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Small-capacity valve-regulated lead/acid battery with long life at high ambient temperature

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Abstract

Valve-regulated lead/acid (VRLA) batteries are widely used as back-up power sources for telecommunications and UPS. These applications require high-reliability under severe environmental conditions. To meet this demand, the authors' company have developed small capacity (12 V, 15–65 A h at C_{20}/20 rate), long-life VRLA batteries which can endure high ambient temperature. These batteries make use of a new alloy and grid design which has improved resistance to corrosion at the positive plate, while at the same time reduce float current at high temperature. As a result, these batteries have a life expectancy of 13 years at 25°C, and inhibited thermal runaway even under ambient temperatures up to 75°C. The batteries can be installed in outdoor and underground environments. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

Due to the rapidly increasing use of computers as well as the widespread use of communication terminals, the telecommunications network is now increasingly larger and more complex. In this higher information-orientated society, valve-regulated lead/acid (VRLA) batteries now play an extremely important role as backup power supplies for information and telecommunications facilities, while at the same time provide a much higher level of quality and reliability than would be expected from conventional batteries.

In Japan, in order to carry a large capacity and wide band of information, the use of optical fibre cables in the information communication network is now being stressed mainly by the Nippon Telephone and Telegraph (NTT). In addition to the power backup purposes for communications buildings, backup power supplies for optical communication terminals are required. Conventionally, large-capacity VRLA batteries (200 to 6000 A h) with long life have been used in telecommunications systems. The current market, however, requires a small capacity, long-life VRLA battery that has excellent heat resistance characteristics and is designed to suit outdoor use for remote terminals. The authors' company has developed such small capacity VRLA batteries to meet these requirements. The technical details of these batteries are reported in this paper.

2. Failure modes in floating service

The failure modes of small capacity, VRLA batteries used in floating service are listed in Fig. 1. The two major deterioration causes are:

(i) deterioration of the close contact between the positive grid and the active material, or generation of a passivation layer; both related to elongation of the positive grid caused by corrosion,

(ii) decrease in electrolyte amount caused by moisture permeation through the walls of the battery container.

3. Preventative measures for achieving longer life

The following preventative measures have been taken in the newly developed battery with respect to the abovementioned life-deterioration processes.

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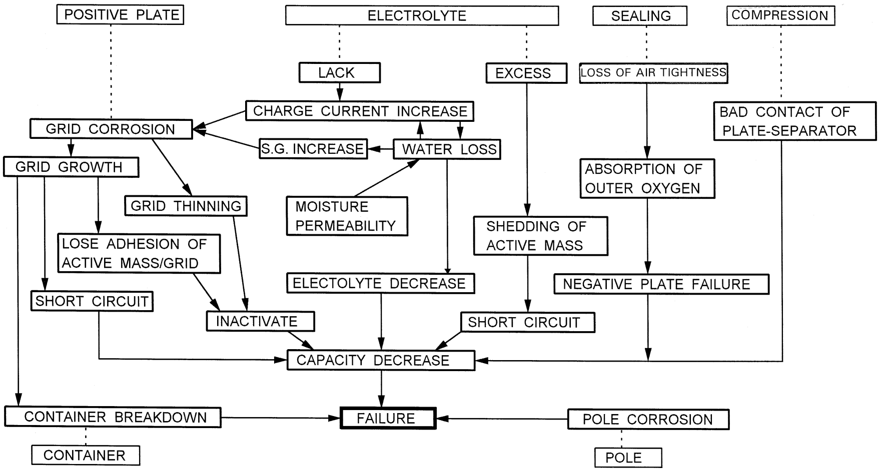

Fig. 1. Failure modes of VRLA batteries.

3.1. Grid corrosion

3.1.1. Alloy

It is a common practice to use a Pb–Ca–Sn alloy in VRLA battery grids. The amounts of Ca and Sn in the positive grid alloy determine the grid elongation due to corrosion. We have therefore employed an alloy containing optimum amounts of these elements to improve the corrosion resistance of the positive grid as well as to inhibit the grid elongation.

