

Improving the performance of deep-cycling, valve-regulated, lead/acid batteries

Eberhard Nann

HAGEN Batterie AG, Research and Development, Coesterweg 45, O-4770 Soest (F.R.G.)

Abstract

Several characteristics of the well-known lead/acid battery can be improved by developing valve-regulated units (VRLAS) with absorptive glass mat (AGM) separators. In spite of the fact that antimony-free alloys are used, very good cycle-life is achieved. The performance of conventional flooded systems of the same design is inferior. Additional advantages of VRLAs are: absolutely maintenance-free operation during battery service life; very low self-discharge; ability to be used in any position; excellent charge acceptance; deep-discharge resistance. Furthermore, the VRLA system may be designed to meet stated, specific requirements. Different test results show that VRLAs with AGM separators can be used for standby, automotive, and deep-discharge cycling applications.

Introduction

The advantages of valve-regulated lead/acid (VRLA) batteries compared with flooded systems has been the subject of a recently published paper [1]. In the latter, it was considered to be a disadvantage that VRLA batteries can, at present, be used only for applications with relatively shallow discharges. The market shows, however, a continuously rising demand for maintenance-free batteries. Although VRLA batteries now occupy a prominent position in standby operation, their application as automotive or traction batteries is still in its infancy.

The work presented here shows that the performance of existing flooded systems can be markedly improved by using VRLA batteries in which the electrolyte is fixed in an absorptive glass mat (AGM) separator.

Fundamentals of valve-regulated batteries

During the recharge of a lead/acid battery, first oxygen, and then hydrogen, is evolved. This fundamental electrochemical fact is applied to advantage in VRLA batteries through use of the oxygen recombination reaction [2-4].

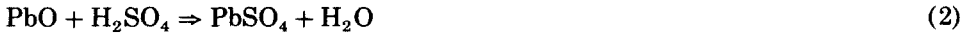
VRLA batteries operate according to the following principle. During charging, oxygen evolving at the positive plate reacts with the negative electrode to produce water, provided the gas can reach the surface of this

electrode. To guarantee this conversion, channels must exist within a fixed electrolyte so that gas transport can take place from the positive to the negative electrode. In the case of AGM separators, this is achieved by filling up the separator with a specific amount of acid. The remaining free pore volume is available for gas transport. Oxygen diffusion is possible, but is reduced by the highly active, micro-porous, negative lead electrode that has a very high specific surface area.

The exact mechanism of the oxygen recombination reaction is still unknown. Two alternatives are proposed [5–11]. In the first, oxygen is considered to react directly with lead to form PbO which is then immediately converted to PbSO₄ which, in turn, is reduced back to lead, i.e.,



(exothermic, chemical reaction)



(exothermic, chemical reaction)



(electrochemical reaction)

The second mechanism involves the direct, potential-dependent, reduction of the oxygen, i.e.,



(electrochemical reaction).

Due to the above reactions, very little hydrogen evolves — but only so long as the battery is charged at a potential at which no more oxygen evolves than is consumed by diffusion and conversion at the negative electrode, otherwise the internal gas pressure will rise. Because of this, cells have a pressure relief valve that protects them from oxygen in the atmosphere. An accidental passage of air would, according to eqns. (1) and (2), result in sulphation and discharge of the negative plates.

Absorptive separation: the key element for recombination

The properties and performance of the AGM are extremely important in the functioning of VRLA batteries. The AGM consists of borosilicate glass fibres of short length and small diameter. No binding agent is added.

The AGM must serve as a separator to insulate the plates, i.e., the size of pores and the structure must be designed in such a way as to prevent short circuits and dendrite growths. This means that the material must be resistant to both sulphuric acid and oxidative attack. Furthermore, it must not release any substances into the system that will increase the gassing and self-discharge rates. Other requirements of the separator are: high overall porosity for a low internal resistance; good wettability; easy processibility; good compressive resistance against active-material particles during manufacture of batteries.

The absorptive material must also be able to absorb sufficient sulphuric acid when the battery is in use so that the required battery capacity can be achieved. Finally, the AGM must contain sufficient free pores, without electrolyte, to allow rapid transport of oxygen between the positive and negative plates.

Acid absorption is a key characteristic, i.e., the dependence of the maximum absorbed quantity of acid on the thickness of the separator at a given surface [12]. A further significant role is played by the capillary activity; this enables the required quantity of acid to be held above a certain separator height [13].

