

Failure modes of valve-regulated lead/acid batteries

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Abstract

The decline in the cycle-life performance of lead/acid batteries is often caused by deterioration of the positive plates. When batteries are used in electric vehicles, however, the decline in performance is due not only to positive-plate degradation, but also to serious problems with the negative plates. This is because electric-vehicle batteries are used in the form of a pack and their temperature rises excessively (especially during the hot weather) which, in turn, causes decomposition of the lignin additive in the negative plates. Deterioration of the negative plates limits vehicle-running performance even in hybrid electric vehicles (HEV). When batteries are used in this way, charging is achieved during travel via regenerative current and the generator. Thus, the batteries are charged by large currents, and charging is irregular. This causes the accumulation of lead sulfate in the negative plates. Such behaviour can be suppressed by increasing the amount of carbon, one of the negative-plate additives. As a consequence, cycle-life performance is improved significantly. On the other hand, in small valve-regulated lead/acid batteries for trickle use, contact between the plates and separators is impaired and this results in a decline in the high-rate discharge performance. This occurs because transmission of water vapour from the battery container lowers the amount of electrolyte in the separators, which then contract.

Keywords: Valve-regulated lead/acid batteries; Positive plates; Negative plates; Failure mode

1. Introduction

The decline in cycle-life performance of lead/acid batteries is often caused by deterioration of the positive plates [1,2]. This behaviour is also experienced with valve-regulated lead/acid battery (VRLA) designs. We have found, however, that the decline in performance of batteries in electric-vehicle (EV) and uninterruptible power supply (UPS) applications, which offer promise as major markets for VRLAs, is caused not only by positive-plate deterioration, but also by problems with the negative plates, separators, and other parts. Apparently, this is because these applications involve loads and usage conditions that differ from those experienced heretofore. Here, we shall present some examples of these, and shall also discuss deterioration mechanisms and ways to limit them.

2. Failure modes in EV applications

Batteries for EV applications are used under deep-discharge and overcharge conditions. Many of the failures are associated with softening of the positive active-material, positive grid corrosion and growth, and passivation of the bound-

ary between the positive grid and the active material [1,2]. Examination of batteries that have actually been used in EV service, however, reveals that positive-plate deterioration is not the only problem. This is demonstrated by the following experiments.

2.1. Field tests

A battery field test was conducted in a HIJET van (Daihatsu Motor Co., Ltd.) This vehicle was fitted with eight, 12 V, 60 Ah ($C_3/3$ rate) batteries of the starved-electrolyte, VRLA design. The specific energy of the batteries was 35 Wh kg^{-1} at the $C_3/3$ rate. The depth-of-discharge (DOD) was 70%. The test was conducted for 3 months (Aug. to Oct.), i.e., for about 50 cycles.

The charge and discharge currents during vehicle operation are given in Fig. 1. The discharge current was about $5C_3$ when accelerating, and about $1/3C_3$ when running at a constant speed. The acceleration current is quite large because small-capacity batteries were used in order to speed up the test. Additionally, the battery temperature during the test frequently exceeded 50 °C for various reasons, including execution of the test during a hot summer.

The discharge capacity of the batteries after the van had driven under these conditions for 50 cycles is given in Fig. 2.

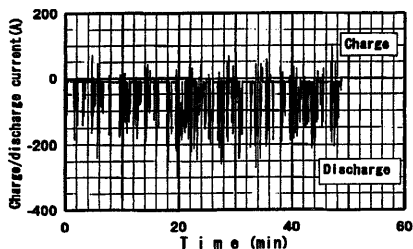


Fig. 1. Charge/discharge current during vehicle operation.

The discharge capacity at $1/3C_3$ was virtually the same as that at the beginning of the test, but the capacity at $3C_3$ had fallen by about 30%. The single-charge driving range decreased by about 40%, and correlated more with the $3C_3$ discharge capacity than with the $1/3C_3$ value.

One of the batteries was selected and the discharge capacities of its cells were determined; these are given in Fig. 3. The capacity of the central cell was found to have dropped substantially; the capacity was limited by the negative electrodes. A possible explanation for this behaviour was a rise in temperature that, in turn, decomposed the lignin additive in the negative active-material. An analysis of the amount of lignin in the negative active-material (obtained by the UV absorbance of the solution that eluted the lignin) showed (Fig. 4) that the central cell, which suffered the largest capacity drop, contained little residual lignin.

