CYCLE LIFE OF STRESSED LEAD–ACID BATTERIES

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Summary

An original lead–acid battery structure incorporating a special set of separators and a device to exert mechanical pressure on the plates is described. An additional arrangement on the positive plates reduces shedding. Such batteries were cycled using thirty minute rapid charges, and cycle lives of between 300 and 3000 are reported. According to porosity measurements, it seems that positive active material ceases to change after a few hundred cycles.

Résumé

Une structure originale d'accumulateurs au plomb, caractérisée par une séparation particulière et la présence d'un dispositif permettant d'appliquer sur les plaques une contrainte mécanique, est testée en cyclage. Une disposition supplémentaire permet d'éviter la chute de la matière active positive. Le cyclage mis en oeuvre comporte une charge rapide c'est à dire en 30 minutes. L'expérience montre que la durée de vie des cellules testées dépend fortement de la contrainte exercée et peut atteindre des valeurs élevées. Les durées de vie relevées varient entre 300 et 3000 cycles. Des mesures de porosité conduisent à penser que la matière active positive n'évolue plus après quelques centaines de cycles.

Introduction

This paper originated from research on the rapid charging of lead–acid traction batteries. After unsuccessfully attempting to design a special charging process as suggested by the literature [1], we began to study the structure of lead–acid batteries.

We built small, 3-electrode cells ($C_{10} = 2$ A h), comprising standard separators and plates used by battery constructors [2]. Nine main combinations of separator disposition, nature, and number were tested. One of the

parameters monitored was the pressure on the plates and separators necessary to maintain the structure. It will be shown that this parameter, adjusted to 0.15 bar, has important implications for cycle life.

The cells were subjected to the following uninterrupted cycle:

- constant current charge I_c = 6 A (*i.e.*, 3 C_{10}) for 15 min,
- constant current discharge I_d = 1 A (*i.e.*, 0.5 C_{10}) maintained until cell voltage fell to 1.7 V.

Under such conditions, cell cycle life varied from a few cycles to 600 cycles.

The five longest-lasting structures were selected for further experiments with large cells comparable with those of commercially available traction batteries (C_5 = 34 A h). Despite varying the experimental conditions — especially the cycling — it was not possible to repeat the results obtained on the smaller cells using the larger cells. After studying some possible causes, *e.g.*, gas flow rate and electrolyte ratio, we attributed the difference to the pressure on the plate and separator set; it significantly affected the cycle life of one of the selected structures. It must be pointed out that the pressure was reduced when we changed the cell scale because of the greater forces involved.

A study was then made of the effect pressure had on cycle life, and the results of this study are presented below.

Experimental

Mechanical pressure is exerted onto the cell stack by means of adjustable, calibrated springs *via* metallic flanges (see Fig. 1(a)). The containers are flexible enough not to affect the pressure, and the flanges are sufficiently stiff so as not to buckle, and therefore the pressure is transmitted uniformly.

The separator set is shown in Fig. 1(b); it consisted of a microporous separator, corrugated, perforated PVC sheet, and glass fibers (all commercially available industrial materials, provided by the CEAc*). It is obvious that, at a critical pressure, the PVC sheet will collapse. This point will be discussed later.

The cells had a 5-hour-rate capacity, C_5 = 34 A h, and consisted of 5 electrodes: 2 positive and 3 negative, FULMEN 198 designed by the CEAc for electrical propulsion. The outer dimensions of the grid were 145 × 175 mm and the thicknesses of the positive and negative plates were 2 mm and 1.8 mm, respectively.

These cells were subjected to a cycling regime different from the one described previously for the following reasons:

- When submitting these large-scale cells to the previous cycling regime, some problems associated with scale change appear (charge acceptance drop, gas flow rate increase...).

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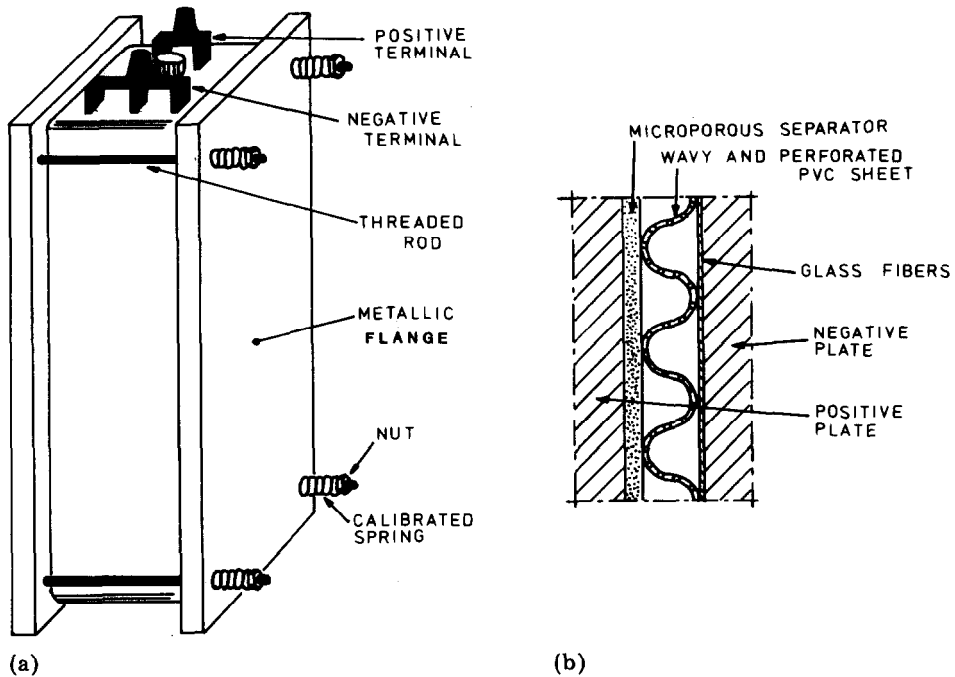
Fig. 1. (a) Apparatus for exerting stress on the cell; (b) schematic representation of the cell internal structure.