The electric resistance of AGM separators is much lower than that of traditional types [14]. Thus, a high voltage state can be expected at a high current load.

Design fundamentals of VRLAs using AGM separators

The design principles of VRLA cells using micro glass-fibre separators are compared in Fig. 1 with those of flooded cells.

In order to ensure that VRLA cells operate as maintenance-free units, it is necessary (as mentioned above) to hold the hydrogen overpotential at the highest possible level. This is normally achieved by using grids made from lead-calcium-tin alloys and by ensuring that the whole system is free from contaminants that influence the hydrogen overpotential, e.g., antimony.

For the recombination of oxygen, active lead must be available on the negative electrode. In addition, both the separator and the plates must have

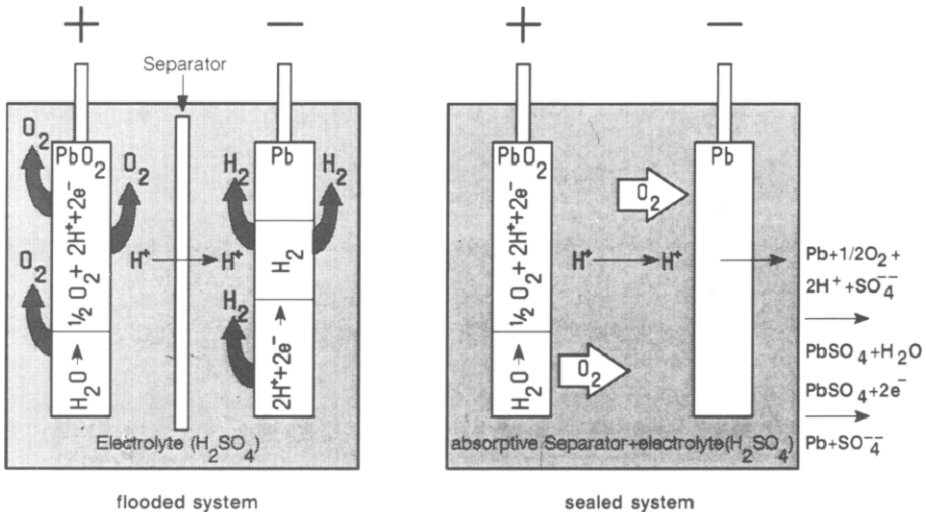


Fig. 1. Design principles of VRLA cells with micro glass-fibre separators, in comparison with flooded cells.

a free pore volume. It is also important that the separator is in good contact with the plates. The latter is achieved by compressing the separators slightly. This results in a good exchange of sulphuric acid. It also prevents gas bubbles from forming on the surface of the plates, and the occurrence of so-called 'dry areas'. The good contact between the positive plate and separator favours cycling performance by binding the positive active material to the grid structure, and thus preventing the sludging that is found in flooded cells. On the other hand, over-compression reduces the void volume of the separator and, thereby, lowers the performance of the batteries. Compression of the separator by more than 35% is generally considered to be excessive [14, 15], while less than 5% is too low. This means that the actual distance between the plates and the resulting separator thickness is generally between 70% and 90% of the initial thickness of the original separator material. Controlling plate thickness is a crucial factor in the manufacture of such batteries.

As the ability to recombine oxygen in a VRLA cell depends upon the electrolyte quantity in the cell [13, 14], it is important to know the amount of acid in both the separator and the cells. The electrolyte stored in the plates depends upon two factors, namely, the weight and the porosity of the active material. As a rule [15], for VRLA cells with AGM separation, about 10–11 cm³ sulphuric acid of sp.gr. 1.285–1.295 must be stored in the element per ampere-hour (*C*/20 rate) in order to achieve good performance and sufficient oxygen recombination. The latter depends mainly upon the filling ratio of the cell, the oxygen partial pressure, and the type of separator. Electrolyte concentration and separator compression exert little influence on the rate of oxygen recombination [15], but have a distinct effect upon electrical performance.

Results and discussion

Various batteries, using the container shown in Fig. 2, were designed and tested in accordance with present specifications and their expected application, viz., standby, starter and traction. Partial cycles with discharges up to 100% were conducted in order to determine the cycle performance. The findings for this design of the VRLA battery were then transferred to other battery sizes, and the manufactured batteries were tested using the same procedure.

