

## SEALED LEAD/ACID BATTERIES: THEORY AND APPLICATIONS

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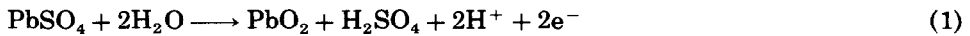
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### Introduction

The development of sealed, valve-regulated lead/acid batteries started more than 30 years ago as a leak-proof, maintenance-free battery generation that could be used in portable equipment. Subsequently, the technology was successfully introduced into larger units, and now sealed batteries challenge their conventional counterparts in almost all applications.

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

*positive electrode*



*negative electrode*



The rate of water-decomposition, reactions (2) and (4), relates to the hydrogen overvoltage, which, in turn, is controlled by the antimony concentration in the grid alloy. The evolution of gas from an antimony-free cell is only about 10% of that from a cell containing 4 wt.% Sb in the grid alloy. It should be pointed out, also, that because the self-discharge of lead/acid cells is due to reaction of the negative mass with sulphuric acid, which is accompanied by hydrogen evolution, the rate of self-discharge also depends on the antimony content of the grid alloy (Fig. 1). Finally, because in conventional lead/acid cells the antimony content influences the cycle life, the elimination of antimony in order to reduce maintenance requirements is not without its problems.

### Valve-regulated systems

In general, valve-regulated batteries can be distinguished from conventional lead/acid batteries by the use of antimony-free grid alloys and immobilized electrolyte. The first system of this type was developed by Sonnenschein in the 1950s and used a gelled electrolyte. The gel was formed by adding

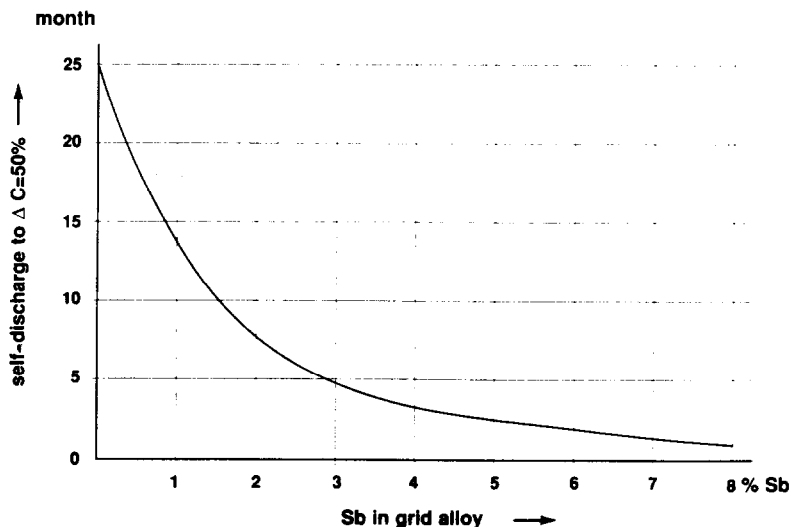


Fig. 1. Influence of antimony on the self-discharge of lead/acid batteries.

highly dispersed silica to the electrolyte. This system is still in use today for batteries in sizes up to 1500 A h. In later years, a second system was introduced in which the electrolyte was immobilized on porous, glass-fibre separator material.

### *Gas evolution*

The use of antimony-free grid alloys with high hydrogen overvoltage in sealed batteries is the main reason for negligible gas evolution in comparison with conventional lead/acid cells. Because of the general construction of sealed batteries, which gives rise to a three-phase-boundary of gas/electrolyte/electrode, oxygen produced at the positive plate is reduced to water at the negative plate. This reaction is favoured over the reduction of protons (eqn. (4)) to hydrogen owing to the lower reaction energy. Figure 2 shows that the potential of the negative plate becomes depolarized by oxygen as soon as the gas can penetrate to the plate surface. As a consequence, the end-of-charge current increases. The rate of oxygen penetration into the plate determines the gas evolution in a sealed cell. To achieve a high recombination rate cells of the adsorbed system are not completely filled with electrolyte.

As can be seen from the data of Fig. 3, the gas recombination of cells with adsorbed electrolyte is complete only up to about 80% saturation of the separator which provides about 75% of the total capacity. Therefore, so-called starved electrolyte batteries with adsorbed electrolyte have about 20% free pores in the separator. Clearly, because of this incomplete filling condition, there is an equilibrium between capillarity of the separator and gravity. Especially with tall cells, therefore, electrolyte limitations may cause problems of unequal mass reaction and current density between the upper and the lower zones of the cell.