The relationship between the Pb–Ca–Sn phase diagram [1] and growth of the positive grid is shown in Fig. 2. With corrosion resistance and productivity taken into account, we have determined the optimum Ca and Sn levels. Fig. 3 shows cross-sectional areas of positive plates, which employ this new alloy and the conventional alloy, after a constant-current overcharge test (0.1 C A for 1000 h) at 75°C. The new alloy, compared with the conventional alloy, has fewer grain boundaries in its structure, and this suggests that the corrosion resistance of the grid has increased due to the decreased number of locations subjected to intergranular corrosion.

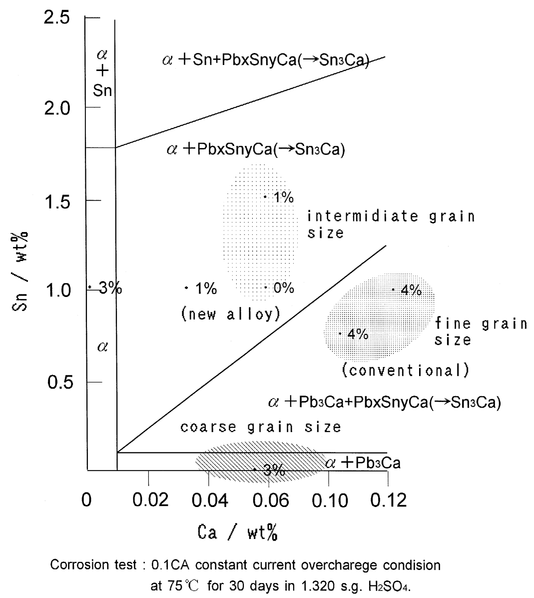

Fig. 2. Relationship between Pb–Ca–Sn phase diagram and growth (%) of positive grid.

3.1.2. Grid structure

In order to prevent a deterioration in the contact between the active material and the grid due to grid corrosion, the grid shape was investigated. As a result, it was found that changing the conventional grid shape by increasing the cross-sectional area of the vertical grids, while decreasing that of the horizontal grids, is effective in extending the grid life [2]. The results from an accelerated float life test at 45°C are shown in Fig. 4. For the conventional grid configuration, the grid elongates in both the vertical and horizontal directions to create a gap between the grid and the active material in both directions. It is expected that this would decrease the discharge capacity. This gap formation between the grid and the active material is related to the grid corrosion, namely, to the rate of elongation. As the grid elongates, the close contact between the grid and the active material deteriorates and this results in failure to obtain the specified capacity. The grid of the new structure, designed to allow the grid elongation due to corrosion to take place only in the vertical direction, provides maximum contact between the vertical grid and the active material, compared with the conventional grid. This occurs even if the grid corrosion has progressed, suggesting a slower decline in the discharge capacity.

3.1.3. Specific gravity of electrolyte

The sulfuric acid of the electrolyte is a reactant in VRLA batteries, along with the positive and negative active materials. The acid concentration affects greatly

