Ten minutes-rechargeable, valve-regulated, lead/acid battery after deep discharge and stand

T. Yasaki, Y. Ehara, K. Asai and J. Takahashi
Japan Storage Battery Co., Ltd., Small Battery Division, 1 Inobaba-cho, Nishinosho, Kisshoin, Minami-ku, 601 Kyoto (Japan)

K. Matsumoto and S. Kubotani
AIWA Co., Ltd., Technical Headquarters, 4-2-20 Harigaya, Urawa-shi, 338 Saitama (Japan)

Abstract

Ten minutes-rechargeable, valve-regulated batteries for headphone stereos were released on to the market in 1990. These were very thin batteries, i.e., the PF2V0.28 (2 V, 0.28 Ah) unit was 6 mm thick and the PF2V0.55 (2 V, 0.55 Ah) unit was 8.5 mm thick. The systems were well accepted for normal operation, but the batteries could not be recharged rapidly after overdischarge and long stand. Therefore, batteries have been developed that can be recharged quickly, even after being subjected to the most severe operating conditions experienced with portable electronic appliances. In order to simulate the operational problem, the batteries were evaluated in an overdischarge condition that consisted of one-week discharge through a resistor and long-term standing at open-circuit at high temperature. The batteries have now been improved to accept charge current in a few minutes, even under the most severe of overdischarge conditions. The improved batteries also display good performance with respect to storage, overcharge and cycle life.

Introduction

The demand for small batteries has been increasing because electronic equipment, through down-sizing and reduced power consumption, is becoming portable and cordless. As a consequence, the market for rechargeable batteries is expanding, particularly for nickel/cadmium units. Small, valve-regulated lead/acid batteries (VRBs), of slightly lower energy density, display the following advantages over nickel/cadmium counterparts when used for headphone stereos, cordless telephones and portable compact disc players:

(i) higher cell voltage, therefore fewer cells are required for a given size of battery pack;

(ii) about one-tenth the self-discharge rate;

(iii) terminal voltage is proportional to the state-of-charge and, therefore, residual capacity can be evaluated;

(iv) no memory effect under shallow-discharge cycling.

Small VRBs with a high energy density (the PF series) were developed in the authors' laboratories in 1987 [1]. A ten-minute, fast recharging system was developed for headphone stereos that used these batteries. This system was placed on the market in 1990. A photograph of the PF Series batteries, together with a headphone stereo, is given in Fig. 1. Despite further technological advances, VRBs are still considered

0378-7753/93/$6.00

Fig. 1. PF-type batteries.

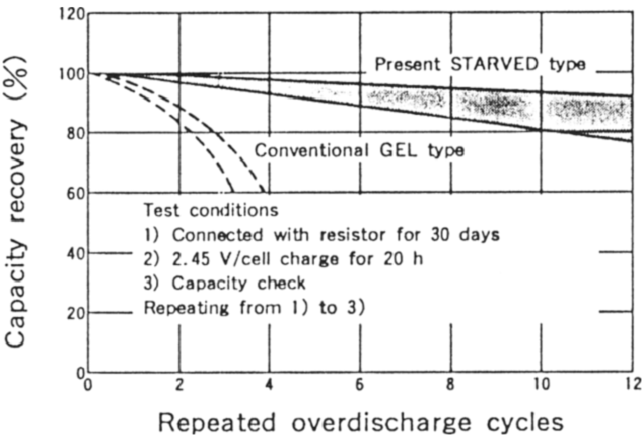

Fig. 2. Overdischarge durability of small VRBs.

to be inferior to nickel/cadmium batteries, particularly with respect to overdischarge performance.

The overdischarge performance can be divided into two principal features, namely: overdischarge durability and charge acceptance after overdischarge. Overdischarge durability means that the batteries should maintain a stable performance even if they are repeatedly overdischarged or stood for a long time under overdischarge conditions. Figure 2 shows the overdischarge durability of standard small VRBs. In this test, the batteries were connected to a resistor for one month, then charged at a constant voltage for 20 h and the capacity was evaluated. These tests were repeated 12 times. The present standard types of VRBs have been improved to withstand this treatment. This was not the case with older-technology, gelled-electrolyte batteries. The batteries displayed poor durability (Fig. 2). Therefore, the new VRBs should pose no problems in practical use.

