Journal of Power Sources, 23 (1988) 143 - 155

SEALED MAINTENANCE-FREE LEAD/ACID BATTERIES: PROPERTIES AND APPLICATION OF A NEW BATTERY GENERATION

H. TUPHORN

Accumulatorenfabrik Sonnenschein Batterie GmbH, Thiergarten, D-6470 Büdingen (F.R.G.)

Introduction

Over the past 10 years, the need for maintenance-free systems in lead/acid battery technology has become more and more evident — not only to reduce high labour costs (particularly in European countries), but also for service in areas with little or no infrastructure.

When discussing maintenance-free batteries, it is necessary to define first the term 'maintenance'. For automotive batteries, maintenance-free refers to a system with electrodes containing low, or no, antimony in the grid alloy. These batteries experience little loss of water during their life and thus normally do not require periodic "topping up". However, the batteries suffer from serious performance limitations when subjected to deep-discharge cycling regimes.

In addition to the periodic control and adjustment of electrolyte level by water addition, battery maintenance involves: (i) periodic recharging after extended storage because of self discharge; (ii) charging of the battery immediately after discharge; (iii) avoidance of overcharge because of antimony poisoning; (iv) avoidance of deep-discharge conditions.

While water addition and items (i) and (iii) are controlled directly by the antimony content, items (ii) and (iv) are also valid for lead/acid batteries of conventional construction.

The electrode reactions in lead/acid cells during charging are:
positive electrode:

$$PbSO_4 + 2H_2O \longrightarrow PbO_2 + H_2SO_4 + 2H^+ + 2e^- \qquad (1)$$

$$H_2O \longrightarrow 2H^+ + \tfrac{1}{2}O_2 + 2e^- \qquad (2)$$

negative electrode:

$$PbSO_4 + 2H^+ + 2e^- \longrightarrow Pb + H_2SO_4 \qquad (3)$$

$$2H^+ + 2e^- \longrightarrow H_2 \qquad (4)$$

During charging, the water decomposition reactions (2) and (4) are in direct competition with reactions (1) and (3) of the active masses. The rate of the parasitic reaction (4) is controlled by the amount of antimony in the grid

0378-7753/88/$3.50

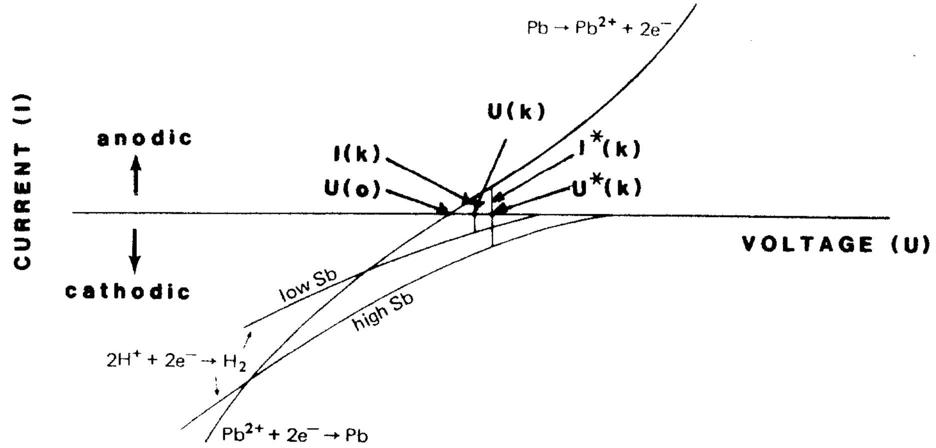

Fig. 1. Influence of H_2 overpotential on self-discharge of negative plates in lead/acid batteries.

alloy. As is shown schematically in Fig. 1, the H_2 overpotential at a lead electrode increases with decreasing antimony concentration, so that the amount of H_2 evolved at the negative electrode correspondingly decreases. In addition, a reduction in the antimony content shifts the equilibrium potential, U(k), of the lead-oxidation and proton-reduction reactions to more negative values. As a result, the corrosion current, I(k), which controls the rate of self-discharge of the electrode, becomes smaller. This is the underlying reason for the very low self-discharge rate of antimony-free batteries (see below).

