FACTORS INFLUENCING THE PERFORMANCE OF GAS-RECOMBINATION LEAD/ACID BATTERIES

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Introduction

Lead/acid batteries, both traditional and maintenance-free, suffer water loss due to electrolysis at the end of charging. As a result, batteries with Pb–3wt.%Sb grids require periodic addition of distilled or demineralized water.

At the beginning of the investigations into sealed lead/acid batteries reported here it was necessary to optimize various parameters so as to eliminate hydrogen evolution on the negative electrode or, in other words, to make the reaction of spongy lead oxidation proceed on the negative electrode [1].

During charging and discharging of lead/acid batteries the following reactions proceed on the anode:

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

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

and on the cathode:

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

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

together with an additional reaction of spongy lead oxidation:

$$Pb + \tfrac{1}{2}O_2 \longrightarrow PbO \qquad (5)$$

$$PbO + H_2SO_4 \longrightarrow PbSO_4 + H_2O \qquad (6)$$

Design of sealed lead/acid batteries

One of the essential components of the design of sealed lead/acid batteries is a glass microfibre separator. This allows immobilization of the electrolyte and recombination of gases. A series of glass microfibre separators (fibre diameter = 2.2 μm) was made in the Institute of Cellulose and

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TABLE 1

Physical and chemical properties of microfibre-glass separators

Parameter	UWS 1.5	UWS 2.2
Separator thickness at 3.5 kPa (mm)	1.5	2.2
Average fibre diameter (μm)	2.2	2.2
Electrical resistance (Ω cm^2)	0.04	0.08
Basic weight (g m^{-2})	160	240
Acid absorption — H_2SO_4 sp. gr. 1.28 g cm^{-3} (cm^3 g^{-1})	9	9
Acid wetting time (s)	1	1

Papermaking, Łódź, in cooperation with the authors' laboratories [2, 3]. These separators feature high porosity, low electrical resistance, good chemical resistance to oxidation, and freedom from organic impurities. The physical and chemical properties of the separators are given in Table 1.

Gas recombination depends on the absorptivity of the separator and the degree of its saturation with electrolyte. When designing a sealed battery, the thickness of the separator and the degree of its saturation should be carefully chosen so that the appropriate quantity of electrolyte per unit capacity is available. Due to immobilization of the electrolyte in the separator and the pores of the electrodes, sealed batteries are unspillable and can operate in any position.

A further important factor that affects gas recombination is the selected ratio of the active material in the positive and negative electrodes. This ratio should allow the positive electrode to reach a fully charged state in advance of the negative electrode.

The correlation between recombination efficiency and the lead alloy used for the grids is also important since both the overpotential of hydrogen evolution on the positive electrode and the gas overpressure depend on the type of alloy used. West European battery manufacturers prefer to use lead–calcium alloys. Figure 1 shows the influence of separator saturation and the type of grid alloy on gas overpressure during charging of laboratory-scale cells. The lowest overpressure is observed for lead–calcium alloys and pure lead at 85% saturation of the separator.

Gas generation is also affected by the charging parameters, *i.e.*, constant voltage and limited current. The final design problem is sealing of the battery in the form of a unidirectional pressure safety valve. The latter releases excess gas generated during overcharge and oxidation of organic components, and is then closed automatically.

Factors affecting cycle life of sealed batteries

The first series of cells tested for cycle-life performance contained positive and negative grids made from low-antimony alloy. Poor cycle life

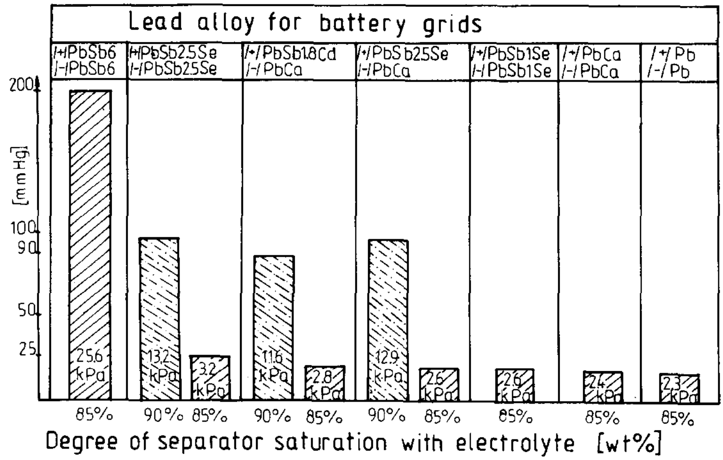

Fig. 1. Influence of separator saturation and type of grid alloy on gas overpressure in lead/acid cells.

($\sim$100 cycles) resulted from positive grid corrosion. This is in agreement with earlier statements [4, 5] that low-antimony alloys contribute to high oxygen evolution, causing excessive grid corrosion.

A second series of tests was conducted on cells with lead–calcium and pure lead (99.99%) grids. The behaviour of pure lead grids was particularly interesting since after 100 cycles no corrosion was observed (data of April, 1989).

Other important factors affecting cycle life are the electrical parameters. Typical charging and discharging characteristics of a sealed lead/acid battery are given in Fig. 2. This battery type requires constant-voltage charging at 2.3 - 2.35 V/cell and a maximum current of 0.2 $C/20$. During charging at a constant voltage of 2.35 V/cell, the water loss is zero and the oxygen-recombination efficiency is 100% [6].

Similar charging conditions are specified in the IEC Publication No. 21 (Central Office/38 of 2 Feb. 1989), the only difference being an initial current limitation of $I_{max} = 0.3\ C/20$ or, in other words, $I_{max} = 6\ I/20$. Charging should be carried out at 25 ± 2 °C. According to this document, cycle life shall be a minimum of 200 cycles.

The cells in the present study were charged at a constant voltage of 2.4 V/cell. Therefore, it might be expected that the excess of generated gases caused premature corrosion of the positive grids.

It is expected that low-antimony alloys could also be used in sealed lead/acid batteries, but this would require the development of a new charging procedure. Investigations into low-antimony alloys for sealed lead/acid batteries are in progress at the authors' laboratories.

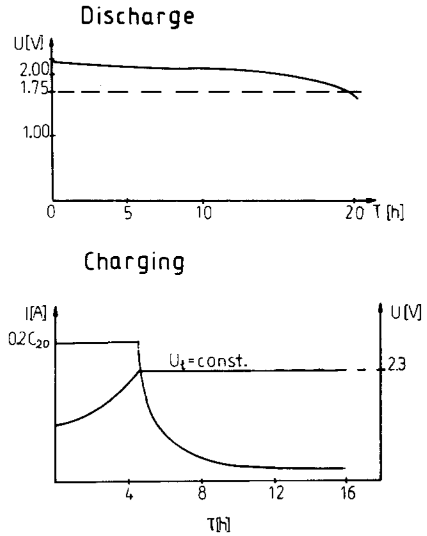

Fig. 2. Typical charging and discharging characteristics of recombination lead/acid cell.

Conclusions

In order to design a sealed lead/acid battery, the following conditions must be fulfilled:

(i) the battery should contain a highly absorptive glass microfibre separator, partially saturated with electrolyte;

(ii) the proportions of the active materials should be selected in such a way that the positive plate reaches a fully charged state in advance of the negative plate;

(iii) it is concluded that lead alloys for battery grids have not been developed satisfactorily and therefore require further investigation;

(iv) the battery should be equipped with a unidirectional safety valve;

(v) charging should be carried out at constant voltage of 2.30 - 2.35 V/cell and a limited current of 0.2 $C/20$ - 0.3 $C/20$.

References

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