Charge acceptance after overdischarge was also improved so that a charge current could be accepted within several hours. This was achieved by modifying the lead-alloy composition of the positive grids.

Batteries for portable electronic appliances, however, were used with a quick charging system and were charged for only one hour or so in the field, even after overdischarge. This resulted in a number of battery failures. As a consequence, batteries that can be recharged rapidly, even after severe overdischarge, were developed. This was made possible by modifying the positive grid alloy, as well as both the electrolyte and the active-material composition. Test data from these fast-charge studies are reported below.

Experimental

The charge acceptance was first examined under normal operating conditions, and then after overdischarge. In normal practice, headphone stereos have electronic circuits that prevent overdischarge; the discharge ceases when the battery voltage falls to 1.8 V. In the experimental test, however, the batteries were discharged very deeply with a 25-Ω resistor (similar to the stereo's load) for 7 days. The batteries were then stood at 40 °C (to accelerate corrosion at the grid/active-material interface) for a maximum of 90 days, and their charge acceptance at constant voltage was evaluated.

The capacity recovery after overdischarge is remarkably dependent upon the charge conditions. The capacity recovery after a 1-h charge with the stereo's charger was evaluated. The charger has a fast, two-step, quasi-constant voltage, charging system. The batteries were recharged again for 1 h and the capacity was redetermined. Batteries that had not recovered their capacity, even after the second charge, were recharged for 6 h and then discharged. The headphone stereo's batteries (PF2V0.28: 2 V, 0.28 Ah) that had been improved through modifications to the positive grid alloy, electrolyte and active materials were tested and compared with the performance of conventional designs.

Results and discussion

Charge acceptance immediately after discharge

Figure 3 shows the characteristics of VRBs of PF2V0.28 design that were charged with the stereo's charger immediately after discharge to 1.8 V under a load similar to that of the stereo.

The improved and conventional batteries showed almost the same charge acceptance; the first charge step was completed within 13 min.

The relationship between charge time and capacity recovery immediately after discharge is given in Fig. 4. In this test, the batteries were discharged to 1.8 V, charged for 10 to 60 min, and then discharged to assess the capacity retention for each charging time. Even for a 10-min charge, the capacity recovered by more than 75%. Full recovery was achieved with a 1-h charge. Under these conditions of normal operation, there is no difference in capacity recovery between the improved and conventional batteries.

Charge acceptance after overdischarge

Figure 5 shows the relationship between the standing time at 40 °C (after overdischarge with a resistor) and the open-circuit voltage (OCV) of the batteries. The OCV of the improved batteries is about 0.95 V. This value is very stable and is independent of the standing time. By contrast, the OCV of conventional batteries decreased to about 0.15 V after 14 days of standing. This was caused by a change in the potential of the positive plates. The improved batteries exhibited good electrical conductivity between the current collector and the residual lead dioxide in the positive

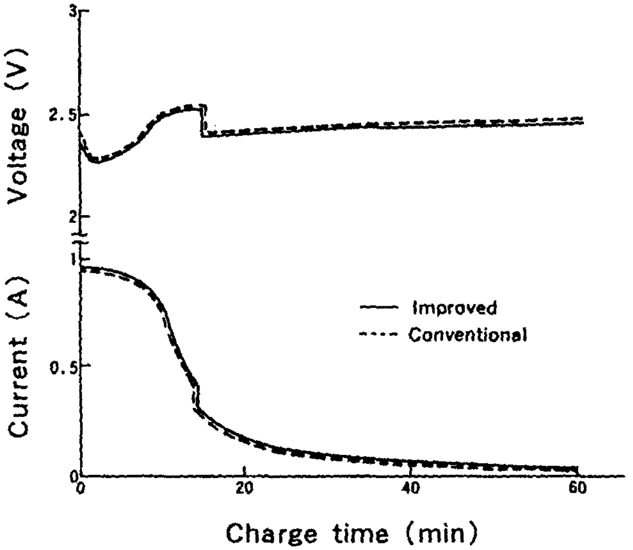

Fig. 3. Charge characteristics with headphone stereo's charger (PF2V0.28).