Figure 2 shows the influence of antimony on the charging characteristic of lead/acid cells under a constant-current regime. Because of the higher H_2

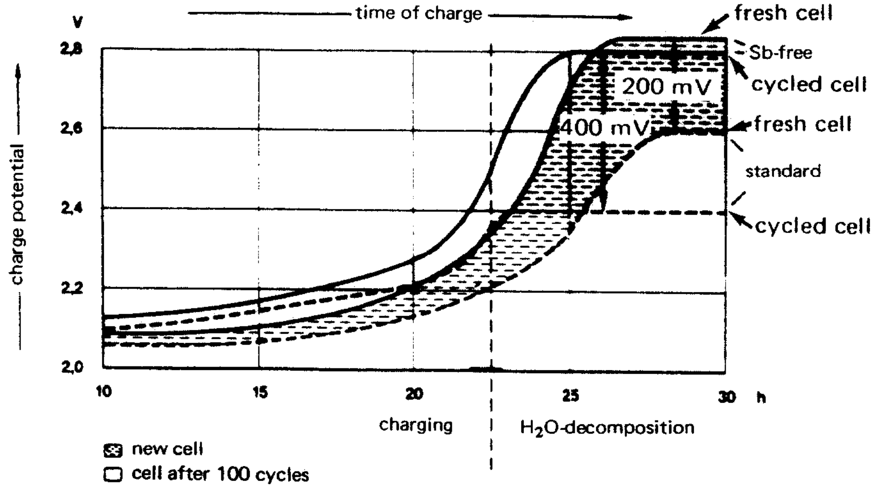

Fig. 2. Influence of antimony on recharge characteristics of lead/acid cells (constant-current charging).

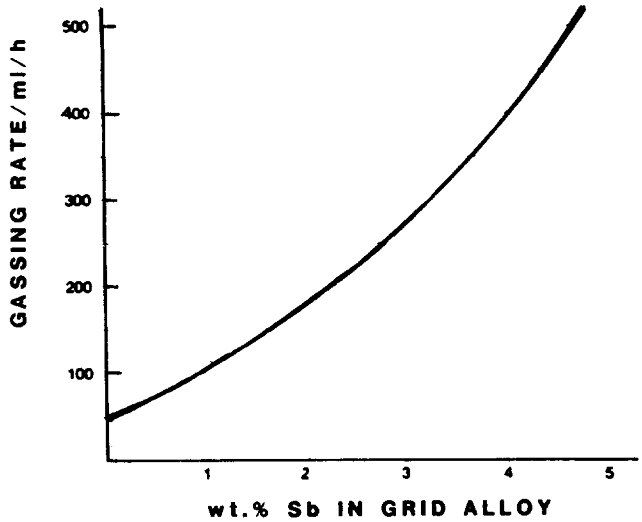

Fig. 3. Influence of grid antimony content on electrolyte decomposition.

overpotential, the water decomposition voltage of antimony-free cells is approximately 250 mV higher than that of standard antimonial cells. By virtue of the antimony-poisoning effect, this difference in voltage becomes greater with cycling, *i.e.*, 400 mV in Fig. 2. Given that charging of batteries without water decomposition has to be carried out at a voltage that is higher than that of the reactions of the active masses, but below that of water decomposition, it is evident that maintenance-free batteries require antimony-free alloys with a marked difference between these two voltage limits.

In a test on automotive batteries, it was found that reduction in the antimony content from 4.5 to 0 wt.% resulted in an approximate 10% decrease in the gassing rate (Fig. 3).

On the other hand, the cycle-life of batteries is enhanced by the presence of antimony. This is the reason for using high antimony-concentrations in conventional traction cells, namely, 6 - 8 wt.% Sb. The data of Fig. 4 show that battery cycle-life is markedly decreased by the elimination of antimony. This is known as the 'antimony-free' effect, and has been the subject of numerous and extensive fundamental investigations. The basic cause of the effect is considered to be the development of a passivating 'barrier' layer of lead sulphate at the grid/active-material interface in positive plates.

Sealed batteries: general properties

The first type of sealed lead/acid battery — the gelled-electrolyte system — was developed thirty years ago by Sonnenschein in the F.R.G.

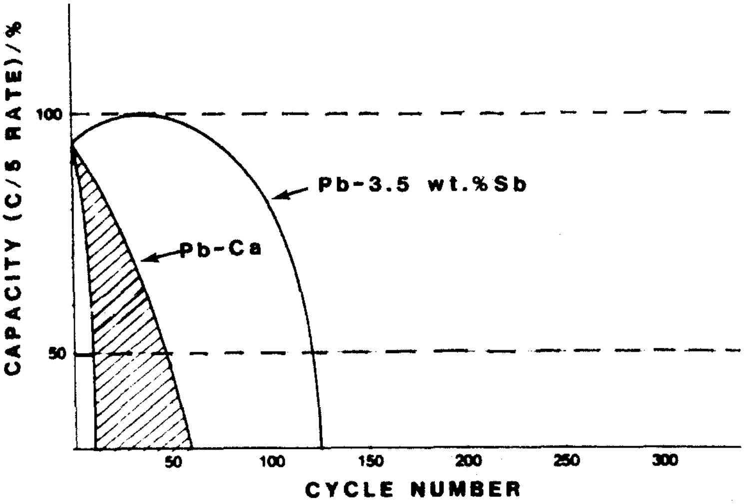

Fig. 4. Cycle life of lead/acid batteries with differing grid alloys.

