Valve-regulated lead/acid batteries: systems, properties and applications

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Abstract

The first types of small gel-batteries were first produced over 35 years ago. Today, however, two technologies for valve-regulated lead/acid batteries are used. The special properties of gelled-electrolyte and absorptive glass mat systems are compared in this work. Gel-batteries are presently made in sizes up to 3000 Ah. In addition to stationary applications for emergency power supplies, these batteries are used in cycle applications. The advantages and limitations of gelled-electrolyte batteries in new applications are discussed.

Introduction

The lead/acid battery is the oldest existing battery system. It was discovered about 130 years ago and has been used for energy storage for over 100 years. The specific energy of lead/acid batteries is 35 Wh kg^{-1}. This value is rather low in comparison with other systems. That, in spite of this, lead/acid batteries are still the most commonly used system must be due to other factors. These are:

(i) the cost of the batteries is only 65–70% that of nickel/cadmium batteries;

(ii) the charge characteristic is simple, because the current is controlled by the state-of-charge;

(iii) environmental problems are less than for nickel/cadmium batteries and lead is fully recycleable.

Since the mid-1970s, there have been strong demands for producing low-maintenance, or maintenance-free, batteries. As a consequence, the high antimony alloys have become replaced by low-antimony and antimony-free systems with a high hydrogen overvoltage. Forty years ago, Sonnenschein in Germany developed a system for valve-regulated, maintenance-free, lead/acid batteries using gelled-electrolyte technology. The battery sizes were between 1 and 20 Ah. This system was used for both cycling and stand-by applications. Until ten years ago, however, these batteries secured only niche-products. In the 1980s, when the technology was scaled-up to 3000 Ah, a high state of interest was shown in such designs and a worldwide development for valve-regulated batteries commenced [1].

Valve-regulated batteries

The basic differences between valve-regulated and conventional batteries are as follows: (i) grids are free of antimony; (ii) electrolyte is solidified, which enables oxygen recombination; (iii) vent plugs are replaced by valves.

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An antimony-free, lead–calcium alloy with high hydrogen overvoltage inhibits the decomposition of water to hydrogen and oxygen. Small amounts of oxygen, that are still formed by oxidation of the electrolyte water, become reduced to water again at the surface of the negative plates, because this reaction requires less energy than the reduction of hydrogen ions to hydrogen gas (Fig. 1).

In order for oxygen to be reduced, it is necessary, for the gas to flow from the positive to the negative plates, and for a three-phase boundary (electrode/electrolyte/gas) to be present.

There are two technologies of valve-regulated batteries (VRBs) in commercial production. In the gel design, the electrolyte is gellified by dispersion with SiO_2 [2]. This gel has good thixotropic properties so that it can be poured into the cells. After a short time, the gel solidifies and, during ageing, develops cracks for oxygen. The second valve-regulated technology corporates the so-called absorptive glass mat (AGM) design. In this, liquid electrolyte is adsorbed in a porous separator and the passages for oxygen are obtained by undersaturation of the separators with electrolyte. Figure 2 indicates that, for up to 85% saturation, the cells exhibit full gas-recombination. At higher saturation, the recombination rate decreases.

In general, the limitation of electrolyte to 85% reduces the performance to about 80% in comparison with other VRBs.

In AGM batteries, the oxygen penetrates directly through the separator to the negative plate. In gelled-electrolyte batteries, however, the way for the oxygen is through the gas space above the elements because of the presence of a microporous separator with pore diameters of 0.5 μm.