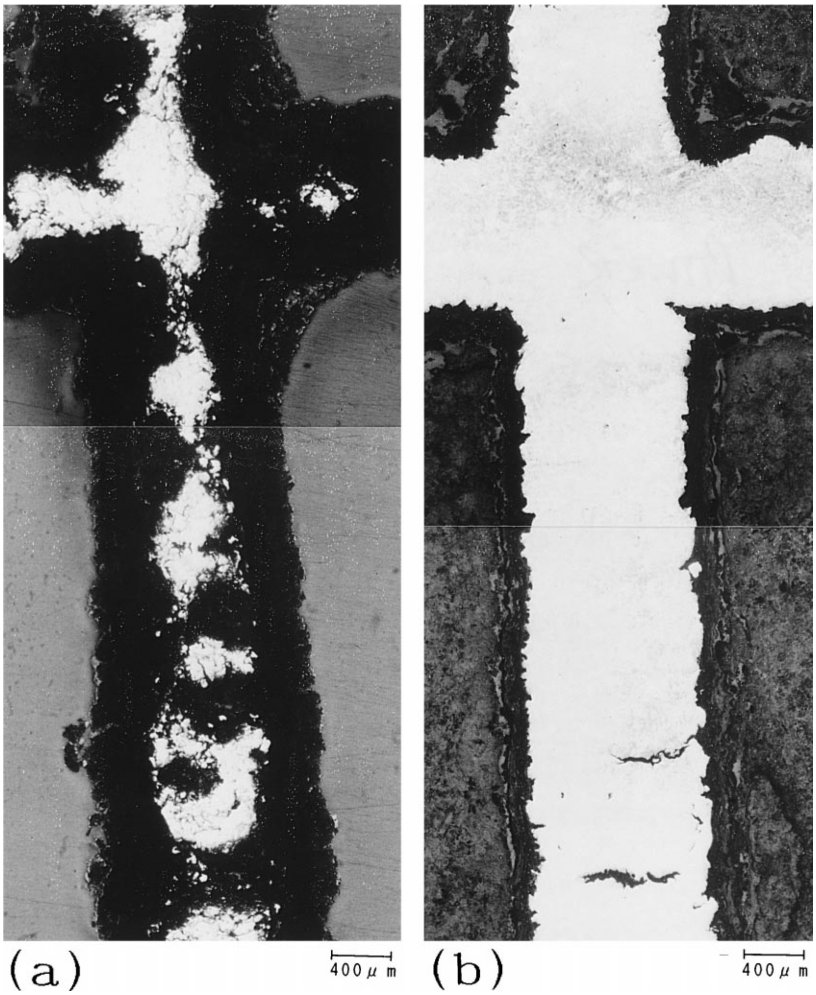

Fig. 3. Cross-section of positive plates after constant-current overcharging (0.1 C A for 1000 h) at 75°C: (a) conventional alloy; (b) new alloy.

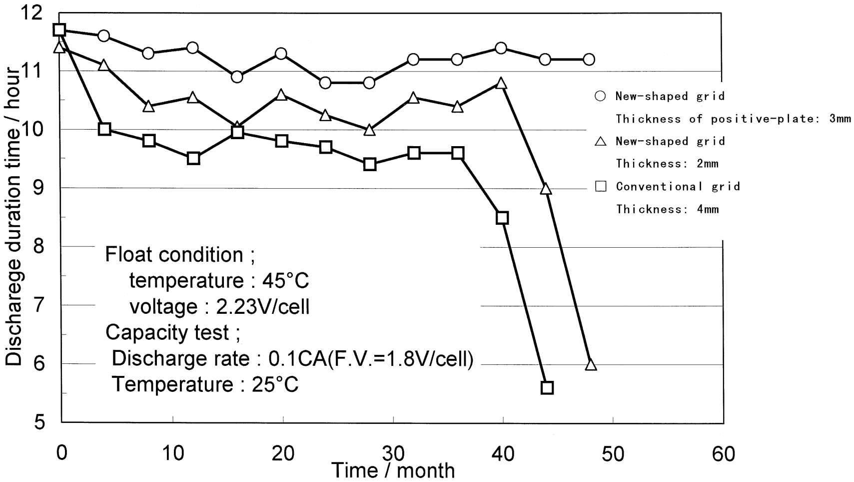

Fig. 4. Results of accelerated float life test at 45°C.