Today, it is well known as the 'Dryfit System'. More recently, sealed maintenance-free systems have attracted considerable attention with the introduction of larger units in new and more diverse applications.

In general, sealed systems can be distinguished from conventional lead/acid batteries by the following criteria: (i) the use of non-liquid electrolytes, either by gelling or by adsorption in porous materials; (ii) the introduction of low-antimony or antimony-free grid alloys; (iii) the replacement of vent caps by pressure-release valves.

The information in Fig. 5, which is valid for batteries with a flat-plate construction, demonstrates that the cycle life of Dryfit batteries is about twice that of standard automotive types, even though the former do not contain antimony. The high cycle life is achieved by the use of phosphate stabilizers in the gelled electrolyte; these react favourably with the positive mass during charging. Because of the above-mentioned high H_2 overpotential on antimony-free electrodes, the self-discharge rate of Dryfit batteries is very low. While conventional batteries lose ~50% of capacity after ~3 months of storage, even after 2 years of storage Dryfit batteries deliver more than 50% of their initial capacity (see Fig. 6.).

In general, sealed batteries have to be charged at constant voltage with a value that has to be higher than the mass-reaction voltage and lower than the water-decomposition voltage. The optimum charging voltage at room temperature is 2.3 V/cell. It can be seen from Fig. 7 that if a battery is charged with unlimited current, 80% of the capacity is replaced within about 3 h, while the last 10% requires more than 10 h of charging time. The high voltage step between the charging and overcharging reaction of antimony-free lead/acid batteries is an important advantage of this system.

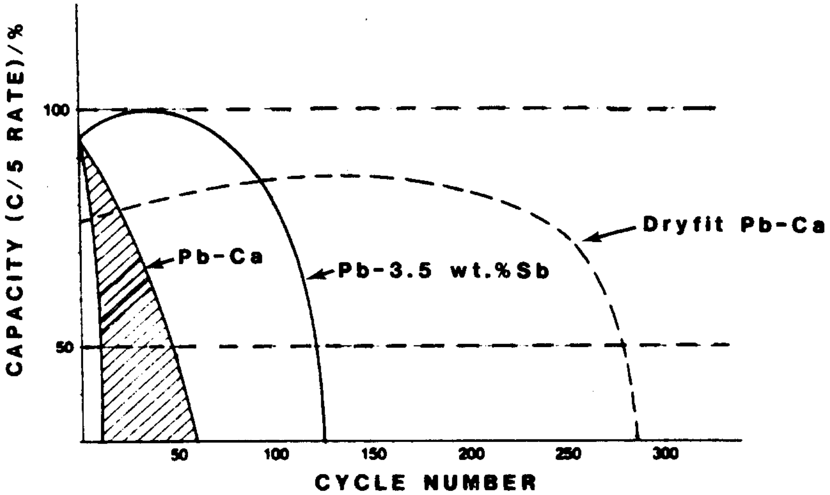

Fig. 5. Cycle life of Dryfit (gelled) batteries compared with that of flooded batteries.

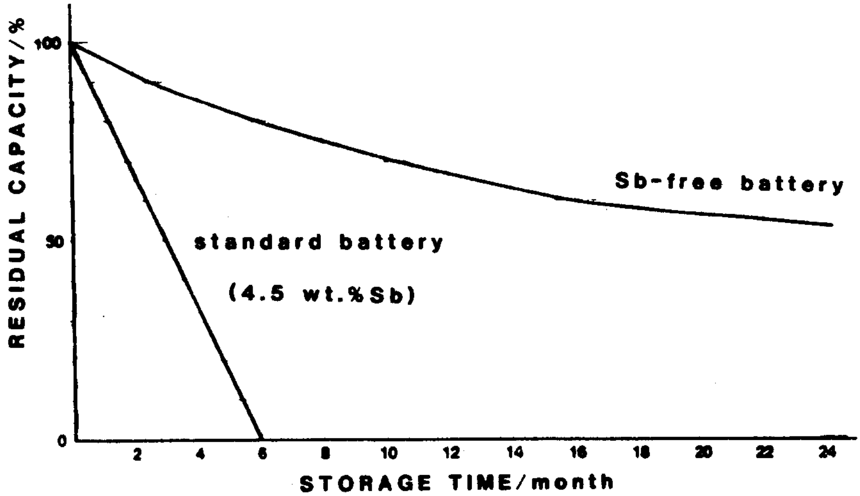

Fig. 6. Self-discharge of lead/acid batteries at 20 °C.

Because of this large difference in voltage, the charging current is self-regulated by the state-of-charge, which controls the cell voltage. So chargers for this type of battery do not require special current-regulating systems.