The shorter way for oxygen penetration in AGM batteries accounts for the fact that the recombination rate of AGM cells is about 20 times higher than that of gelled-electrolyte cells (Fig. 3). Nevertheless, because the float current of gelled batteries is below 0.5 mA/Ah, this low recombination current is no disadvantage in field application. On the contrary, as illustrated in Fig. 4, a high recombination rate depolarizes the

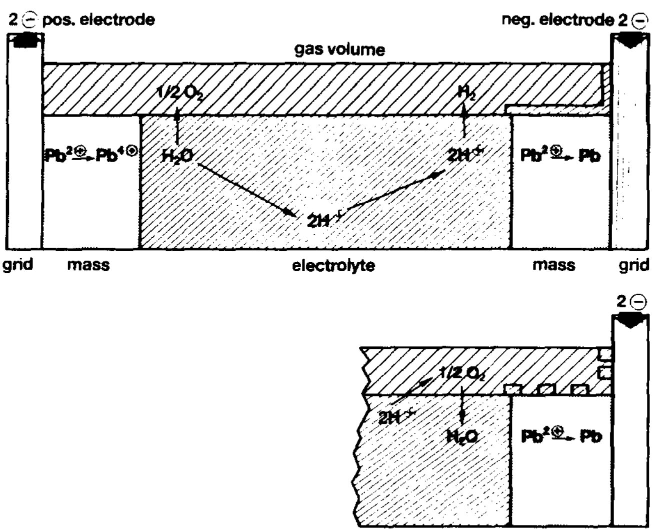

Fig. 1. Oxygen recombination in valve-regulated lead/acid batteries.

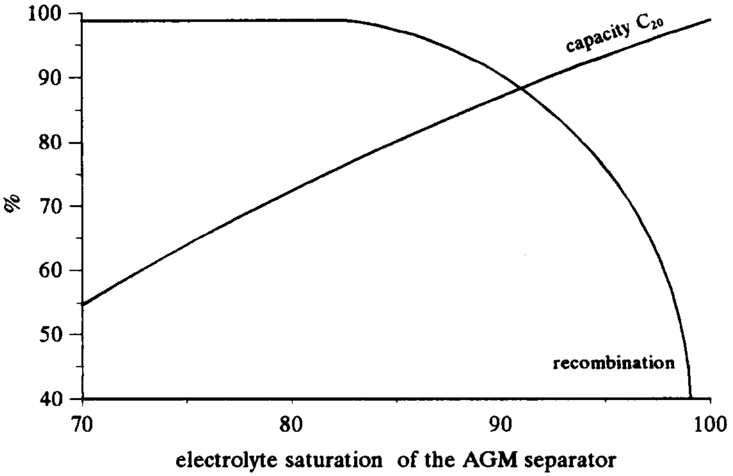

Fig. 2. Influence of saturation of the electrolyte on recombination and performance of AGM batteries.

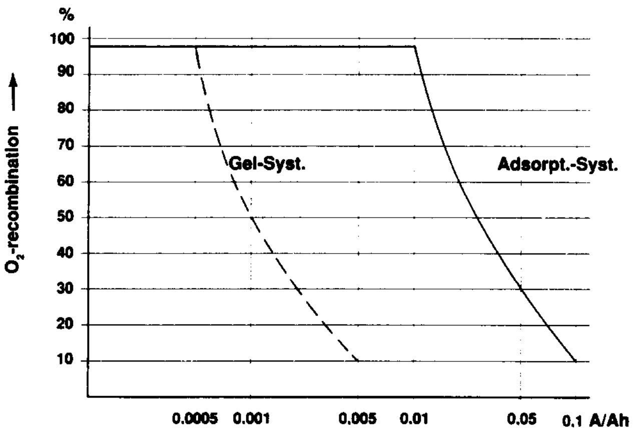

Fig. 3. Oxygen recombination in valve-regulated lead/acid cells. (Source: NTT-Elec. Com. Lab., Tokyo.)

negative potential and, consequently, causes higher polarization of the positive plate and an increased evolution of oxygen.

Therefore, in AGM batteries, more oxygen is circulating during float charge. Because of the exothermic nature of oxygen recombination, the batteries will operate at higher temperatures, and this will have a negative influence on life.

The difficulties indicate that requirements for recombination rates, which are included in some specifications, do not make sense. Rather than a requirement for a certain recombination rate, it is better to define the gas loss with time and the Ah during overcharging with a specified float voltage.

