HIGH-PERFORMANCE MAINTENANCE-FREE LEAD/ACID BATTERIES

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Introduction

The term 'maintenance-free' when applied to lead/acid batteries must be defined very clearly as the meaning differs for automotive, standby, and cycling batteries. This paper deals with stationary batteries of the gas-recombination type. These batteries are suitable for both standby and deep-cycling applications.

A problem in the development of gas-recombination batteries, both the gelled-electrolyte and glass-mat separator types, has been the inferior service life compared with conventional lead/acid batteries. Since a standby battery of the tubular type nowadays provides a service life of 1200 cycles or 15 years (whichever occurs first), this is the performance goal for the new generation of recombination batteries.

Design principles

The design of the recombination battery under discussion was based on flat, pasted plates for both the positive and negative electrodes. The design included optimization of both material flow during casting and electrical conductivity. The grids, for obvious reasons, were cast from antimony-free lead alloys using calcium as a hardening agent. While the negative grids were prepared by a simple gravity-casting process, a more sophisticated procedure was employed for making the positive grids.

Since grid quality is known to be critical to service life, production methods such as gravity casting, expanding, or punching were not considered to be suitable. Thus, die casting was chosen. This process offers high precision and a smooth grid surface with a fine-grain size. Unfortunately, grain-size refining agents, such as selenium for low-antimony grids, are not known for lead–calcium alloys.

The electrolyte can be immobilized either by the addition of silica (*i.e.*, gelled electrolyte) or by absorption in the micropores of a glass-fibre separator. Both methods are well known and were used for the first generation of

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sample batteries. The glass-fibre cells showed the following significant advantages:

(i) excellent recombination from the commissioning charge onwards;
(ii) lower sensitivity to final charging voltage;
(iii) better performance due to lower internal resistance;
(iv) no problems with deep-discharge service;
(v) in the event of charger malfunction whereby water is lost due to abusive overcharge, glass-fibre batteries can be "repaired" by adding water.

Taking these advantages into account the gelled-electrolyte batteries were clearly the second choice, despite the high price of the glass mats.

The new generation must meet the dimensions for stationary batteries according to DIN 40 739, at least for the German market. The reinforcement of the container walls reduces the internal dimensions. Monoblocs of 6 V/18 A h and 4 V/32 A h are available. Intercell connection is made through the partition wall as in automotive batteries. A fully leak-proof design was already available since the terminals also suited the requirements of internal overpressure.

Cell performance

The maintenance-free type of industrial lead/acid battery must be shipped with electrolyte in a charged condition. Thus, shelf life is an important property and depends mainly on the storage temperature. Assuming that a residual capacity of 70% is sufficient for most installations, the minimum storage times at various temperatures are as in Table 1. As expected, the rate of self discharge follows the Arrhenius law.

Many battery applications require a constant-power supply rather than a constant current. This is often used to characterize the performance. Figure 1 shows a typical constant-power diagram for a section of a cell comprising one pair of positive and negative plates. For a minimum voltage level of 15% less than nominal, *i.e.*, cell voltage = 1.70 V, the available energy from the 18 A h plate is 19 W h and 23.5 W h for the 30 min and 1 h rates, respectively. These values correspond to 51% and 63%, respectively, of the energy at the

TABLE 1

Storage conditions and shelf life for type OGi 75-DC batteries

Storage temperature (°C)	Shelf life (months)
10	24
20	12
30	6
40	3

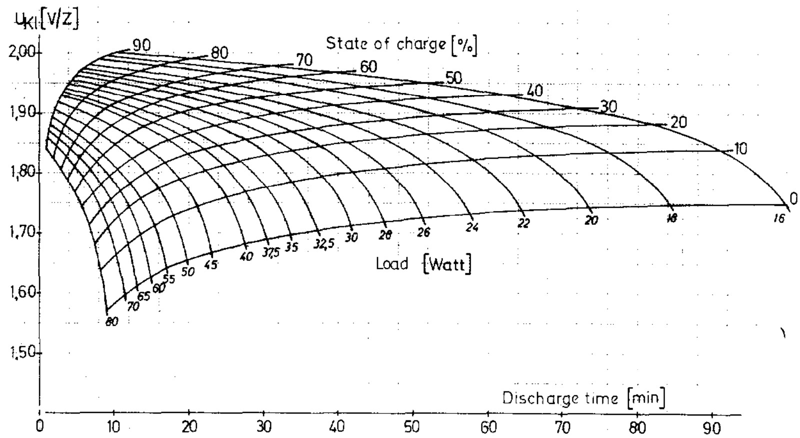

Fig. 1. Constant-power performance for type OGi 20 sealed lead/acid battery at 20 °C.