The gelled structure of the electrolyte provides Dryfit batteries with a good deep-discharge capability. Even after connecting the positive with the negative terminal for 4 weeks, Dryfit batteries are not damaged and can be recharged within 15 h at a normal charging voltage.

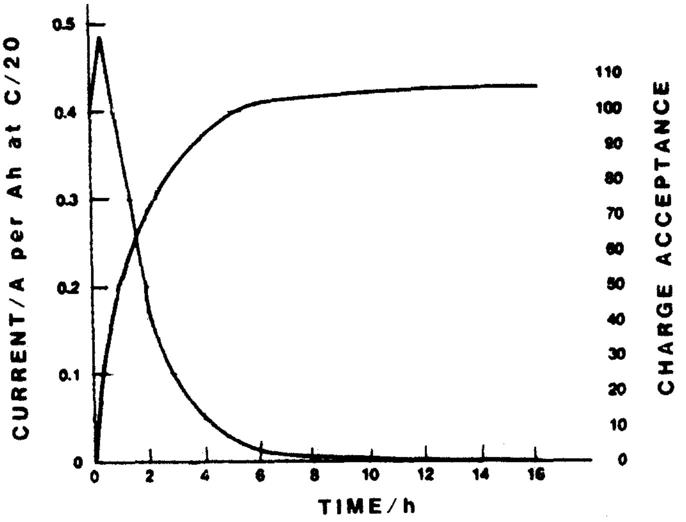

Fig. 7. Charging characteristic of Dryfit batteries. Charging voltage = 2.3 V/cell after discharge at $C/20$ rate.

Small Dryfit batteries

The first Dryfit batteries were developed about 30 years ago and are still produced in an optimized flat-plate construction with sizes between 1 and 36 A h. The Dryfit A200 type contains phosphoric acid and is especially designed for long cycle-life (*i.e.*, at least 250 full cycles). These batteries are used for various applications such as: type recorders, portable video recorders, portable television sets, electronic flash-lights, etc. In more recent times, float applications have become significant. Today, more than 50% of the batteries in these sizes are used for un-interruptible power supplies (UPS), data back-up, emergency lighting, and alarm equipment.

The float life of A200 batteries is approximately 4 years at normal temperatures. Battery aging is influenced by temperature and can be represented by the law of van't Hoff. The data in Fig. 8 indicate that up to 50 °C, the rate of ageing is doubled by each 10 °C increase in temperature. The stronger influence of temperature above 50 °C suggests that there is a change in the life-limiting reaction at this value.

The maintenance-free operation, high cycle-life and good cycling capability have, together, been responsible for gelled technology being introduced into military applications. Because most tank batteries have been destroyed not by cycling, but during standing through deep discharge by the electronic system, the deep-discharge capability of the gelled system is an important advantage in such applications. Today, the tanks of the German army are fully equipped with Dryfit batteries, type 6TN (12 V/100 A h).

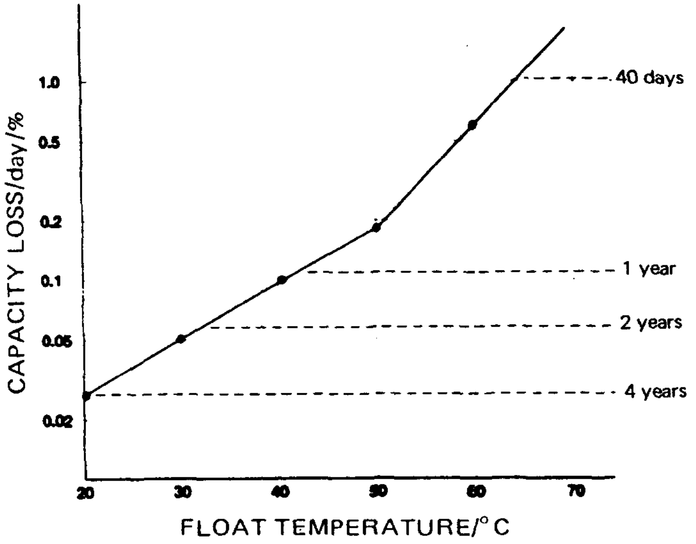

Fig. 8. Influence of temperature on float life of A200 Dryfit batteries with flat plates.

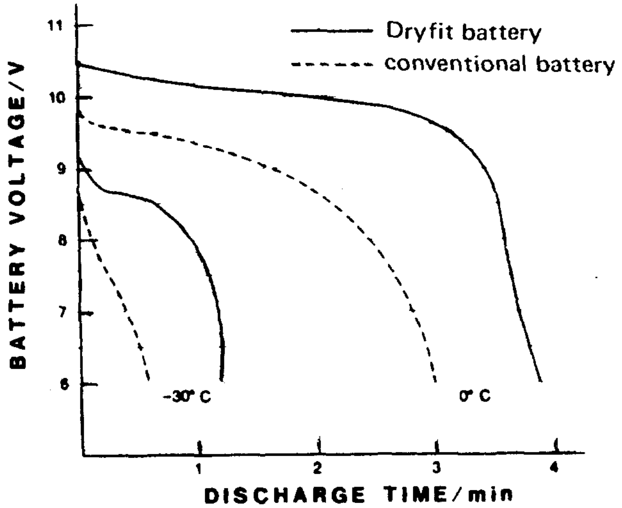

Fig. 9. Performance of conventional and Dryfit batteries under 100 × C/20 discharge at different temperatures.