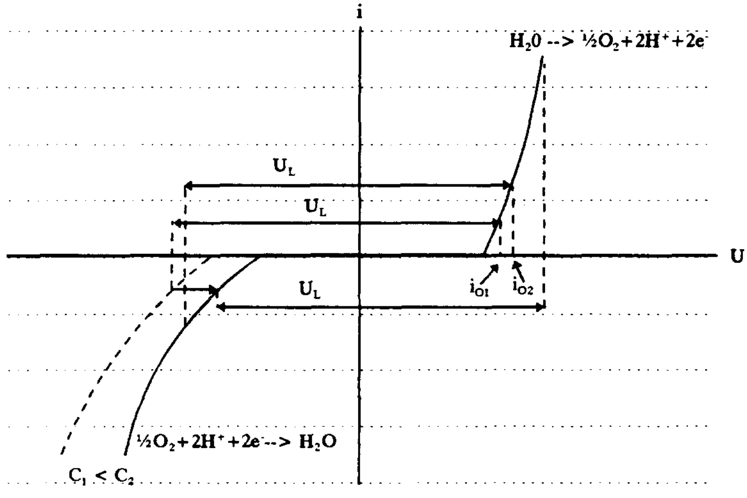

Fig. 4. Influence of cathode depolarization on oxygen formation at the positive plate.

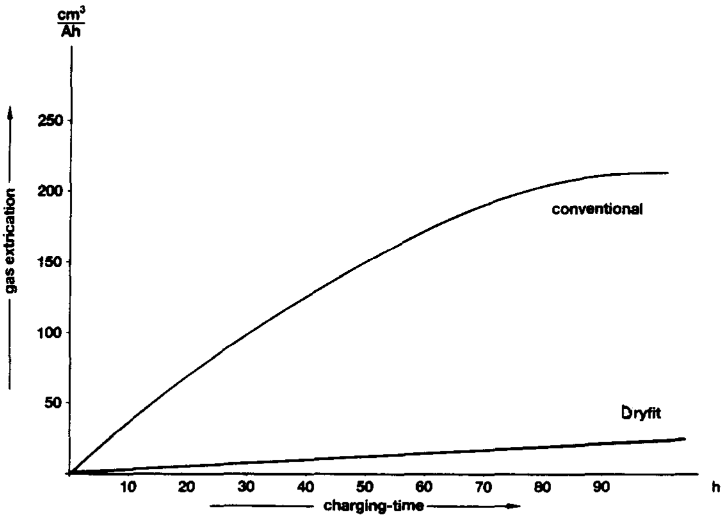

Fig. 5. Gas extrication from gelled-electrolyte and conventional batteries during float charging.

Properties

Valve-regulated batteries are maintenance-free. Apart from this, they can be distinguished from conventional batteries through following features.

Gas extrication

Figure 5 shows the gas extrication of a Dryfit® battery in comparison with conventional batteries. In the initial state, the gas extrication is 10% of a flooded battery. This decreases further during life because of electrolyte ageing [3]. The low gas extrication of VRBs has been incorporated into the security specifications of battery rooms. For such batteries, only 25% ventilation is required [4].

Self-discharge

Because of the usage of an antimony-free alloy with a high hydrogen overvoltage, VRBs have a low self-discharge. After two years storage at 25 °C, the residual capacity is at least 75%; this corresponds to a daily self-discharge rate of 0.08%.

Life

Gelled-electrolyte batteries with pasted plates and a construction similar to automotive designs have a life of 250 cycles. This is about four times more than that for flooded batteries. The cycle life is achieved in spite of the usage of antimony-free plates. Addition of phosphate stabilizers to the electrolyte is required to achieve this performance.

Deep discharge

Conventional batteries are destroyed by deep discharging, because there is an increase in the solubility of lead ions in the diluted electrolyte. Failure is due to the formation of short circuits that are caused by the precipitation of lead dendrites during charging. By contrast, VRBs are highly resistant to deep discharging. In some specifications, a 4-week deep-discharge performance at the 5-h rate is required (IEC-1056-1).