standard 10 h rate (37.3 W h). Comparative data for wet batteries in the same container are 41% and 51% for the 30 min and 1 h rates, respectively. The superior performance of the glass-mat type is due to the oversizing of the grid in both the positive and the negative plates and to the diagonal design for the main current leads: a principle well known from automotive battery manufacture.

Recharge time is also a very important feature, especially for UPS and similar emergency power supply systems. This parameter should be defined as the time required to regain full performance. Due to diffusion effects, this time is not identical with the time for full recharge, as only 100% of the discharged current must be charged back. The time for full recharge depends on the actual discharge (in terms of % nominal capacity), the available maximum current, and the boost-charge voltage. Typical behaviour for a maximum voltage of 2.40 V/cell is given in Fig. 2. It can be seen that for full discharge at the 1 h rate (~60% of the 10 h capacity), the required charge time is 3 h and 6 h for charge currents of 3 I_{10} and I_{10}, respectively.

Service life

Standby applications

Recombination batteries require a higher float voltage than conventional types in order to maintain the capacity at the maximum level. For example, the new cells should be operated at 2.27 V at 20 °C, while standard cells require only 2.23 V. Nevertheless, the float currents are significantly lower, *i.e.*, 10 mA, compared with 15 - 20 mA for low-antimony batteries, per 100 A h capacity.

Because of obvious time constraints, actual life tests cannot be conducted. Thus, comparative corrosion studies were carried out using grids and

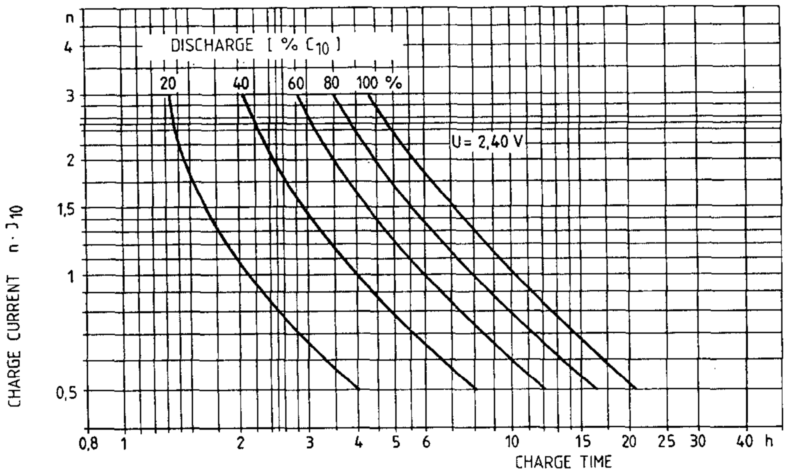

Fig. 2. Charge time *vs.* charge current for sealed lead/acid battery. Tapered charge at 2.4 V/cell; charge = 100% discharge.

full plates made from conventional materials (where the service life is well known) as a reference. Results from accelerated life tests were also taken into account. From these studies, the expected service life of the recombination cells is 10 - 12 years and 5 - 6 years at 20 °C and 40 °C, respectively.

Cycling applications

Pasted positive plates are not popular in Europe for traction-battery design; tubular plates are preferred. Thus, for cycle-life testing under deep-discharge conditions, it was inappropriate to rely upon accelerated tests (*e.g.*, with elevated temperature) but on data based on normal operating conditions only.

Thirty cells in series were subjected to a cycle-life test. Only one cycle per day could be accomplished. This involved a discharge for 4 h at the 5 h rate (*i.e.*, 80% depth-of-discharge) followed by a charge for 16 h. Intensive charging was essential in order to maintain the actual capacity at a high level. Nevertheless, the studies showed that a charge time of 10 h was sufficient. Capacity tests were conducted at the 5 h rate after successive periods of 100 cycles. The results, shown in Fig. 3, represent technology that is already three years old, as 1000 cycles have been completed to date.