2.2. Discussion

An experiment was performed to confirm the effect of temperature on cycle-life performance. The test battery was a 2 V, 25 Ah starved-electrolyte VRLA unit with ratios of

negative-to-positive active material of 70, 80 and 90%. Discharging was carried out at the $1/3C_3$ rate for 2.4 h to 80% DOD. Charging was achieved with a two-step, constant-current procedure with an overcharge factor of 110%. The test temperature was 40 °C for the first 300 cycles, and 50 °C thereafter.

The C_3 discharge capacity dropped precipitously when the temperature was raised from 40 to 50 °C (Fig. 5). The capacity was limited by the negative electrodes. Within the chosen experimental conditions, the capacity declined even if the amount of negative active-material was increased. Nevertheless, the rate of capacity loss was decreased as the amount of negative active-material was increased. The results from this test and the above field trials clearly indicate that lignin decomposition is responsible for the degradation in battery performance. Thus, in order to increase the cycle life of lead/acid batteries used in EVs, it is very important to improve not only the positive plates, but also the negative plates. In particular, it is essential to develop additives that can withstand high temperatures.

3. Failure modes in HEV applications

In HEV applications [3], which combine batteries and engines, the batteries experience the following conditions: (i) repeated large discharges for several seconds to several tens of seconds, in order to assist the engine during starting and accelerating; (ii) charging in accordance with the state-of-discharge when travelling at constant speed or when idling while stopped, and (iii) charging by a large current through regenerative braking when decelerating or stopping. Investigations were made on VRLA batteries taken from a HEV that had been subjected to this charge/discharge pattern. Just as with the EV described above, battery performance was restricted by the negative plates. The cause was not the

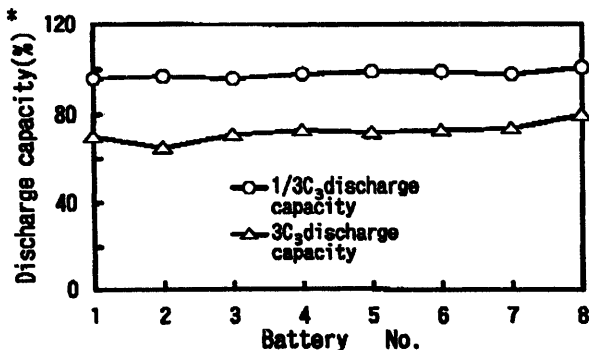


Fig. 2. Discharge capacity after 50 cycles of the driving test; (•) ratio with respect to initial capacity.

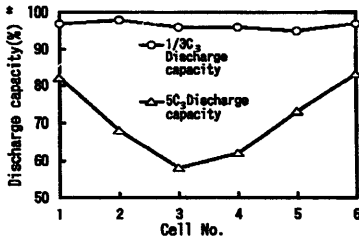


Fig. 3. Cell capacity of tested batteries; (*) ratio with respect to initial capacity.

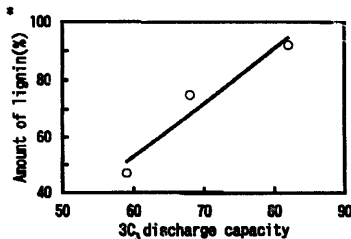


Fig. 4. Relationship between residual amount of lignin and 3C₂ discharge capacity. (*) ratio with respect to initial amount of lignin.

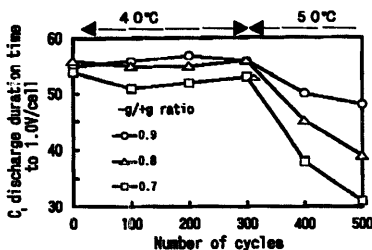


Fig. 5. Effect of ratio of negative-to-positive active mass and temperature on cycle life.

decomposition of the lignin additive, however, but an accumulation of lead sulfate. The reasons for this behaviour in such an application were related to the fact that the batteries are charged with a large current, undergo irregular charging, and continue to be used without having been fully charged.

To reproduce the above failure mode, experiments were performed on 2 V, 2 Ah starved-type VRLA cells. The amount of carbon (a negative electrode additive) was increased to 3 or 10 times the standard amount in attempts to prevent the accumulation of lead sulfate. The simulated charge/discharge pattern of batteries in the HEV is shown in Fig. 6. The pattern was repeated until the final discharge

voltage fell to 1.5 V. The state of the plates was examined both on termination of the cycles (stage (b), Fig. 6) and when the batteries had been charged to 200% of their rated capacity subsequent to the final cycle (stage (a), Fig. 6).