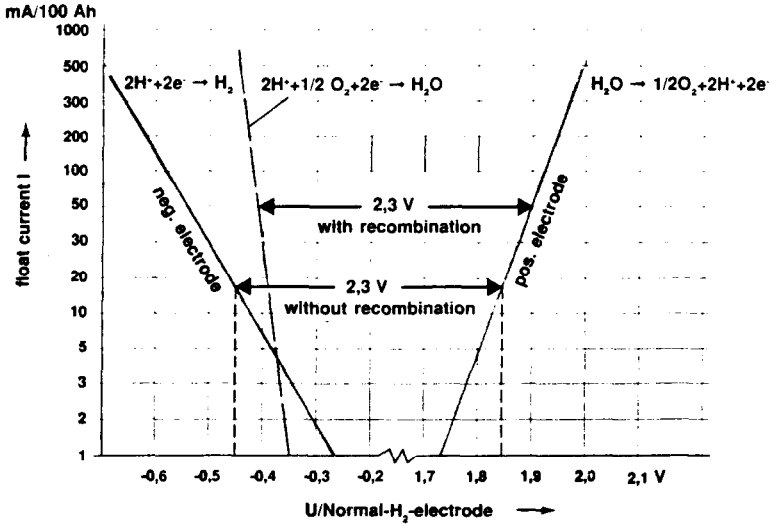


Fig. 2. Distribution of charging voltage in lead/acid batteries.

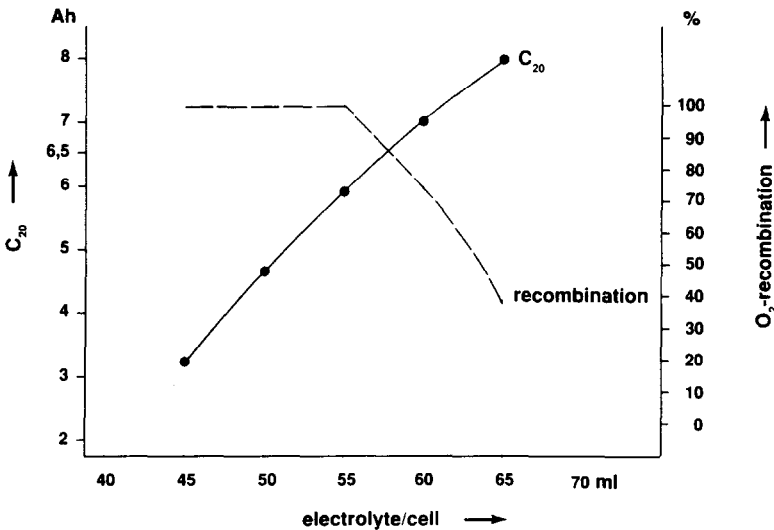


Fig. 3. Influence of electrolyte volume on  $O_2$  recombination in valve-regulated lead/acid batteries.

By contrast, gelled-electrolyte cells are completely filled. For this reason, the oxygen recombination in new gel cells is lower than that in adsorbed-electrolyte systems. By virtue of a shrinking effect of the electrolyte during ageing, however, small cracks appear in the gel and the oxygen recombination increases. This is demonstrated in Fig. 4 which shows the

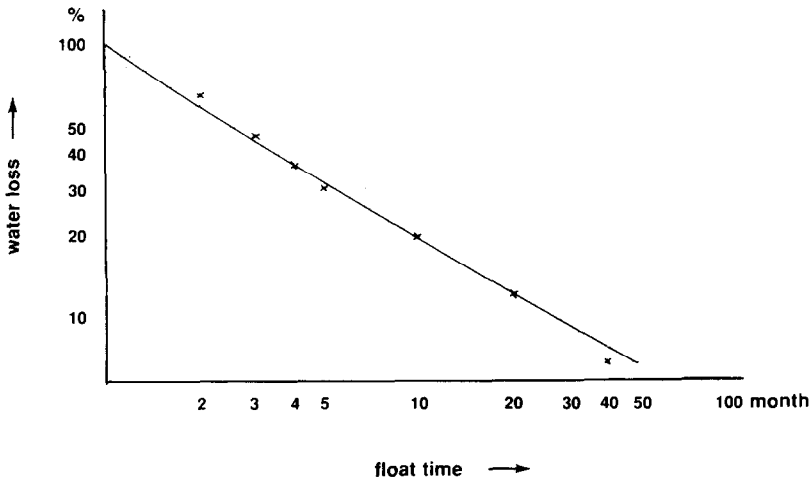


Fig. 4. Ageing influence on water decomposition in gelled lead/acid cells in float operation (2.23 V/cell).