Automotive battery testing

The test used above (Fig. 2) had specifications for a standard battery with ratings: 12 V, 36 A h (*C*/20), 175 A (Type 536 21). A high-current optimized battery with a flooded system and ratings 12 V, 40 A h, 220 A (Type 540 45) was also put in the same container. Testing of VRLA batteries was performed according to the standard DIN 43 539, Part 2 procedure for automotive batteries. The same test was also used for the flooded systems. The

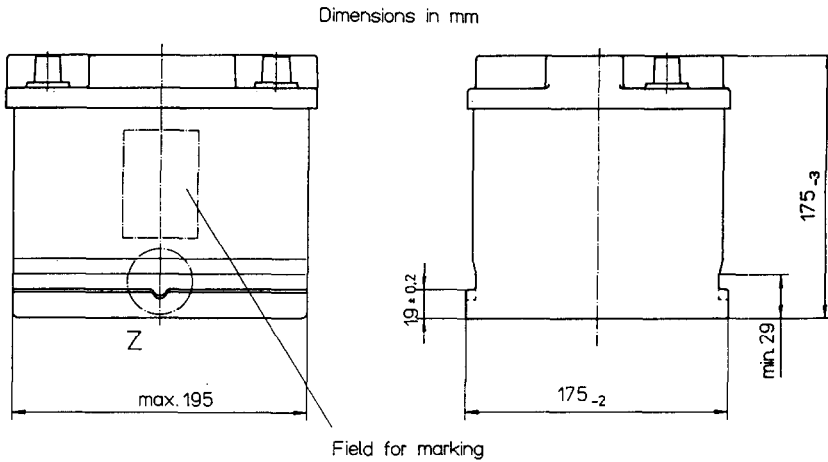


Fig. 2. Container for VRLA battery (12 V, 30 A h, VG 96 924, Part 12).

results of capacity, cold-cranking and charge acceptance tests are given in Fig. 3 and cycle-life data are presented in Fig. 4.

The findings show that VRLA systems can be used as automotive batteries and have performance characteristics that are superior in many respects to present standard batteries, DIN 72 311, Parts 13, 16, 18. Cold-cranking rates are equivalent to those of the high-current optimized batteries, in terms of 30-s voltage. This is brought about by the extremely low resistance of the glass-fibre separator. Furthermore, cycle-life data clearly show that the durability of the VRLA system is considerably greater than that previously found with standard automotive batteries. This is demonstrated by comparison with the results given in Table 1.

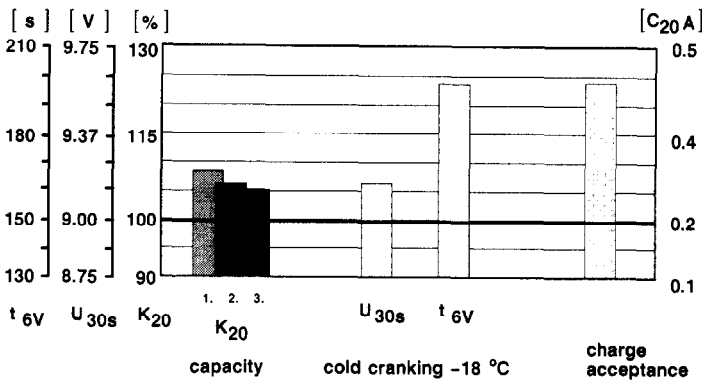


Fig. 3. Test results for automotive application with rated values 12 V, 40 A h (C/20), 220 A.

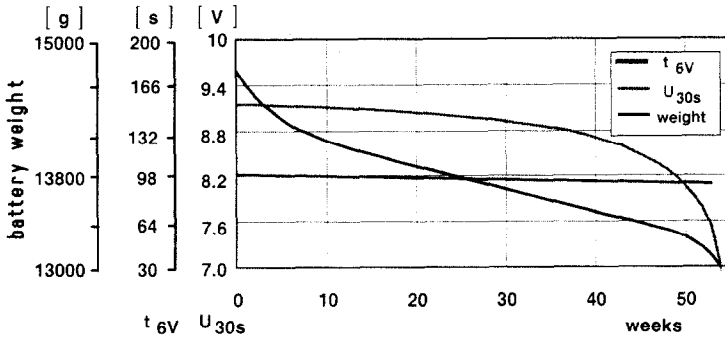


Fig. 4. Cycle-life according to DIN 43 539, Part 2 with rated values 12 V, 40 A h (C/20), 220 A.