Incomplete recharging

In contrast to conventional batteries, gelled-electrolyte VRBs have a high resistance to incomplete charging. Figure 6 shows the life of a 100-Ah Dryfit battery and conventional batteries from different sources in a cycle test that involves incomplete charging, i.e., only 60% nominal capacity. It can be seen that gelled-electrolyte batteries are substantially suited for storage of alternative energy, because in such applications the charge condition depends on the weather conditions and full recharging cannot be guaranteed.

Acid stratification

Acid stratification is often the reason for the failure of batteries with low values of water decomposition. Batteries that are charged without gas evolution can register stratification values 1:1.7 within ten cycles.

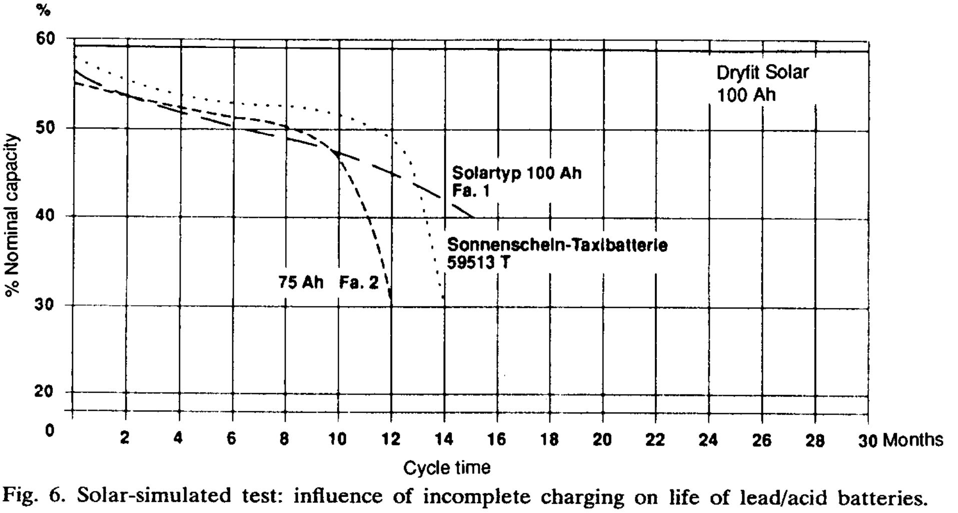

Fig. 6. Solar-simulated test: influence of incomplete charging on life of lead/acid batteries.

This is indicated in Fig. 7. The data were obtained on cells of 50 cm in height. It is obvious that the AGM design decreases the stratification by 50%. There is no stratification in batteries with gelled-electrolyte. This is one of the main advantages of gelled technology for VRBs. The highly dense acid, formed during charging, is prevented from sedimentation by adsorption in the gel structure.

Charging technique

Valve-regulated lead/acid batteries generally have to be charged with constant voltage. The current is decreased with increasing charge condition automatically. Nevertheless, the charging technique for VRBs is rather simple.

At 20 °C, the recommended voltage for Sonnenschein gelled-electrolyte batteries is 2.3 to 2.35 V/cell. The voltage, U, has to be compensated for temperature according to (Fig. 8): $U = -5$ mV/K.

In float applications, where the batteries are always on charge, it is especially important to recognize the temperature influence on the voltage.

Because of the exothermic nature of oxygen reduction, charging is generally accompanied by heat production [5, 6]. Because the current during float charging is very low, with maximum rates of 0.5 mA/Ah, gelled-electrolyte batteries pose no thermal problems during stand-by applications.

The cycling of single battery modules does not create heating problems. This is because of the good relation of the surface area to the battery volume. Traction batteries (where the cells are compactly packed in containers) have a poor ratio between surface and volume and, therefore, the battery needs a rest for cooling before recharging. This is the reason that only one-shift-operations are permitted for traction batteries, if the voltage is not controlled automatically by the battery temperature. Harmful heating of traction batteries during charging is promoted by a low charge efficiency, which can be observed on positive, antimony-free, tubular plates under worst case conditions.