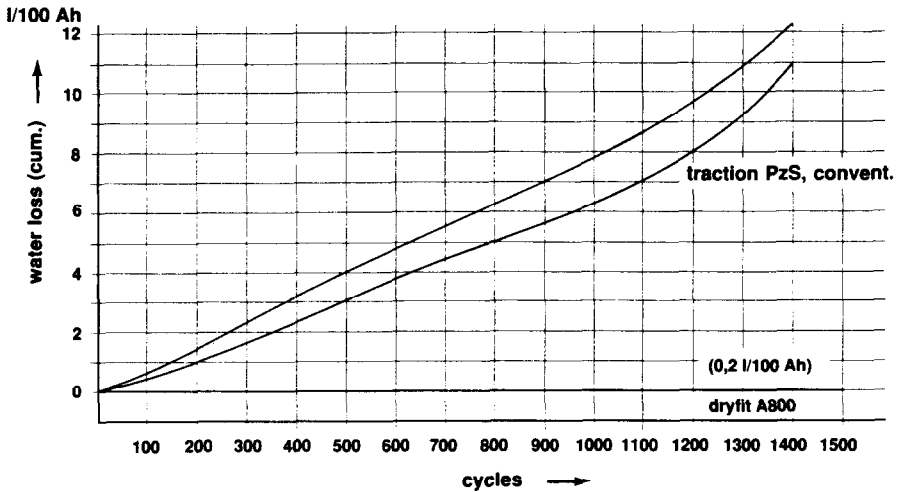


Fig. 5. Loss of water from valve-regulated, gelled-electrolyte lead/acid cells during service life.

behaviour of gelled cells under float conditions. The life of these cells is not limited by water loss. Furthermore, the completely filled situation results in gelled cells having no problems with electrolyte-limited discharge rates in the upper parts of the plates. Thus, the gelled system is particularly suitable for tall cells.

In Fig. 5, the water loss in sealed, gelled traction cells (A800, tubular-plate type) is compared with that experienced in equivalent conventional (PzS type, flooded electrolyte) cells. It can be seen that the water loss from

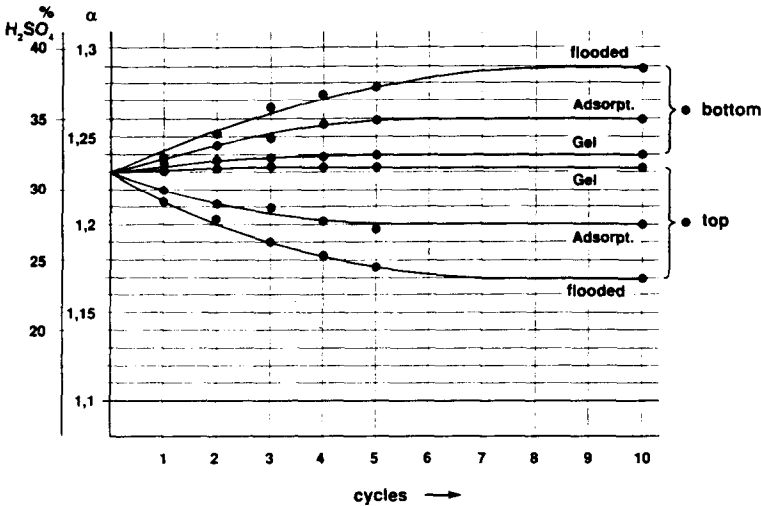


Fig. 6. Electrolyte stratification in 350 A h PzS cells with different technology.

the gelled systems is very low and this reduces the level of ventilation required in battery rooms.

### *Electrolyte stratification*

Electrolyte stratification is a well-known problem when flooded cells are cycled with charge voltages below the water decomposition potential. Under these conditions, no gas is evolved during charging so the electrolyte is not stirred. As a result, the high gravity sulphuric acid formed during charging sinks to the bottom of the cell. This leads to a reduction in capacity through electrolyte limitations, as well as to short life through corrosion and sulphation problems in the lower parts of the plates.