TABLE 1

Comparison of cycle-life of standard, optimized, flooded battery and VRLA system

High-current optimized battery	Grid alloy (wt.%)		Separation	Maximum no. of cycles (weeks)
	Positive	Negative		
12 V, 36 A h, 175 A	Sb(2.5%)	Sb(2.5%)	cellulose	9
12 V, 40 A h, 220 A	Sb(2%)	Sb(2%)	pocket	16
12 V, 70 A h, 370 A	Sb(1.4%)	Pb-Ca	pocket + fleece	25
12 V, 40 A h, 220 A	Pb-Ca	Pb-Ca	absorptive	54

Because of the sealed design with oxygen recombination, the battery is maintenance-free with regard to water consumption. The value is $<0.35 \text{ g (A h)}^{-1}$ in the DIN overcharge test. Similar low values were also achieved during the DIN life test (Fig. 5).

Batteries for military applications

Two versions were made for military applications: a 12 V, 30 A h battery to the standard VG 96 924, Part 12 (battery container according to Fig. 2), and a 12 V, 100 A h battery to VG 96 924, Part 9. The performance of these batteries was examined in accordance with the specialized basic standard for VRLA batteries VG 96 924, Part 2 (Nov. 1985). The most important results are summarized in Figs. 6 to 10.

The results show that VRLA battery designs with AGM separators can be considered safe from deep-discharge. They can withstand a discharge for 28 days without damage through a resistance $R = U_N/I_5$. In addition, cycle-life at a discharge to a final voltage of 1.5 V/cell shows only a slight drop in capacity over a period of 250 cycles.

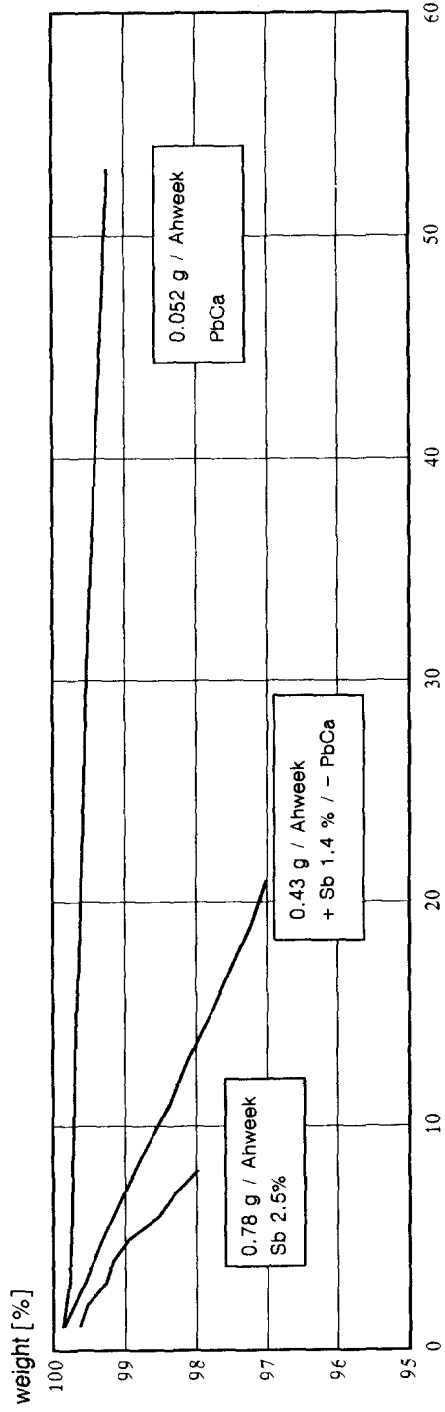
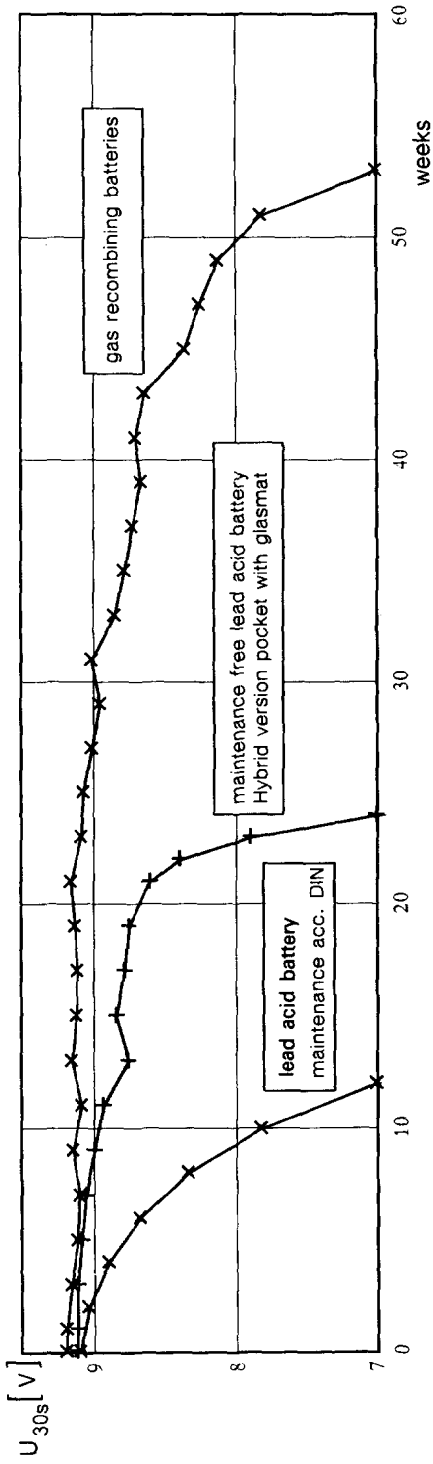