It is believed that the batteries yielding the data of Fig. 3 are nearing end of life. The slight decline in the 1 h capacity indicates heavy grid corrosion, as the behaviour is common to almost all of the 30 cells. It should be noted that the nominal capacity at the beginning of the tests was 12.5 A h per plate. This was set by the grid moulds that were then available. Nowadays, 18 A h is achievable with the same containers because the plates are taller and make use of the sludge and gassing space that is required by traditional batteries.

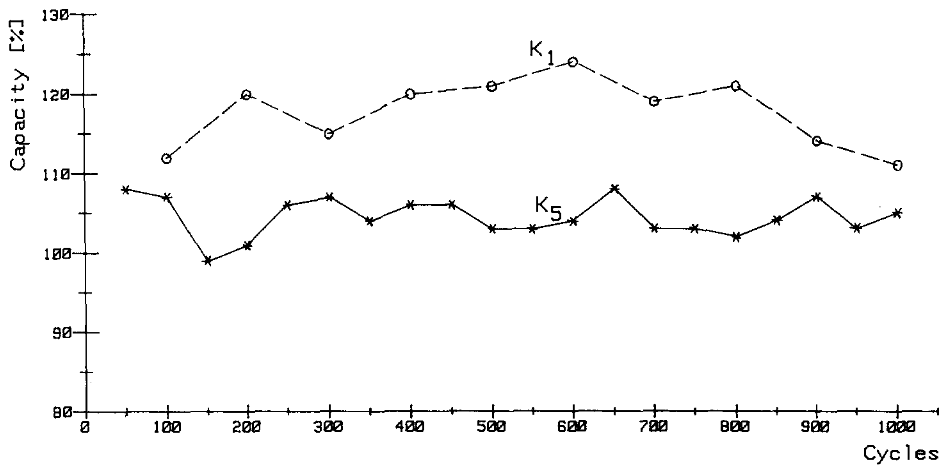

Fig. 3. Service life of type 6 OGi 75-DC sealed lead/acid battery (cycling to 80% depth-of-discharge). $K_1 = 1$ h capacity; $K_5 = 5$ h capacity.

Recombination rate

As mentioned above, intensive charging is required to maintain the working capacity close to the optimum value. Thus, near the end of charging, the voltage was allowed to rise beyond the limit of 2.40 V/cell. The ratio between charge and discharge, in ampere hours, was adjusted to 1.165.

The weight loss was determined after 250 cycles; a typical value was 9.5 g per 6 V module. This is equivalent to 9.4 A h of water electrolysis per cell. With discharge of 55 A h, the total overcharge is:

$$55 \times 0.165 \times 250 = 2269 \text{ A h} \quad (1)$$

This results in a recombination efficiency, *E*, of:

$$E = 1 - 9.4/2269 = 0.996 \quad (2)$$

The achieved efficiency demonstrates that there is no danger of the cells drying out, even with the higher final charging voltage.

TABLE 2

Water loss and recombination efficiencies during float tests for 18 months with type 6 OGi 75-DC batteries

Temperature (°C)	Float voltage (V/cell)	Water loss (g/cell)	Charge (A h)	Recombination efficiency
30	2.40	18.3	5628	0.989
30	2.50	33.7	10466	0.990
40	2.25	5.0	441	0.966
40	2.40	11.0	7807	0.996

Similar measurements were made during float tests at elevated temperatures. From the data of Table 2, it can be seen that there is wide variation in both the total charge and the water loss between cells. The results represent the overall data from a test period of 18 months and show that water loss should not limit the service life. Except at 40 °C and 2.25 V, the recombination rate is high and is significantly improved by increasing the voltage. This is in full agreement with the findings of the cycling tests.

Conclusions

The studies reported here show that, with appropriate design and manufacturing procedures, maintenance-free (or sealed) lead/acid batteries can be produced commercially at a reasonable cost. The performance and service life of these batteries compare favourably with those of traditional batteries with liquid electrolyte.

The service life of maintenance-free batteries now meets that of the system. This has been a major goal. The space requirements of the batteries are smaller compared with those of traditional batteries. The new batteries are also suitable for applications such as solar energy storage because of the good cycling capability and the high gas-recombination rate, even at high ambient temperatures.