The final discharge voltage, i.e. discharge voltage at stage (a), (Fig. 6) is shown in Fig. 7 for three batteries. The final discharge voltage of battery A (with carbon additive in the standard amount) fell to 1.5 V at about 400 cycles. As with in-vehicle use, the discharge capacity was limited by the negative plates. At 400 cycles, analysis revealed accumulations of lead sulfate of about 20% in the positive plates, and about 40% in the negative plates. The same analysis was conducted on a charged battery with the same history (charging amount: 200% of rated capacity). Although almost all of the lead sulfate in the positive plates was eliminated by the charging, but more than 20% lead sulfate still remained in the negative plates. These results were the same as those obtained from field trials. They show that when a battery continues to be used in an incompletely-charged state, it becomes impossible to charge the negative plates because of the build-up of lead sulfate in them and this, in turn, brings about a decline in negative-plate capacity.

By contrast, battery B (with three times the standard amount of carbon) and battery C (with 10 times the standard amount of carbon) completed a greater number of cycles until the final discharge voltage reached 1.5 V (Fig. 6). The cycle life was 700 and 1100 cycles for battery B and C,

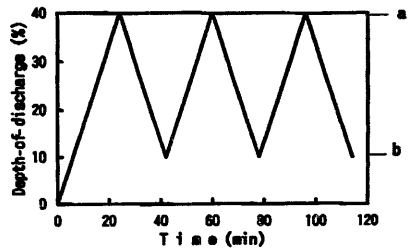


Fig. 6. Charge/discharge pattern.

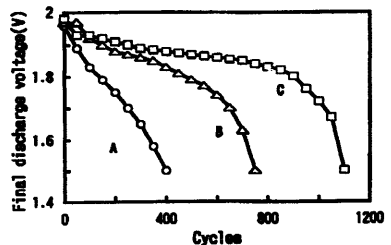


Fig. 7. Change in final discharge voltage during HEV pattern test at 25 °C.

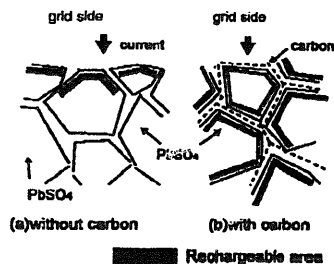


Fig. 8. Schematic of carbon effect on rechargability of negative active-mass.

respectively. Analysis of the amount of lead sulfate at this stage revealed that although these batteries had undergone more cycles than battery A, the accumulation of lead sulfate was less, i.e. about 30%. The amount of lead sulfate accumulated per cycle was 0.1, 0.05 and 0.03% per cycle for battery A, B and C, respectively. This shows that the more the carbon added, the more difficult it is for lead sulfate to accumulate. When charging batteries B and C, the amount of lead sulfate fell to 10%. This result suggests that increasing the amount of carbon makes it easier to charge accumulated lead sulfate. The beneficial effect of carbon is thought to be due to the formation of a conductive network (as shown in Fig. 8) that prevents isolation of active material by lead sulfate and thus facilitates charging.

4. Failure modes in UPS applications

In recent years, VRLA batteries have become widely used in uninterruptible power supply (UPS) systems. As in stationary applications, the batteries are charged at a constant voltage when not in use, and supply power during power outages. The difference with stationary applications, however, is that the batteries are discharged at high-rate currents (at a 5 min rate, for example).

Table 1 shows the discharge capacity of a battery removed from a UPS system in actual use. Even after 36 months, the 5 h discharge capacity is virtually unchanged, but is considerably lower at the 5 min rate. Because ordinary stationary applications do not demand discharges at such large currents, this capacity decline provides no obstacle to actual use. On the other hand, this is a serious problem in UPS applications for computers and the like. Because there was no change in the 5 h capacity, and based on information obtained, for example, from observations of plate condition, it appears that the causes for the poor performance are not the usual positive-grid corrosion and positive-plate deterioration processes.

Discharge curves at the 5 min rate are given in Fig. 9. Batteries with 36 months of use experience a large fall in voltage immediately on commencement of discharging. A

Table 1
Discharge capacity (Ah) before and after operation test of UPS. (final discharge voltage: 10.2 V)

| Discharge time | Initial | After 36 months |
|----------------|---------|-----------------|
| 5 h | 8.1 | 8.3 |
| 5 min | 2.9 | 1.2 |

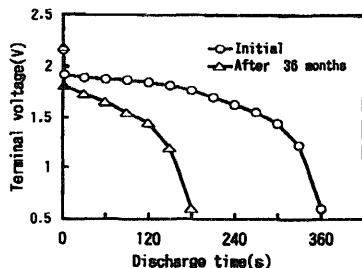


Fig. 9. Discharge curves at 5 min rate.