The data in Fig. 6 show that there is an electrolyte gravity difference of over 0.1 in flooded-electrolyte 350 A h PzS cells after 5 charge/discharge cycles. By comparison, cells using adsorptive glass-mat technology register only 50% of this degree of stratification, while cells with gelled electrolyte are virtually unaffected. The latter is due to the fact that the sulphuric acid formed during charging remains fixed in the porous structure of the gel. This property provides gel systems with a considerable advantage, especially in tall-cell designs.

Figure 7 provides supporting evidence from Japan on the superior performance of sealed batteries. The data show that the loss of capacity due to electrolyte stratification is eliminated through the use of gelled-electrolyte.

### *Performance*

Solidification of the electrolyte does not harm the electrical performance of the battery. On the contrary, especially at low temperatures and high rates (Fig. 8), a superior voltage and capacity can be observed compared

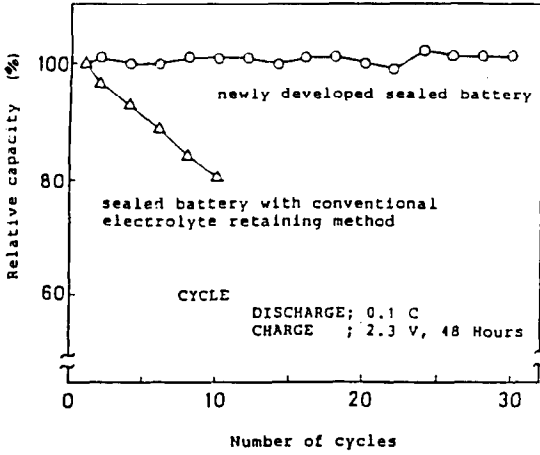


Fig. 7. Loss of capacity through electrolyte stratification. (Source: Matsushima, NTT Electr. Com. Lab., Tokyo.)

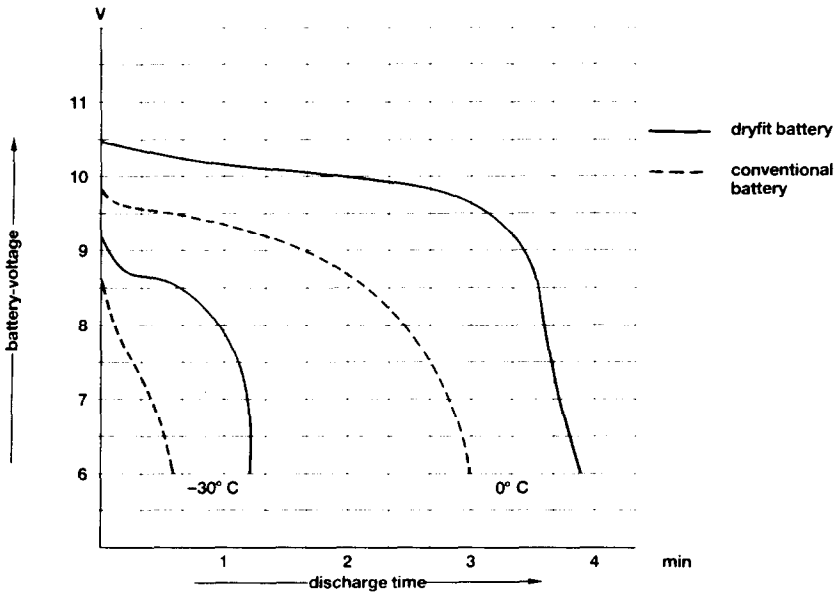


Fig. 8. High-rate behaviour of valve-regulated, gelled-electrolyte lead/acid batteries at low temperatures ( $I = 100 \times I_{20}$ ).

with conventional batteries. This is due to depolarization of the negative plate by oxygen reduction during charging, which achieves a higher charging voltage for the positive plate. Similar behaviour of gas-recombination batteries has been reported in the Japanese literature (Fig. 9).

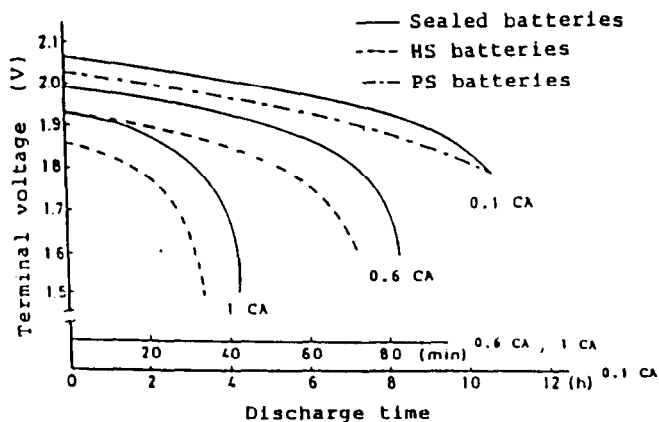


Fig. 9. Discharge characteristics of valve-regulated lead/acid batteries compared with those of flooded cells. (Source: Matsushima, NTT Electr. Com. Lab., Tokyo.)