Compared with conventional batteries, the voltage of 6TN batteries, especially at low temperatures and high rates, is significantly superior to that of flooded types (see Fig. 9). The gassing rate of 6TN batteries is less than 10% of that of flooded types and becomes comparatively smaller during service life due to an increase in O_2 recombination (Fig. 10).

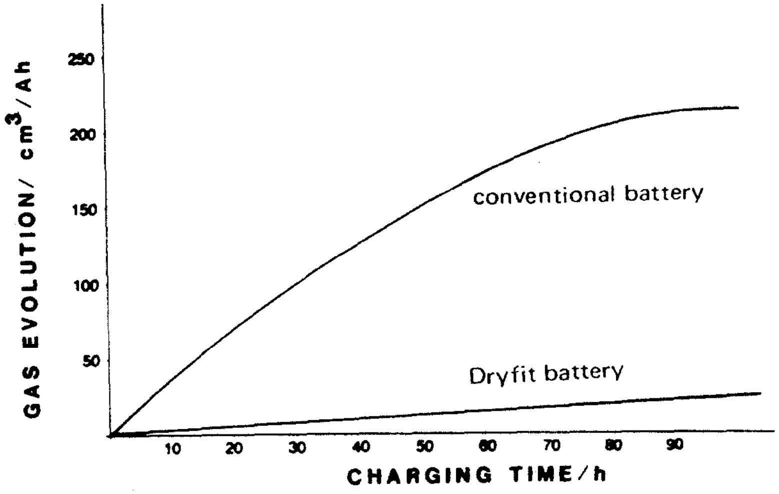

Fig. 10. Gas evolution in conventional and Dryfit batteries during charging at 2.3 V/cell at 20 °C.

Dryfit industrial batteries

A well-known problem with maintenance-free flooded batteries, especially with large sizes, is the phenomenon of electrolyte stratification (Fig. 11).

Because charging is conducted below the water decomposition voltage, the electrolyte does not become agitated. Thus, the sulphuric acid produced during charging accumulates at the bottom of the cell because of its higher gravity compared with that of the free electrolyte. After a few cycles, the concentration of acid at the bottom can be twice that in the upper regions (Fig. 11). This affects battery life by increasing both grid corrosion and sulphation, especially in the lower parts of the plates. Recently, sophisticated cells with electrolyte pumps have been developed to combat this problem.

Sonnenschein A600-type stationary cells have positive tubular plates and gelled electrolyte. Their properties are identical to the Dryfit system in respect of the lead alloy and the basic construction. As Fig. 12 indicates, the gelled structure prevents stratification of the sulphuric acid, so that UPSs fitted with these are not affected by the phenomenon. The life of A600 batteries is limited by the performance of the tubular plates and is thus equivalent to conventional tubular batteries.

As shown in Fig. 13, the life of A600 batteries is not controlled by water loss. The latter decreases during service via a logarithmic function (Fig. 14):

$$W = t^{-0.72} + C \qquad (5)$$

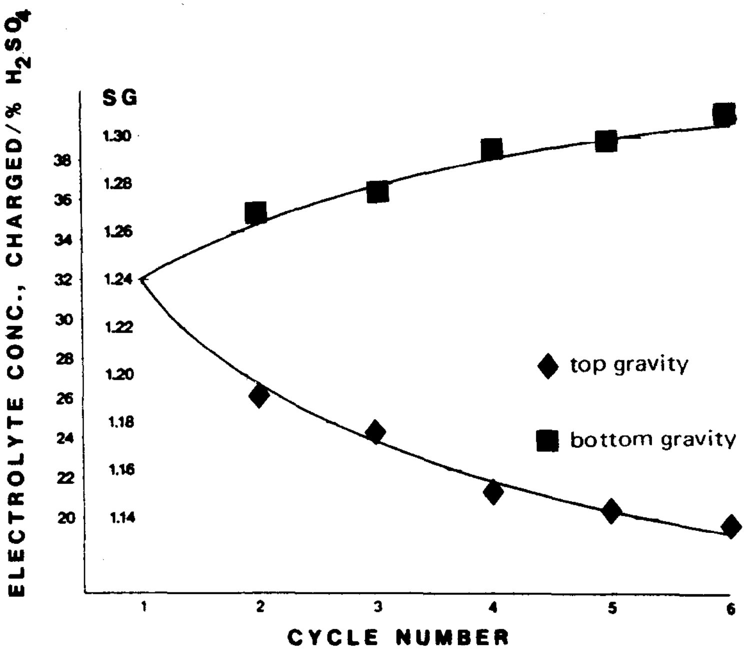

Fig. 11. Electrolyte stratification in a Type 50 PzS350 UPS battery. Charging voltage = 2.3 V/cell; discharge at *C*/10.