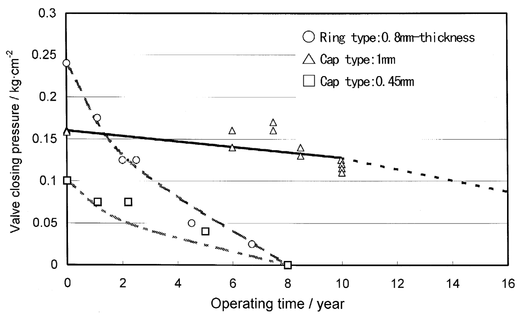

Fig. 5. Relationship between operating time and the valve closing pressure.

both the discharge and the life characteristics. A general means of achieving a longer life is to reduce the electrolyte concentration. Clearly, this will decrease the amount of sulfuric acid, and render it difficult to maintain the specified discharge capacity. Therefore, we selected the upper limit of the electrolyte concentration in which the grid life is optimized.

3.1.4. Float charging current

In floating service, the charging current is affected greatly by the charging voltage, plate construction, the amount of electrolyte, and the battery temperature. As the float charging current increases, the amount of corrosion at the positive grid increases accordingly. At elevated temperatures, the charging current increases, and the battery temperature rises due to recombination of oxygen gas. When the charging current further increases, thermal runaway may take place. Therefore, inhibiting the floating charge current provides an effective means of inhibiting corrosion of the positive grid, and is particularly useful in safeguarding against thermal runaway at elevated temperatures.

We were able to restrict the charging current at high temperatures to below 50% of the conventional value by making improvements to the production method of the negative plate.

3.2. Dry-out

3.2.1. Moisture permeation

ABS (acrylonitrile/butadiene/styrene) resin is often used as a container material for small VRLA batteries. Although this resin is not the optimum material in preventing moisture permeation, we made the wall thickness greater than that of a conventional battery container, and employed a compression control method (to be described later) to inhibit possible electrolyte loss.

3.2.2. Separator

A microglass separator made from fine glass fibers was used to hold the electrolyte in suspension and separate the positive and negative plates. In order to maintain close contact between the plates and the separator, it is necessary to apply a certain level of compressive force to the plates. This force may decrease during the electrolyte filling process, and additionally a decrease in the amount of electrolyte will result in poor contact between the plates and the separators. We have therefore chosen the microglass separator that provides the least decrease in compressive force during filling or use, and have developed a method that allows a battery to be assembled with higher compression.

3.3. Other parts

3.3.1. Safety valve

The relationship between the period of battery use and the valve closing pressure is shown in Fig. 5. Two types of conventional valve shape are used: the ring type and the cap type. We have found that with the cap type, the thicker the valve rubber, the less its deterioration. In our new battery, we have employed a cap type of safety valve because it has an established history of use in large VRLA batteries.

Table 1
Specifications of new batteries

Model number	12V15AH-LHM	12V24AH-LHM	12V38AH-LHM	12V65AH-LHM
Nominal voltage (V)	12	12	12	12
Rated capacity C_{20}/20 rate (A h)	15	24	38	65
Specific energy (W h kg^{-1})	29.0	26.2	28.5	31.0
Outer dimensions				
Length (mm)	181	175	197	350
Width (mm)	76	166	166	166
Height (mm)	167	150	200	175
Mass (approx. kg)	6.2	11.0	16.0	25.2
Terminal types	Faston	Bolt and nut	Bolt and nut	Bolt and nut
Expected life (years) (ambient temp.: 25°C)	13	13	13	13

3.3.2. Terminals

In order to achieve easy connection, we have changed the current bolt and nut type terminal structure to a bolt-buried type or FASTON type.

4. Battery characteristics

4.1. Overview of the battery

The specifications of the newly developed batteries are listed in Table 1. An outside view of the battery is shown in Fig. 6.

4.2. Discharge characteristics

The discharge characteristics of the newly developed battery are shown in Fig. 7 for the 12V38AH-LHM model (12 V, 38 A h C_{20}/20 rate). The discharge characteristics were equivalent to those of a conventional battery, over all ranges.