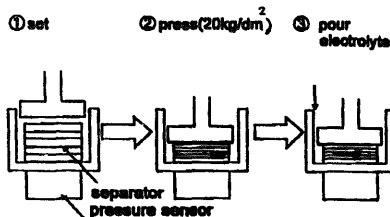


Fig. 10. Schematic diagram of device for measurement of separator contraction.

rise in internal resistance limits the high-rate discharge capacity. It appears that the contact between the separators and the plates worsens as the electrolyte content decreases. Thus, a study was made of the relationship between decreasing electrolyte content in the separators and their contraction. The test setup is shown schematically in Fig. 10. Five glass-fibre separators were used at an initial pressure of 20 kgf dm^{-2} . The holding time after pressurization, i.e. the time before dilute sulfuric acid was added, was 1 h. The amount of electrolyte added to the separators was 50, 80, 90, 95 and 100% of the pore volume.

The change in separator contraction with time is shown in Fig. 11, and the relationship between the amount of electrolyte added and compression after 1 h is given in Fig. 12. Separator contraction decreases when dilute sulfuric acid is added. The decrease in contraction is pronounced when the electrolyte content is under 90%. This decrease in contraction occurs because the glass fibres that compose the glass separators are pulled together by the surface tension of the dilute

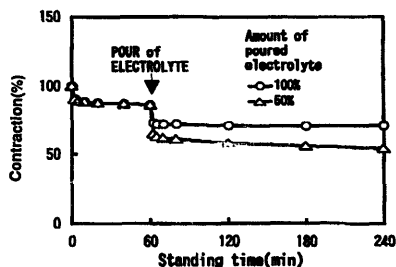


Fig. 11. Change in separator contraction with time.

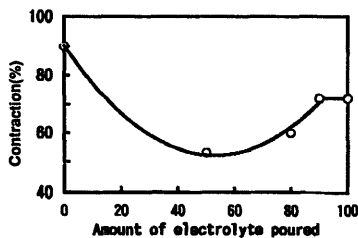


Fig. 12. Relationship between the amount of electrolyte added and separator contraction.

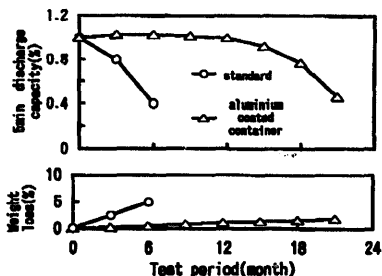


Fig. 13. Effect on battery performance of preventing water-vapour transmission.

sulfuric acid, which brings about separator contraction. The degree of contraction varies with the amount of electrolyte and, within a certain range, it increases as the electrolyte

amount decreases. As separators in actual batteries initially retain about 95% of the electrolyte, separator shrinkage is not appreciable initially. Later, however, the separators shrink considerably because electrolyte is consumed during battery use, and because electrolyte decrease begins in the separators before it begins in the plates (owing to the difference in the pore diameters of the separator and the active material). This shrinkage results in poor contact between the plates and the separators, which increases the internal resistance.

Given the above problem, electrolyte decrease should be minimized in order to prevent the concomitant decline in battery performance. Causes of electrolyte decrease are water decomposition by overcharging, and transmission of water vapour out of the battery container. The effect of the latter is probably large for VRLA in batteries because the containers are made from ABS resin. For this reason, aluminium-deposited containers have been examined as a means for preventing the transmission of water vapour. The data in Fig. 13 show that such an approach is highly effective, and that a substantial improvement in cycle life is obtained.

To improve cycle-life performance, therefore, it would be effective to take steps such as preventing water-vapour transmission (by changing the container material from ABS resin to polypropylene resin, for example), and by applying high compression to improve the contact between the plates and the separators.

5. Conclusions

An investigation has been made of the causes of deterioration in VRLA batteries used in EVs, UPS systems and other applications. In standard bench tests, battery lifetime is often terminated by positive-plate deterioration. Present research and tests have determined, however, that battery life is limited by other causes that include negative-plate deterioration and poor separator-plate contact. These results indicate that as new applications for lead/acid batteries are developed, battery failure modes will diversify and will require improvements to deal with them. In selecting battery configurations to match the use, it will be necessary to establish testing methods that can accurately assess practical service life.

References

- [1] J.G. Ewashanka, *Proc. 19th Intersociety Energy Conversion Engineering Conf.*, Vol. 2, 1984, p. 727.
- [2] B. Culpin and D.A.J. Rand, *J. Power Sources*, 36 (1991) 415-438.
- [3] T. Koike, T. Kato, K. Shimizu, K. Yamaguchi and M. Shiratsuchi, *Proc. 12th Int. Electric Vehicle Symp.*, Vol. 2, 1994, p. 709.