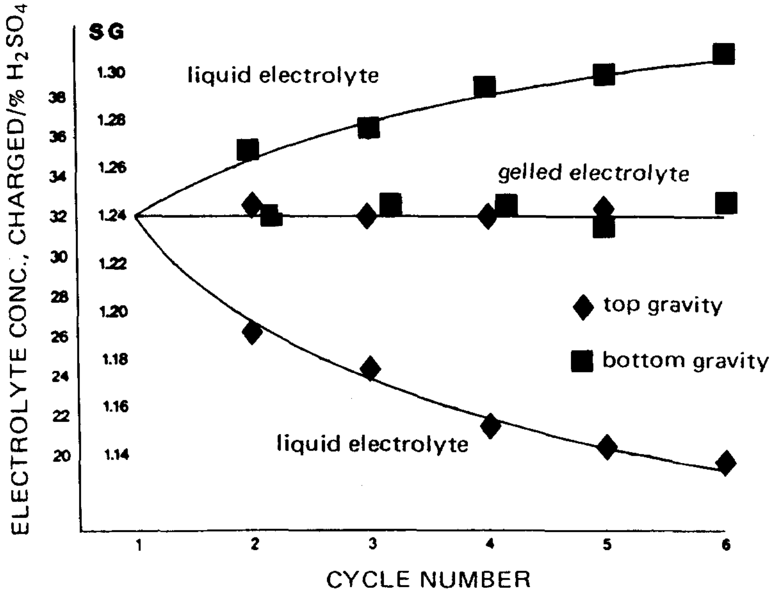

Fig. 12. Comparison of electrolyte stratification in Type 50 PzS350 and gelled batteries. Charging voltage = 2.3 V/cell; discharge at *C*/10.

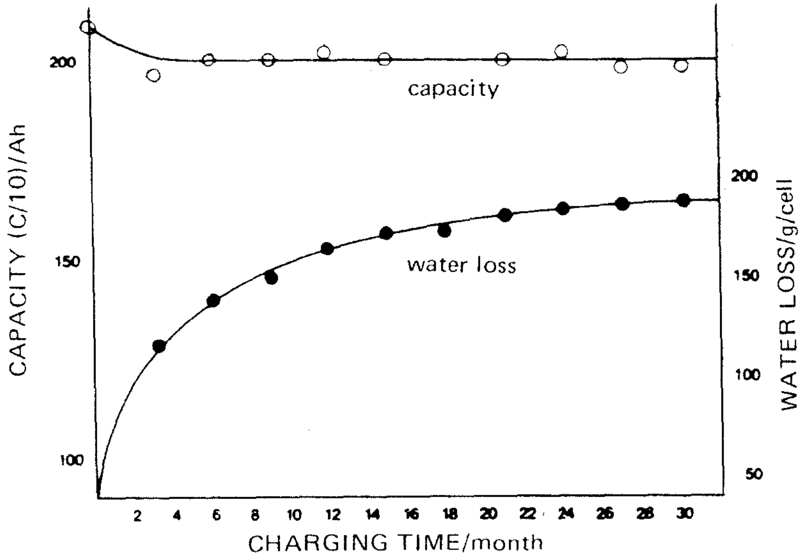

Fig. 13. Float test of Dryfit A600 battery (Type 4/180). Float voltage 2.23 V/cell; charging at $C/10$ to 2.4 V/cell.

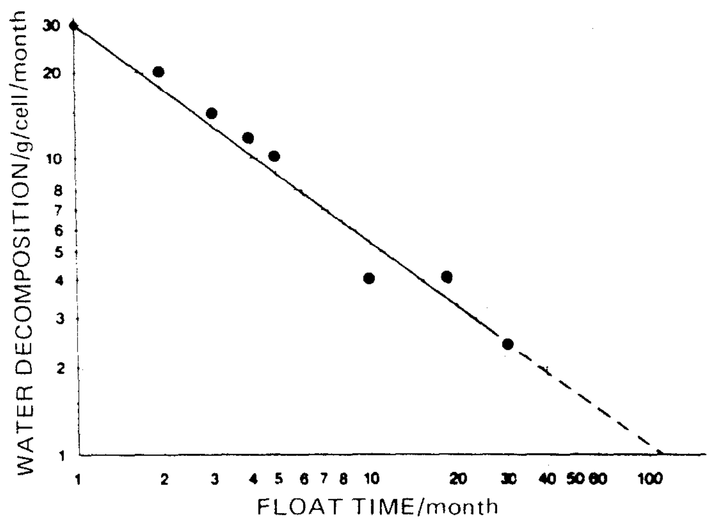

Fig. 14. Water decomposition in a Dryfit A600 battery (type 4/180) during float charge at 2.23 V/cell.

where: W = water loss (g × cell^{-1} × month^{-1}); t = float time (month); c = constant of construction.