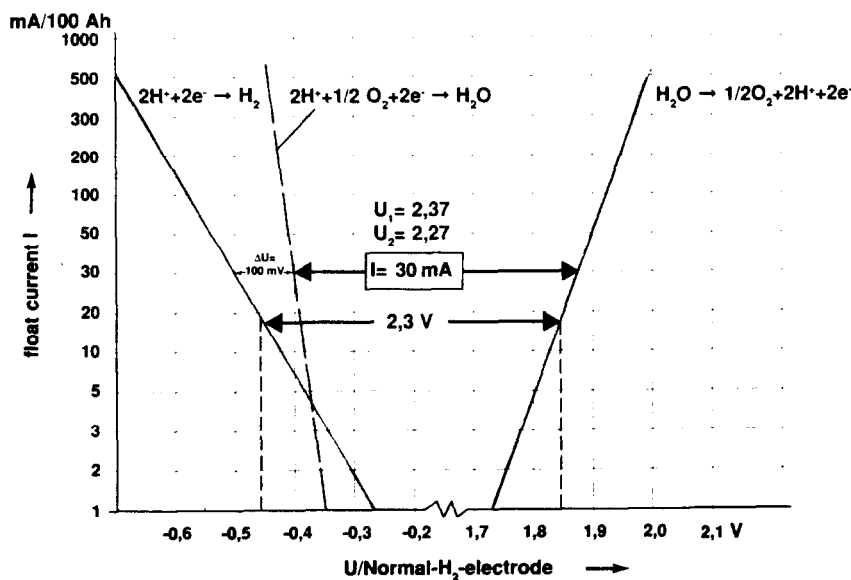


Fig. 10. Influence of  $O_2$  recombination on voltage distribution in valve-regulated lead/acid batteries.

### Voltage distribution

Oxygen recombination can result in an irregular distribution of voltage between cells, especially in new batteries. Because there are two possible cathodic reactions, which have a different reduction energy and which are influenced by the oxygen penetration to the negative plates, the negative plate potential can lie between both reaction voltages. Figure 10 demonstrates

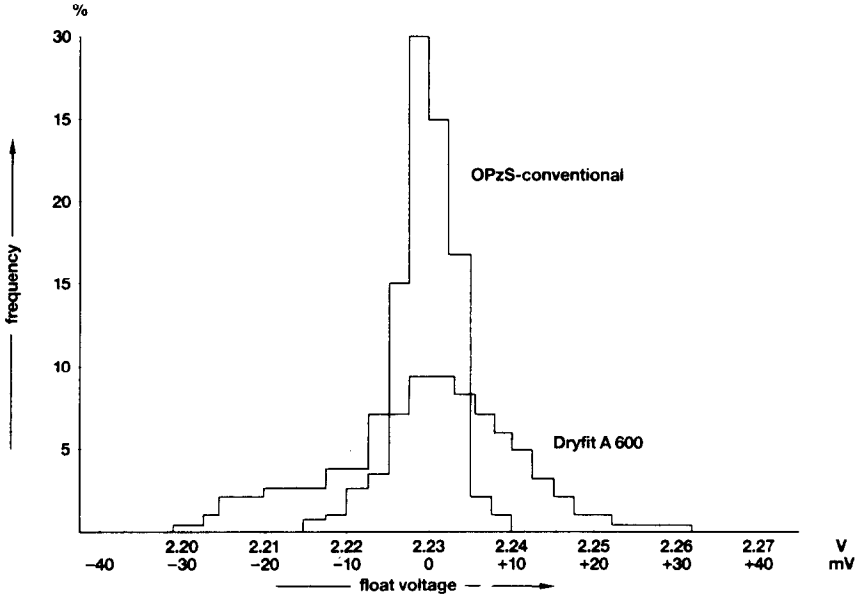


Fig. 11. Voltage distribution of single lead/acid cells in float operation (2.23 V/cell) [1].

that for a battery system where all cells are charged with the same current, the negative voltage can vary by up to 100 mV/cell. Figure 11 shows the voltage distribution of two 48 V batteries in a conventional, and in a gel, system. It must be stressed that the wide range of voltage with the gel battery does not imply that the system has failed.