Fig. 5. Cycle-life according to DIN 43 539, Part 2 (comparison of various types).

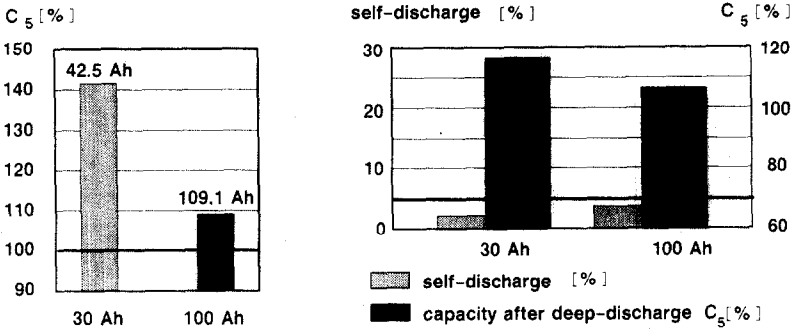


Fig. 6. Test results according to VG 96 924, Part 2: (a) p. 5.2.2 capacity, (b) p. 5.2.4 self-discharge and p. 5.2.8 deep-discharge.

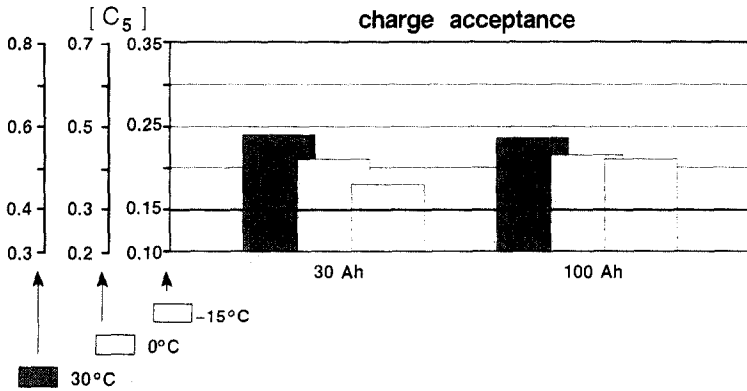


Fig. 7. Charge acceptance test results according to VG 96 924, Part 2, p. 5.2.7.

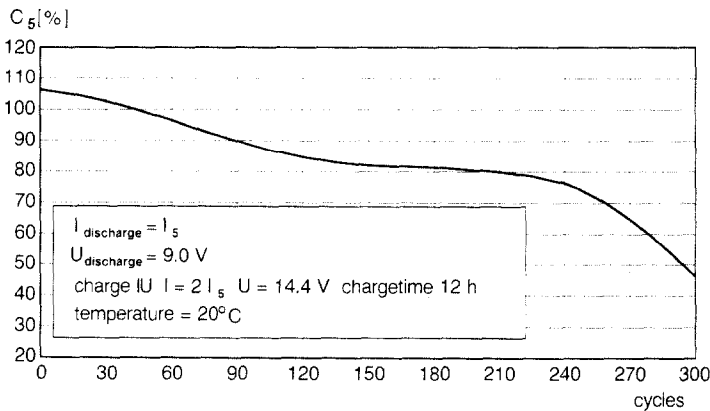


Fig. 8. Cycle-life according to VG 96 924, Part 2, p. 5.2.5.