The decrease in water decomposition is due to a curing effect of the gel during service which results in the formation of cracks. An increase in the number of cracks accelerates the oxygen transport from the positive to the negative electrode. Here the reduction of oxygen to water takes place instead

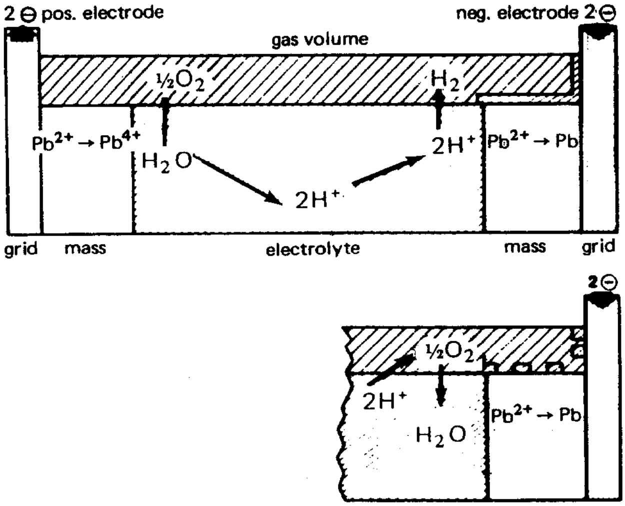

Fig. 15. Oxygen recombination: electrode reactions of sealed lead/acid cells during overcharging.

of the evolution of hydrogen because of the lower reaction energy of the former process. The mechanism is explained in Fig. 15.

A600 batteries are produced in sizes and capacities of DIN 40736 P.1 up to cells of 1500 A h and are used in UPS emergency power supplies (*e.g.*, in public buildings like the Rhein–Main Airport), as power supplies in ships (*e.g.*, in the MS Europa luxury liner), as well as in hospitals. The batteries can be assembled horizontally in racks; this saves space and provides easy access for monitoring single-cell voltages.

The Dryfit block battery (with flat plates) was developed for stand-by application with high discharge rates. These batteries are produced in sizes between 6 V, 20 A h and 4 V, 200 A h, and are designed for a life of more than 10 years without any maintenance.

The A800 Dryfit battery is the first fully maintenance-free traction battery that does not contain any antimony in the grid alloys. These cells have positive tubular plates and are produced in the designs and capacities described in DIN 43567 P.2. The batteries have to be charged with controlled voltage by an IUI-Management. The charger, provided with the system, controls the state-of-discharge, which, in turn, influences the total amount of charging energy. One of the first batteries to be produced has been used at the railway station at Augsburg, F.R.G., for 7 years with a capacity loss of only 20% during this time (Fig. 16). A major advantage of this system is that no special room for maintenance is required. The sealed traction system is also in use in ground-support vehicles at Frankfurt airport. During breaks, the vehicles are recharged at outside stations; these are installed near the terminals. This concept saves the time involved in driving to the special charging and maintenance stations and has worked successfully for over a year.

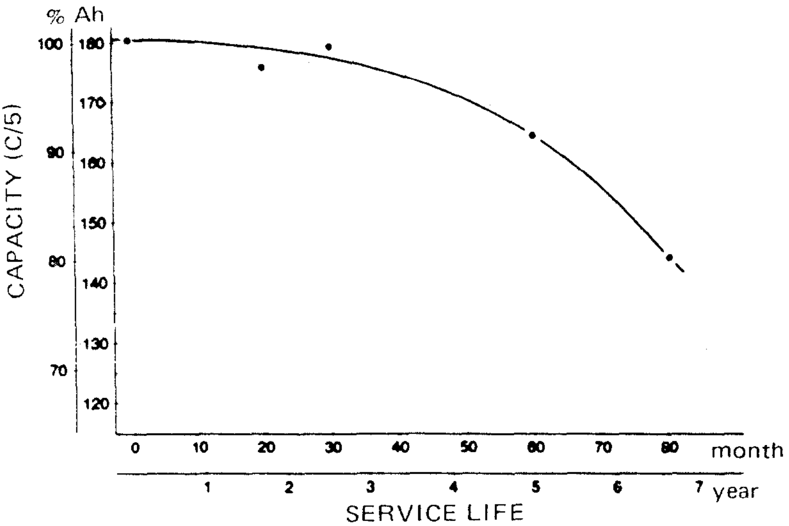

Fig. 16. Service life of an A800 Dryfit traction battery (80 V, 4PzS 180) in operation at Deutsche Bundesbahn in Augsburg, F.R.G.