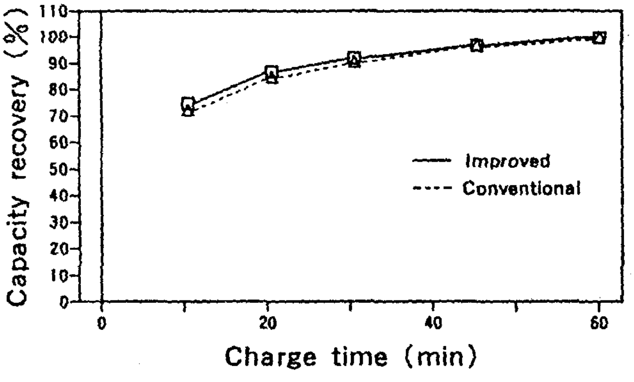

Fig. 4. Relations between charge time and capacity recovery immediately after complete discharge (PF2V0.28).

active material and thus yielded the potential of lead dioxide/lead oxide couple. By comparison, the conventional batteries had a very high resistance at the corrosion layer and displayed the potential of the interface between the corrosion layer and the current collector, including lead oxide, tribasic lead sulfate or monobasic lead sulfate [2].

Figure 6 shows the charging curves after 90 days of standing at 40 °C following 7 days connection with the resistor. The improved battery accepted the charging current within a few minutes and reached the maximum current at 6 min.

The conventional battery, however, did not accept charging during the first 1-h charge (Fig. 6), nor even on the second 1-h charge. The peak charge current was observed at 3 h (total 5 h) during the third 6-h charge.

The relationship between the standing time after overdischarge and the time until the charge current reaches a maximum is presented in Fig. 7. The vertical axis is the

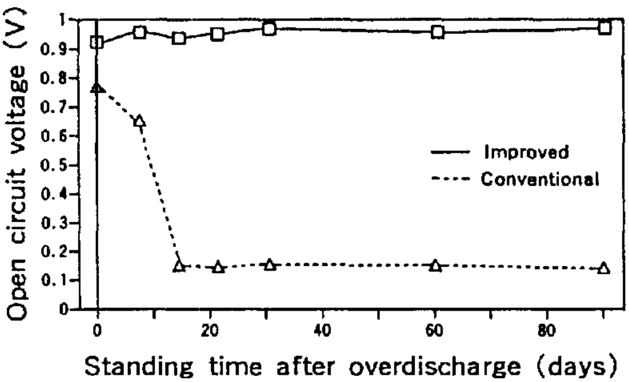

Fig. 5. Relationship between standing time after overdischarge and OCV (PF2V0.28).

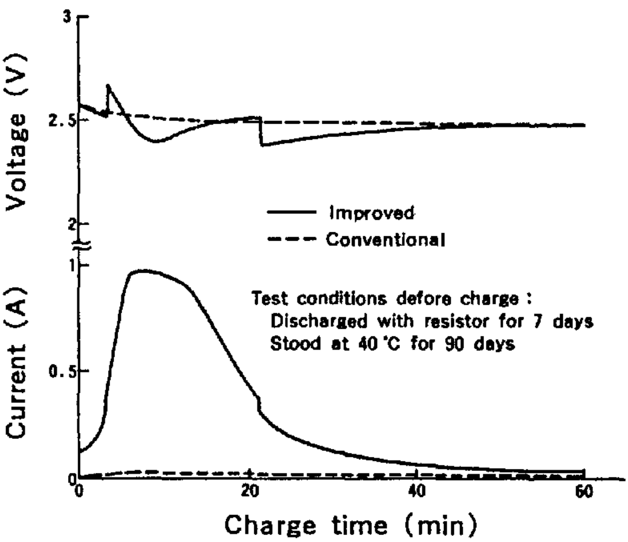

Fig. 6. Charge characteristics after overdischarge and stand for 90 days (PF2V0.28).

total time for three consecutive charges and each point is the average of two test data. All the improved batteries reached a peak current within several minutes, while it took about 1 h or 4 to 5 h to reach the peak current when the conventional batteries were stood for <14 days or >21 days, respectively. The charge-acceptance time was strongly dependent on the OCV, as shown in Fig. 5; that is, the batteries with an OCV of 0.95 V reached a peak charge current in several minutes, while those with an OCV of 0.15 V required about 5 h to charge.