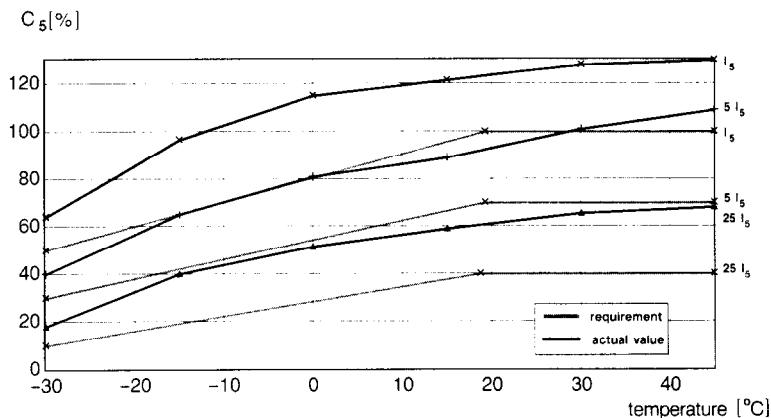


Fig. 9. Discharge test vs. temperature according to VG 96 924, Part 2, p. 5.2.3, for 30 A h battery.

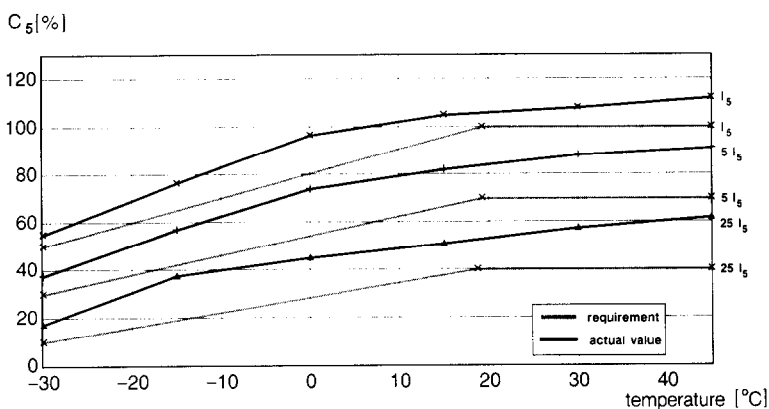


Fig. 10. Discharge test vs. temperature according to VG 96 924, Part 2, p. 5.2.3, for 100 A h battery.

Batteries for cycling applications and standby operation

Two versions were tested for these cycling and standby-power duties: one in a container of the type shown in Fig. 2 with a projected medium cycle-life, and one with a very high cycle-life, i.e., the HAGEN Drysafe® and the HAGEN Drysafe® compact. The former battery had a nominal capacity of 40 A h ($C/20$) or 38 A h ($C/5$) and was subjected to a cycle test under the following procedure at 27 to 30 °C: (i) discharge at $C/5$ up to a final discharge voltage 1.70 V/cell; (ii) charge with an IU-characteristic with $U = 2.4$ V/cell over 16 h. With this method, batteries could supply almost 100% of the rated capacity of 38 A h (Fig. 11) over a period of 300 cycles.

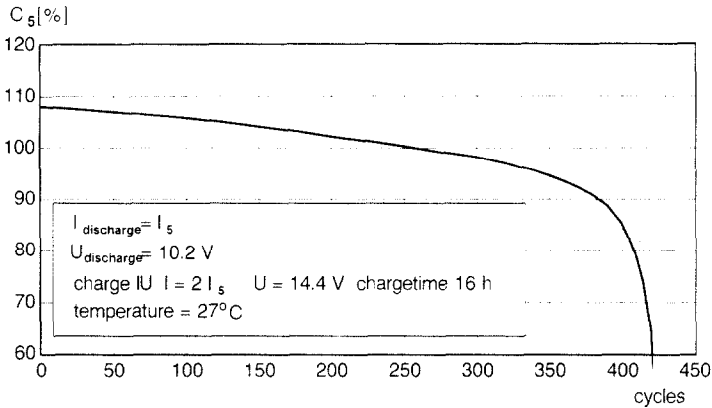


Fig. 11. Cycle-life of VRLA batteries with absorptive glass mat separator (type HAGEN drysafe®).