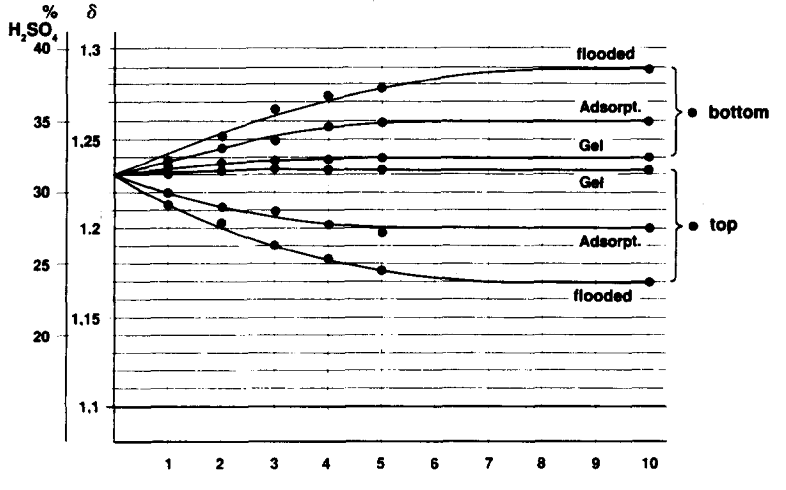

Fig. 7. Acid stratification in 350 Ah tubular cells (height 500 mm).

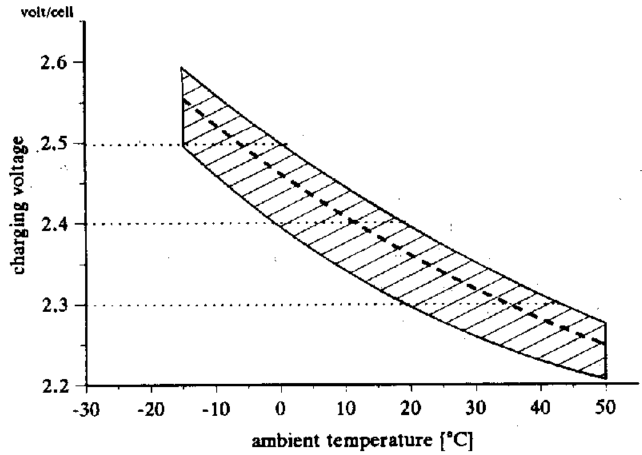

Fig. 8. Temperature influence on charge voltage for gelled-electrolyte batteries.

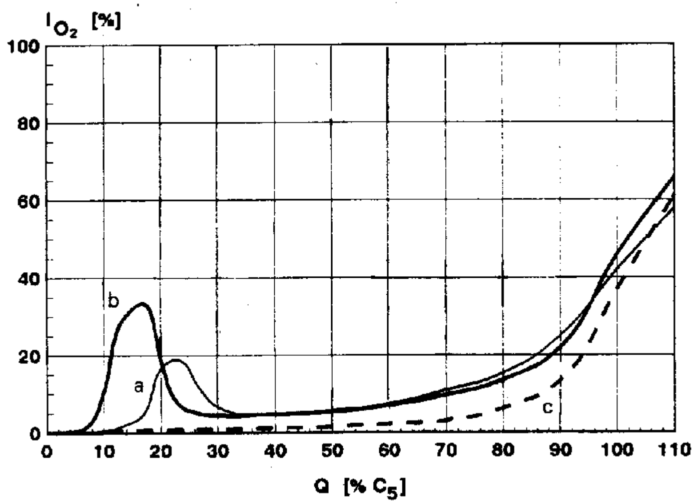

Fig. 9. Oxygen development on antimony-free tubular plates during charging with $I=I_5$: (a) high-tin alloy; (b) low-tin alloy; (c) H_3PO_4-free electrolyte, low-tin alloy.

The data in Fig. 9 indicates that, even at a 20% state-of-charge, up to 35% of the total current may form oxygen. In this low-charge condition, the battery is still in the strong charge phase, so that the formed oxygen is substantially high and the system heats up as soon as the battery comes into recombination.