Figure 8 shows the capacity recovery on repeated charges after overdischarge and standing. All of the improved batteries recovered capacity after the first 1-h charge. On the other hand, the capacities of conventional batteries stood for >21 days did not recover after two consecutive 1-h charges, but all of them recovered by the third 6-h charge.

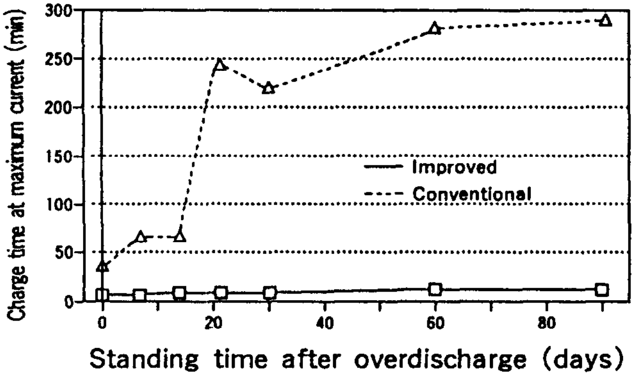

Fig. 7. Relations between standing time after overdischarge and the time until charge current reaches a maximum (PF2V0.28).

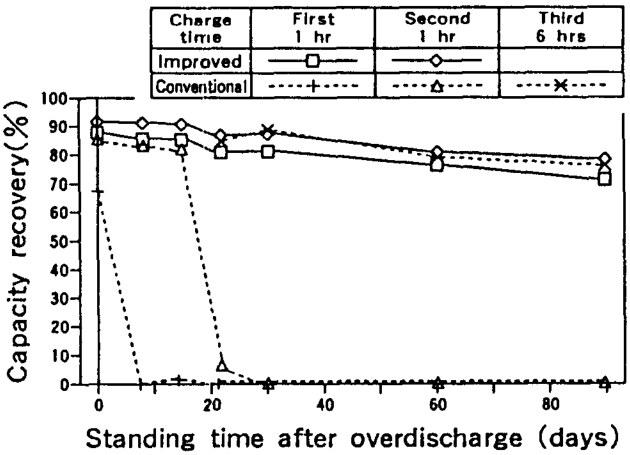

Fig. 8. Capacity recovery after repeated charges following overdischarge and stand (PF2V0.28).

Charge acceptance of other valve-regulated batteries (PF2V0.55)

The technology discussed above is applicable to other VRBs. To examine the overdischarge performance in severe conditions, PF2V0.55 batteries were fully discharged and charged for 100 cycles to grow the corrosion layer at the interface between the positive active material and the current collector. The batteries were then connected to a resistor at 45 °C for one month to effect deep discharge, and then stood at 25 °C for two months. Figure 9 shows the subsequent charge characteristics at a constant voltage of 2.45 V. As this overdischarge condition is very severe, the conventional battery with lead–calcium–tin positive grids needed 15 h and that with a pure-lead positive grids did not accept charge during 24 h. In sharp contrast, the improved battery accepted charge current within only a few minutes.

Other performance characteristics

In addition to charge acceptance, the storage, overcharge and charge/discharge cycle life are very important parameters when using VRBs for portable electronic applications. Figure 10 shows the residual capacity and capacity recovery for a 1-h

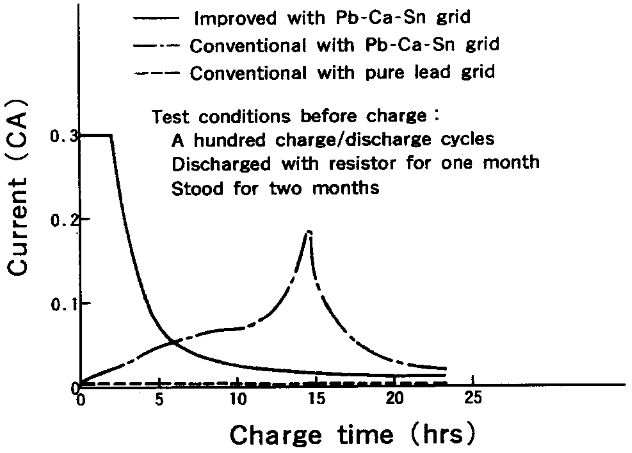

Fig. 9. Charge characteristics after overdischarge and stand (PF2V0.55).