## Products and applications

Sonnenschein produces gelled-electrolyte batteries of size up to 1500 A h for both float and cycling applications. These are sold under the brandname: 'Dryfit'.

### Small batteries

Small batteries are manufactured with a flat-plate construction in sizes between 1 and 63 A h and are used for both float and cycling duties. An emergency power unit (24 V, 63 A h) for a computer system is shown in Fig. 12. A special product line for high-rate discharging has been developed for UPS applications. The service life of these batteries is between 200 and 250 cycles, or 4 - 5 years float life. The batteries have to be charged at a constant voltage of 2.3 - 2.4 V/cell; this is lower than the water decomposition voltage and above the redox potential of the plate material reactions.

### Industrial float batteries

Figure 13 shows sealed batteries with a flat-plate construction and gel technology, that are produced in 4 and 6 V units between 12 and 200 A h. The



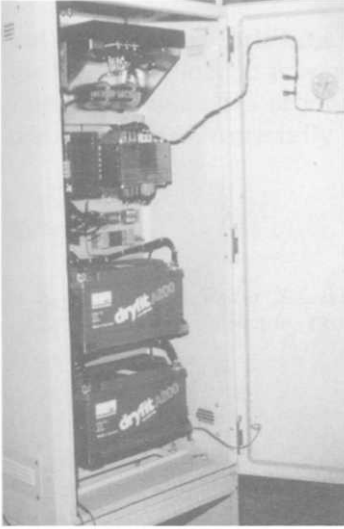


Fig. 12. Dryfit batteries in a UPS system.



Fig. 13. Dryfit batteries for telecommunications applications.

batteries have a float life of about 12 years and their main application is in the telecommunications area. The batteries are floated at 2.23 V/cell and are fully compatible with conventional batteries for emergency power supply. A special series of 12 V batteries with high-rate discharge characteristics is manufactured for UPS systems.

Gelled-electrolyte cells and batteries are also produced with tubular plates. In Fig. 14, such cells are mounted horizontally to save floor space and allow easy access to the terminals for testing procedures. Tubular-plate cells have a service life of 15 years.

#### *Traction batteries*

Traction batteries are produced in 2 V tubular cells. Despite the use of antimony-free grid alloys, these batteries have a cycle life equivalent to that

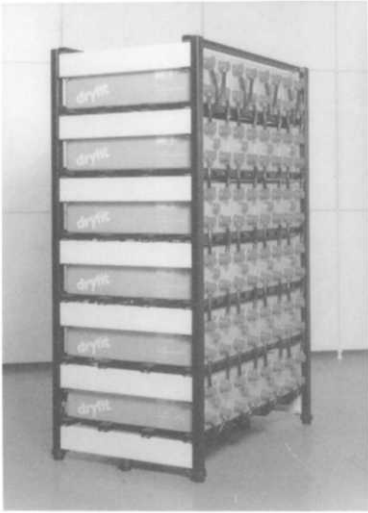


Fig. 14. A600 Dryfit batteries mounted horizontally.



Fig. 15. PANAM electric vehicle at Rhein-Main-Airport, Frankfurt.

of conventional types, *i.e.*, 1500 cycles. This performance is achieved with a current/voltage/current-limiting charging characteristic.

Two years ago, PANAM changed all their vehicles at the Rhein-Main-Airport in Frankfurt to electric versions (Fig. 15). The advantage of the maintenance-free system in this particular application is that the cars need not be serviced in a central battery station. The batteries can be recharged in front of the terminal, so that no extra energy is needed to drive to, or from, the charging station.

In addition to industrial traction batteries, motive-power units are manufactured in 6 and 12 V sizes for propulsion of wheel chairs, golf carts,

and hand-guided fork lifts. Research conducted both by Volkswagen and by the German Electric power company RWE into these batteries operating in electric vehicles has produced excellent results by comparison with conventional batteries, especially with respect to vehicle range and acceleration.

## Reference

- 1 H. Tuphorn, *J. Power Sources*, 23 (1988) 143 - 155; H. Tuphorn, *Proc. 3rd Int. Lead/Acid Battery Seminar, Orlando, 1989*.