The early development of oxygen is influenced by the alloy, the electrolyte and the technology of plate manufacturing. In order to prevent the oxygen peaks at the beginning of the charging regime (see Fig. 9), the current is limited to $0.5 \times I_5$, while the voltage is regulated to 2.35 V/cell. As soon as the current achieves 10% of the initial rate, it is kept constant for a maximum of 4 h (Fig. 10). In this application, temperature control of the charge voltage is recommended.

Battery connections

Switching of batteries in parallel presents no difficulties, even if the cell capacities in the single strings are different. The charge and discharge rates in the single strings will be proportional to their capacity. The number of strings switched together is virtually unlimited, as long as the contacts are in order [7, 8].

Switching batteries in series requires a small range in capacity, in order to prevent single modules from deep discharging. It is also important to allow for an adequate heat exchange, because the charge efficiency relates to the temperature. Because of this, modules at high temperatures would have a lower charge efficiency than cooler cells, and would become deep-discharged during the next discharge operation.

Charging of high-voltage, VRBs show an anomaly at the end of charging and at float charging. By contrast with flooded-electrolyte batteries wide distribution in the voltages of the individual cells is observed. For example, Fig. 11 illustrates that the voltage distribution of gelled-electrolyte modules is twice as large as that for flooded-electrolyte modules. This is because VRBs experience two cathodic reactions, that are in competition, namely, the reduction of protons to hydrogen and the reduction of oxygen to water, which have different energy consumptions. As long as the gel does not have sufficient cracks so that the anodically generated oxygen cannot fully transfer to the negative plate, oxygen reduction is accompanied by hydrogen evolution at high voltages. Therefore, cells with high oxygen recombination decrease in voltage, while the voltage of cells with low recombination increases. With increasing age, the voltage range becomes smaller, because, after initial water decomposition, the oxygen recombination takes place in the weakly recombining cells [9].

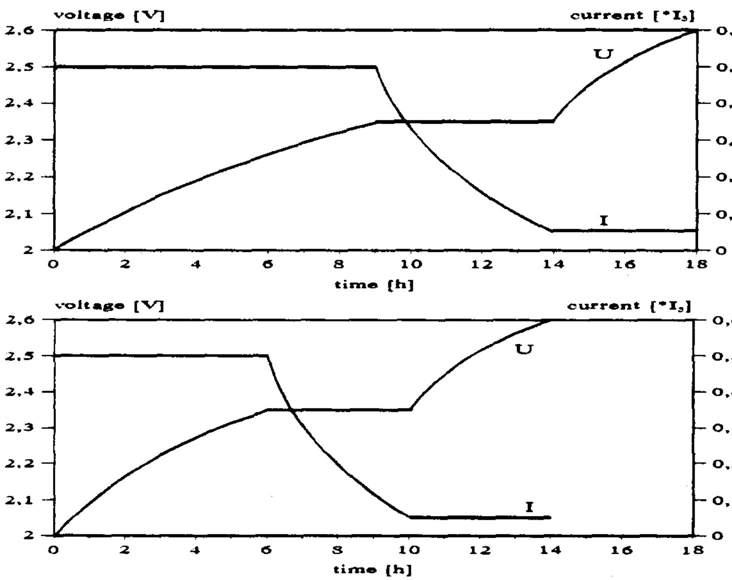

Fig. 10. Charge characteristics of valve-regulated traction cells (Dryfit A800).

