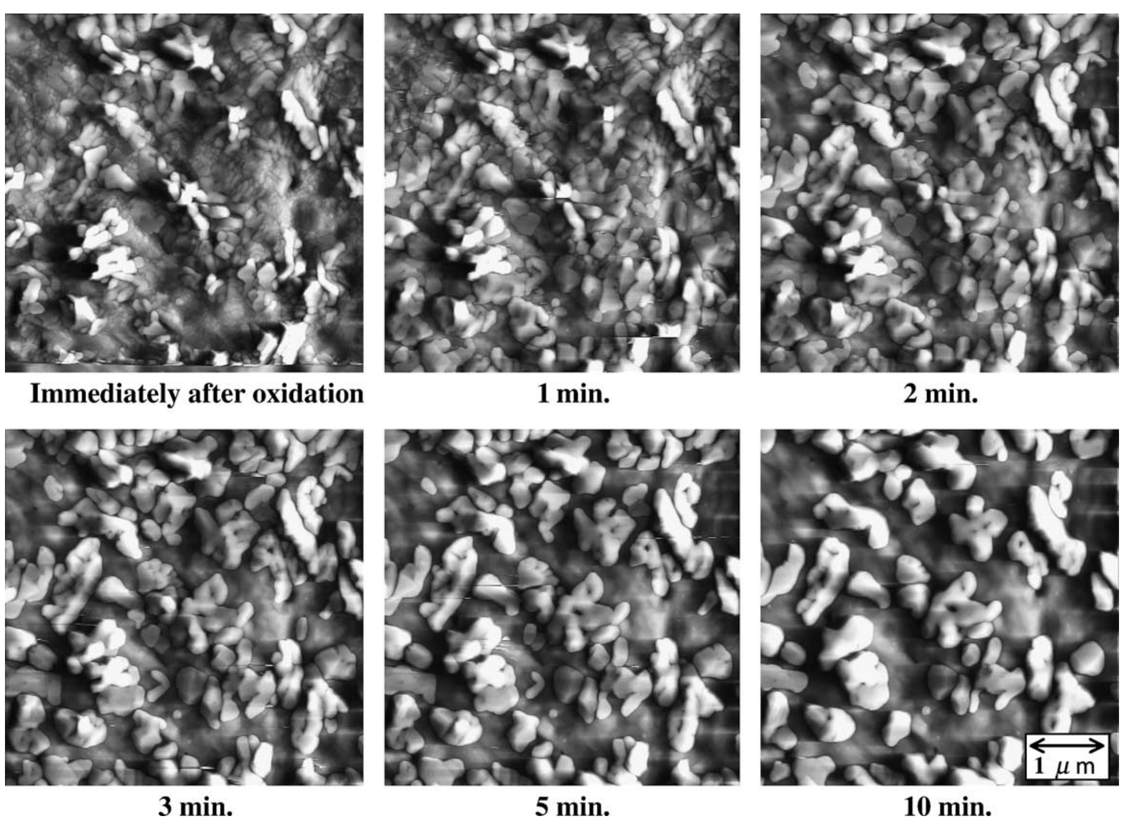

Fig. 7. The crystal growth of lead sulfate during standing after discharge on the negative electrode [4].

after 426 cycles and for the pancake position after 2100 cycles, are indicated in Fig. 6.

Next, we would like to explain why the Type 4 charging pattern, in which the battery was charged 104% against discharge capacity every time, has performed longer life even though they were charged with the same charging capacity in the same pancake position. Recent study using atomic force microscope (AFM) has indicated that it is easy to reduce (charge) lead sulfate crystals formed by electrochemical reaction if the charge operation is made immediately after discharge. However, the crystals become hard to reduce by their growth from recrystallization, when some standing time is applied after discharge (Fig. 7) [3,4].

We consider that the lead sulfates are left without whole reduction by insufficient charge such as charge pattern of Types 1–3 in this study. Then they get recrystallized (see Fig. 7) and become hard to reduce. Therefore, it is assumed that even repeating additional charge promotes decrease of electrolyte as the active materials of negative plates have already turned hard, so that the excess current to the negative plates generates gas.

This decrease of electrolyte causes the following negative aspects to the battery, by promoting grid corrosion of positive plates, which is the main problem to be overcome for LL use battery:

(1) Reduces conductivity between plates and electrolyte by decreasing the tightness between plates and separator.
(2) Accelerates the corrosion of positive grids by increasing the specific gravity of electrolyte.

4. Conclusion

In addition to the three methods previously acquired to improve life performance such as addition of conductive carbon fiber to negative plates, pancake position of plates, and diminution of charge capacity, the investigation results of each charging pattern have proved that applying the charging method of charging 104% against discharge capacity, with no additional charge, shall restrain the accumulation speed of the lead sulfate in negative plates and enable the flat pasted plate design VRLA battery to achieve the life performance of 2000 cycles or more.

We believe that this study has shown us that application of the appropriate charge capacity and pattern enables VRLA battery to achieve much better life performance in addition to the suppression of the grid corrosion of positive plates, sulfation of negative active materials, and stratification of electrolyte at the same time.

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