Miscellaneous

Single cells in sealed lead/acid batteries exhibit a larger voltage distribution during float charging than do flooded types (Fig. 17). This problem is

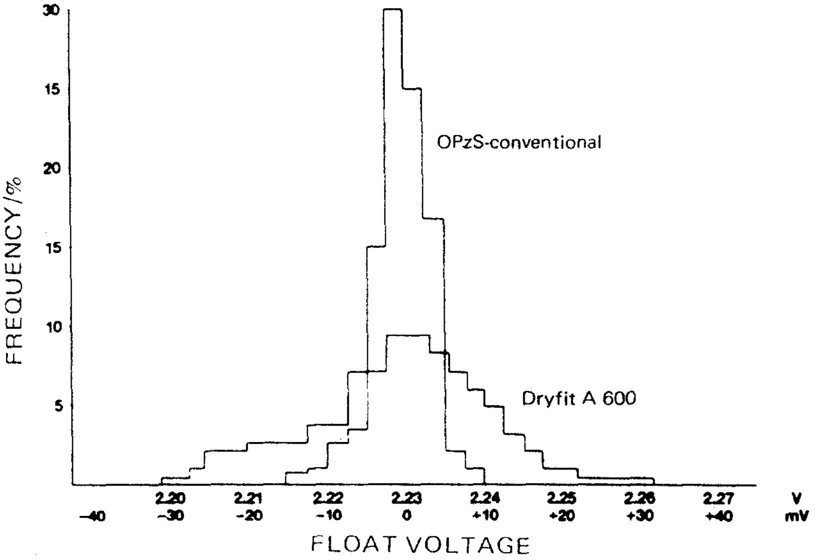

Fig. 17. Distribution of cell voltages during float charging at 2.23 V/cell; 370 V UPS batteries.

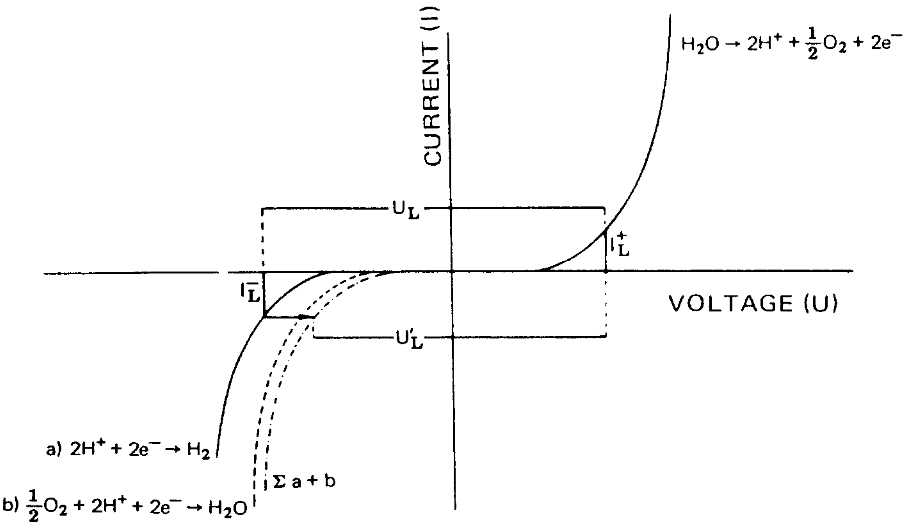

Fig. 18. Influence of O_2-recombination on float voltage.

an inherent feature of the sealed system and does not indicate failure of the individual cells. Whilst voltage variations exhibited by conventional batteries normally indicate antimony-poisoning effects at the negative plates, the cause of the distribution in sealed cells is the competition between two cathodic overcharge reactions, namely, the reduction of protons and of oxygen. As Fig. 18 demonstrates, the negative electrode becomes depolarized by oxygen. Because of the aging effect of the electrolyte during battery service, the oxygen recombination increases in the cells with primarily low recombination and thus the cell voltages tend to equalize.

Conclusions

This paper has reviewed the performance of Dryfit gelled-electrolyte lead/acid batteries. It has been shown that these batteries:

- do not need electrolyte adjustment
- need no periodic recharge during storage because of the low self-discharge rate
- need not be immediately recharged after discharge
- are not destroyed by deep discharge
- do not have an antimony-poisoning effect
- have extremely low gas evolution during charge
- have high float- and cycle-life
- have high voltage stability at low temperatures and high rates
- can be stored and used in any position
- are free from pollution problems
- are supplied in a filled and charged condition.