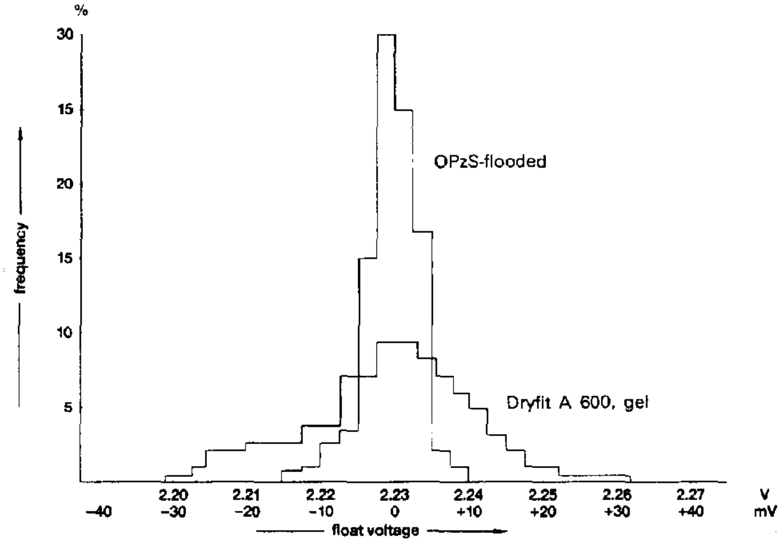

Fig. 11. Distribution of cell voltages of 370-V tubular batteries.

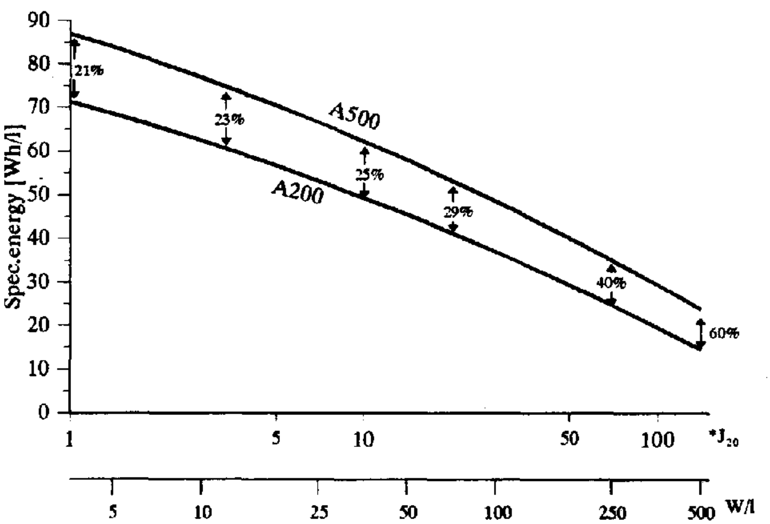

Fig. 12. Specific energy of Dryfit batteries: comparison of A200 and A500 designs.

Dryfit technology — emergency power applications

A500 design

The A500 flat-plate battery was developed for float applications and these modules fulfil the VdS specification in Germany. The float life is at least 4 years with a minimum of 200 cycles. In comparison with the A200 cycling battery, the A500 unit has a higher capacity (Fig. 12), especially at high rates. Thus, the A500 design is suitable for UPS applications.

A400 design

The A400 line is a modification of the A500 line with 8 to 10 years float life. To this line also belong OGiV types (Fig. 13), which are specified in DIN 40741 for capacities between 15 and 256 Ah. The batteries are used mainly for telecommunications applications.

OPzV–A600 design

This industrial line is constructed with tubular plates (Fig. 14). The capacities are between 200 and 3000 Ah, so that the cells are compatible with conventional OPzS types. The cells are used mainly for central power supplies in public buildings. A special construction of the A600 cells allows a horizontal mounting (Fig. 15). This allows a high utilizing of the battery rooms. It should also been noted that VRBs require only 25% of the ventilation of conventional batteries with in flooded-electrolyte construction. The life of A600 batteries is up to 15 years, by virtue of the tubular-plate construction.

Dryfit technology – deep-cycle batteries

A200 design

The A200 line is a cycling battery with a flat-plate construction and a life of 250 cycles. Types from 1 to 25 Ah are specified in IEC standard 1052 and the batteries are used in cordless tools, medical instruments, wheel-chairs, etc. The larger 12-V modules, with capacities between 36 and 200 Ah, are used as starter batteries. Because of their deep dischargeability, good cycle life and reliable cold-cranking performance,