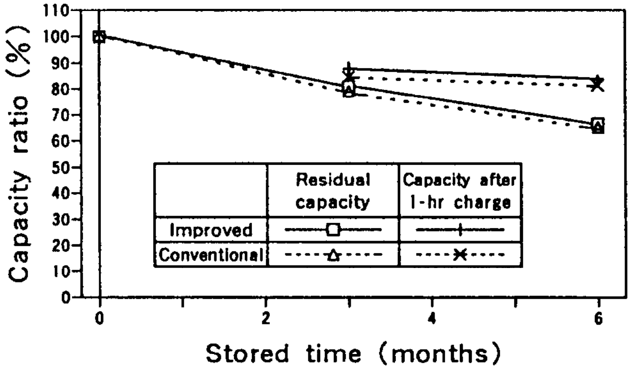

Fig. 10. Residual capacity and capacity recovery on 1-h charge after standing at 25 °C (PF2V0.28).

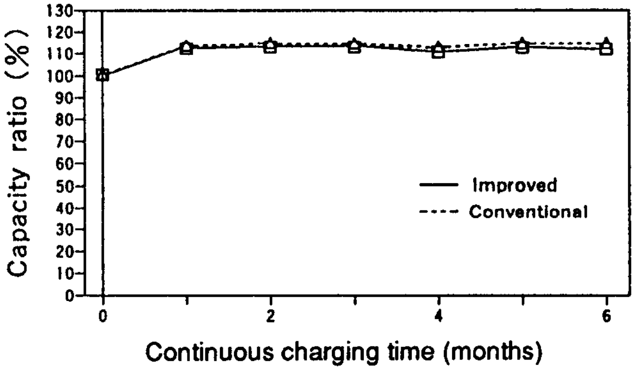

Fig. 11. Overcharge durability by continuous charge at 2.45 V and 25 °C (PF2V0.28).

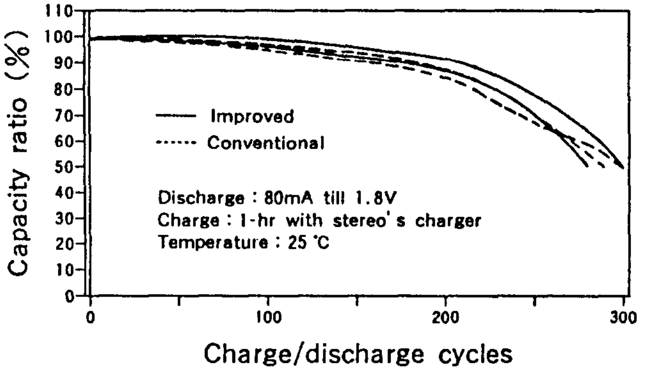

Fig. 12. Life performance under fast-charge cycles (PF2V0.28).

charge after standing at 25 °C. In this test, the fully-charged batteries were stored for 3 to 6 months, discharged to check the capacity, then charged for 1 h and discharged to evaluate the capacity recovery. Both the improved and conventional batteries showed similar self-discharge rates and recovered to about 90% of the initial capacity after only 1-h charge.

The overcharge durability on continuous charge at 2.45 V and 25 °C is given in Fig. 11. Sometimes, consumers leave batteries connected to chargers for a long time. The data demonstrate that even if the batteries are continuously charged for 6 months, the initial capacity is maintained.

Figure 12 shows the life performance of these batteries under fast-charge cycles. The batteries were discharged at 80 mA (i.e., at a rate similar to a stereo's load) to the final voltage of 1.8 V at every cycle and charged for 1 h with the stereo's charger. The capacity was maintained for 250 cycles.

Conclusions

Improved charge acceptance is one of the key factors, for the expanded application of VRBs in portable electronic units such as headphone stereos, compact-disc players, cordless telephones, etc. The overdischarge performance has been improved without sacrificing self-discharge, overdischarge or cycle-life characteristics. The improvement is applicable to all designs of VRBs.

References

1 N. Fujimoto, K. Kobayashi, K. Takeyama and S. Kano, *GS News Tech. Rep., 47-1* (1988) 10.
2 P. Ruetschi, *J. Electrochem. Soc., 111* (1964) 1323.