4.3. Life characteristics

The Arrhenius equation is generally used to estimate float life [3]. Additionally, our battery was subjected to accelerated life tests at elevated temperatures. The results of accelerated life tests at 72 and 60°C are shown in Figs. 8 and 9, respectively, along with the values calculated in terms of 25°C. From these results, the float life at an ambient temperature of 25°C is estimated to be at least 13 years.

4.4. Thermal runaway resistance characteristics

Thermal runaway test results for conventional and newly developed batteries are shown in Fig. 10. The charging current of the conventional battery after 72 h of charge at a charging voltage of 2.275 V/cell increased with ambient temperature, whereas with our newly developed battery, the charging current was restricted to that of an ambient temperature of close to 75°C.

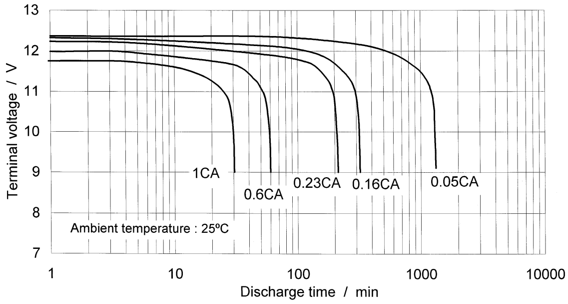

Fig. 7. Discharge characteristics of 12V38AH-LHM battery.

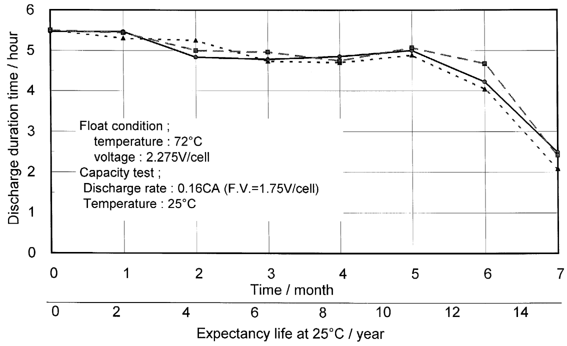

Fig. 8. Results of accelerated float life test at 72°C.

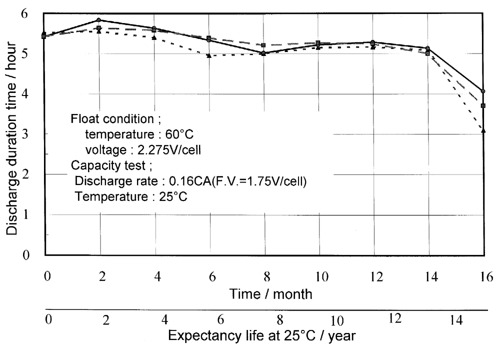

Fig. 9. Results of accelerated float life test at 60°C.

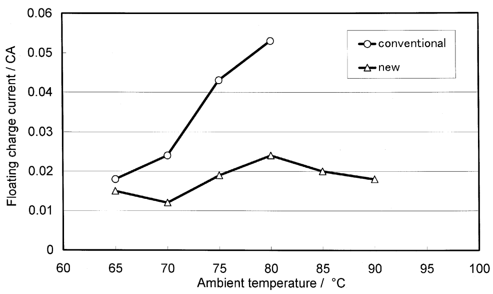

Fig. 10. Relationship between ambient temperature and floating charge current at 2.275 V/cell charge voltage for 72 h.

Fig. 6. Outside view of new VRLA batteries.

5. Conclusions

We have developed small capacity VRLA batteries with an estimated life of at least 13 years. This makes such batteries suitable as backup power supplies for telecommunications. The design features are:

(i) selection of optimum composition and shape of a Pb–Ca–Sn alloy that has less corrosion;
(ii) optimization of electrolyte concentration; and
(iii) inhibition of charging current at elevated temperatures by improving the negative plate.

We intend to employ these technologies in smaller capacity VRLA batteries in order to achieve longer life and higher reliability.

Acknowledgements

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