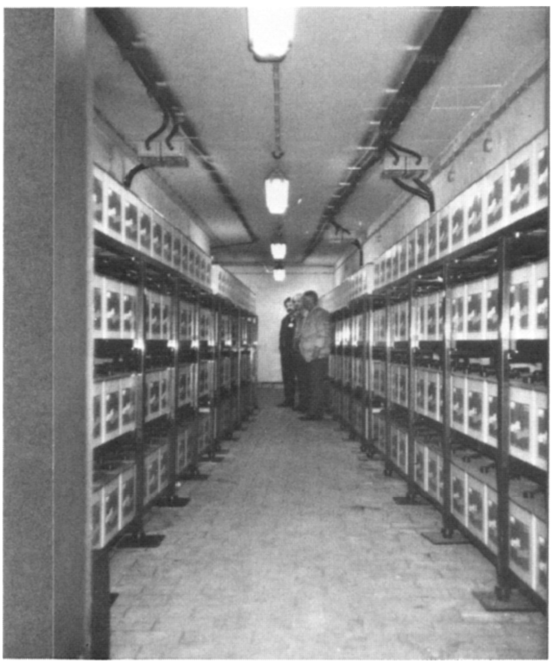

Fig. 13. OGiV 250-Ah energy power battery in a Telecom exchange.

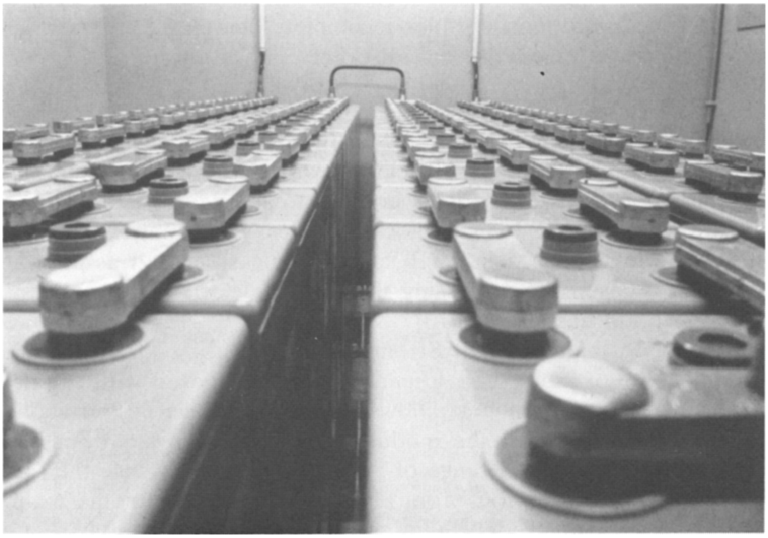

Fig. 14. Central Dryfit A600 battery for emergency power supply in a hospital.

Fig. 15. A600 battery in a horizontal application.

the batteries are employed in high-duty applications, as well as in the military field. The batteries exhibit a good performance under incomplete charging and, those are also used for storage of alternative energy, e.g., in solar applications.

Traction block

The traction block is a flat-plate battery. Due to the plate construction and the formulation of the active mass, an impressive cycle life with 800 cycles is achievable. It is necessary, however, to precycle the modules in order to achieve full performance. The product line includes 6-V and 12-V monoblock batteries with capacities between 50 and 160 Ah. The batteries are used in small forklifts trucks, as well as in street sweepers and wheel-chairs. Given the increasing interest in electric road vehicles, a new and important application has started [10].

Figure 16 shows the boot of a VW CityStromer, which is using Dryfit modules in a 96-V battery pack. A life of more than 4 years has been achieved with the help of a thermal-management system of rubber pillows through which is passed cooling water. The pillows are located between the modules. This cooling system equalizes the temperature of the modules within a range of 5 K, so that they all have the same charge efficiency. One advantage is obvious from Fig. 16; only a space for the battery is required, additional room is not needed for a central water topping-up station or for pump systems to agitate the electrolyte to prevent acid stratification.

A800 design

Traction batteries are also produced with a tubular-plate construction. The sizes correspond to the PzS-line and are between 110 and 1200 Ah.

With batteries that are switched to high energies, heating problems during charging have to be avoided. Excessive heating is prevented by limiting the charging current to $0.5 \times I_5$. Under these conditions at least 1000 cycles can be achieved with this type of battery.

Fig. 16. 96-V 160-Ah Dryfit battery in a VW CityStromer.

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