For the second battery (i.e., that with high cycle-life), the discharge was based on cycle tests for traction batteries, viz., (i) discharge 80% of the $C/5$ capacity at the $C/5$ rate; (ii) charge with IU-characteristic with $U = 2.4 \text{ V/cell}$ over 16 h at 30 °C. The results of the cycle test are given in Fig. 12.

In both cases, the projected cycle-life could be achieved. Due to a low water loss, both types of battery are suitable for stationary applications. In the event of overcharging at 2.4 V/cell for 160 h and 12 weekly units at 45 °C ambient temperature, the batteries showed a loss in weight of less than 0.3%.

These findings clearly demonstrate that VRLA batteries with electrolyte fixed in AGM separators can be used in deep-cycling applications.

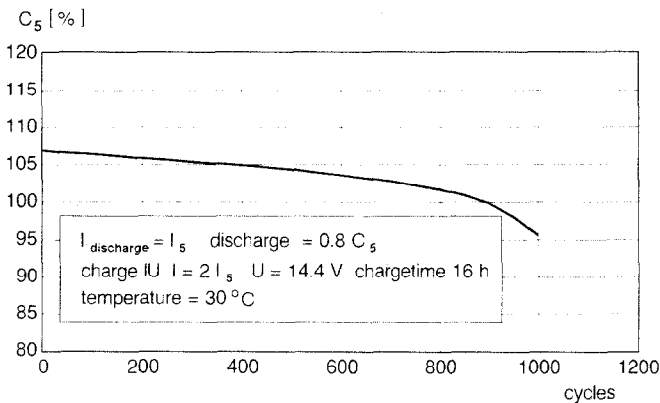


Fig. 12. Cycle-life of VRLA batteries with absorptive glass mat separator (type HAGEN drysafe® compact).

References

- 1 A. M. Hardman, *J. Power Sources*, 23 (1988) 127.
- 2 W. Sunu and B. W. Burrows, in J. Thompson (ed.) *Power Sources 8*, Academic Press, London, 1981 p. 601.
- 3 K. Peters, A. J. Harrison and W. H. Durant, in D. H. Collins (ed.), *Power Sources 2*, Pergamon, Oxford, 1968 p. 1.
- 4 A. J. Harrison, *Chem. Ind.*, (Mar. 17) (1986) 201.
- 5 B. K. Mahato, E. Y. Weissmann and E. C. Laird, *J. Electrochem. Soc.*, 121 (1974) 13.
- 6 J. Atkin, R. Bonnaterre and J. F. Laurent; in D. H. Collins (ed.), *Power Sources 6*, Academic Press, London, 1977, p. 91.
- 7 A. N. Fleming, J. A. Harrison and J. Thompson, in D. H. Collins (ed.), *Power Sources 5*, Academic Press, London, 1974, p. 1.
- 8 J. Thompson and S. Warrell, in J. Thompson (ed.), *Power Sources 9*, Academic Press, London, 1983, p. 97.
- 9 R. D. Armstrong and K. L. Bladen, *J. Appl. Electrochem.*, 7 (1977) 345.
- 10 E. A. Khomskaya, N. F. Gorbacheva and N. B. Tolochkov, *Sov. Electrochem.*, 16 (1980) 48.
- 11 E. A. Khomskaya, N. F. Gorbacheva, T. V. Arkhipova and N. F. Burdanova, *Sov. Electrochem.*, 21 (1985) 331.
- 12 *Chemical and Physical Properties of Absorptive Glass Mat (AGM)*, Evanite Battery Separator, Inc., Corvallis, OR, U.S.A.
- 13 B. Culpin and J. A. Hayman, in L. J. Pearce (ed.), *Power Sources 11*, Int. Power Sources Symp. Committee, Leatherhead, U.K., 1987, p. 45.
- 14 K. J. Wandzy and G. W. Taylor, *The Battery Man*, 28 (1986) 7, 16.
- 15 J. Badger, *IBMA 50th Convention, Chicago, IL, U.S.A., Oct. 27-29, 1987*.