● The purpose of the small-scale experiment was to compare several cells, and an accelerated failure due to rapid, deep discharge cycling is an experimental advantage. In the case of the larger cells, the objective is to measure the cycle life of a defined structure, and accelerated tests could falsify the measurements.

Accordingly, the large-scale cells were subjected to the following uninterrupted cycle:

(a) Thirty minute charge: first, the current was limited to 100 A (*i.e.*, 3 C_5), then, the voltage was adjusted to 2.65 V.

(b) Constant current discharge (20 A, *i.e.*, $C_5/1.7$) continued until the cell voltage fell to 1.5 V. Thus, the average discharge was $C_c = 0.65 \, C_5$.
It should be mentioned that the cycle life was fixed according to the terms of our contract with the EDF (Electricité de France), whereas the charge voltage was the result of an optimisation study [3].

In Fig. 2, we show the change of cell voltage (a), and current (b), during a cycle.

We define cycle life as the number of cycles for which the measured capacity remains greater than 0.8 C_c, the dotted line on Fig. 3. We measured cell cycle life, using the conditions just mentioned, as a function of the pressure exerted on the plates, and the results are plotted in Fig. 3.

Figure 4 shows cycle life as a function of pressure from data obtained over a number of tests performed in two different series, one after the other.
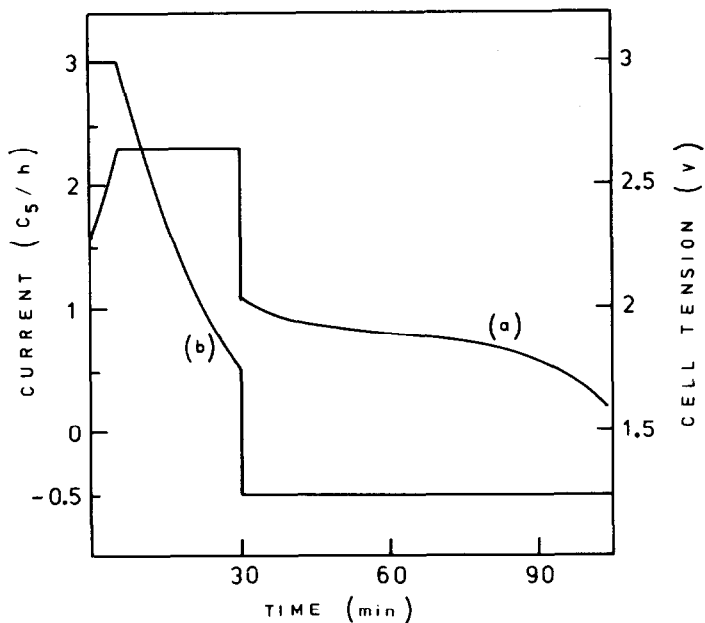
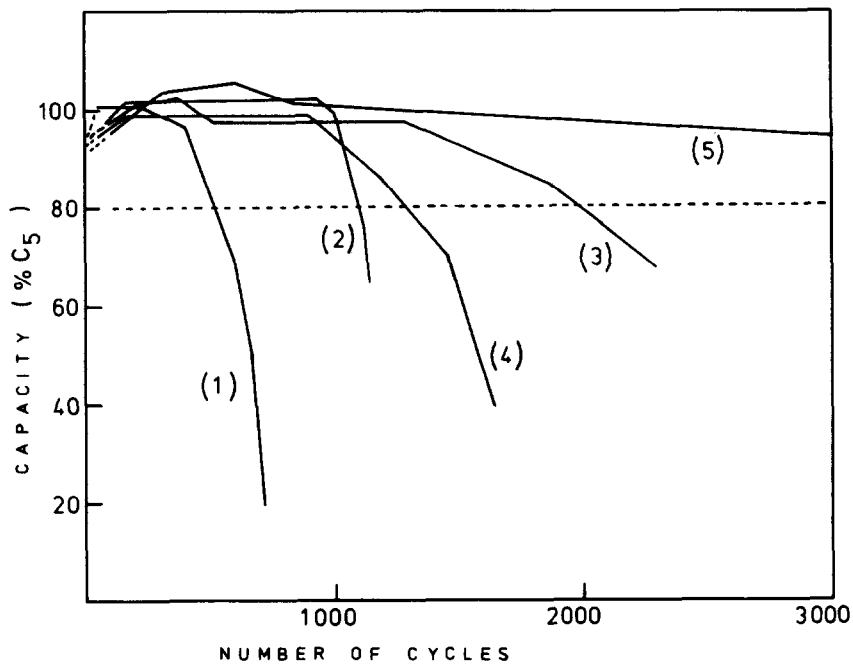Fig. 2. Evolution of cell tension (a), and current (b) during a cycle.

Fig. 3. Capacity profiles corresponding to some stresses. First series of experiments: (1), 5×10^{-2} bar; (2), 0.4 bar; (3), 1 bar; (4), 1.5 bar. Second series of experiments: (5), 0.75 bar.
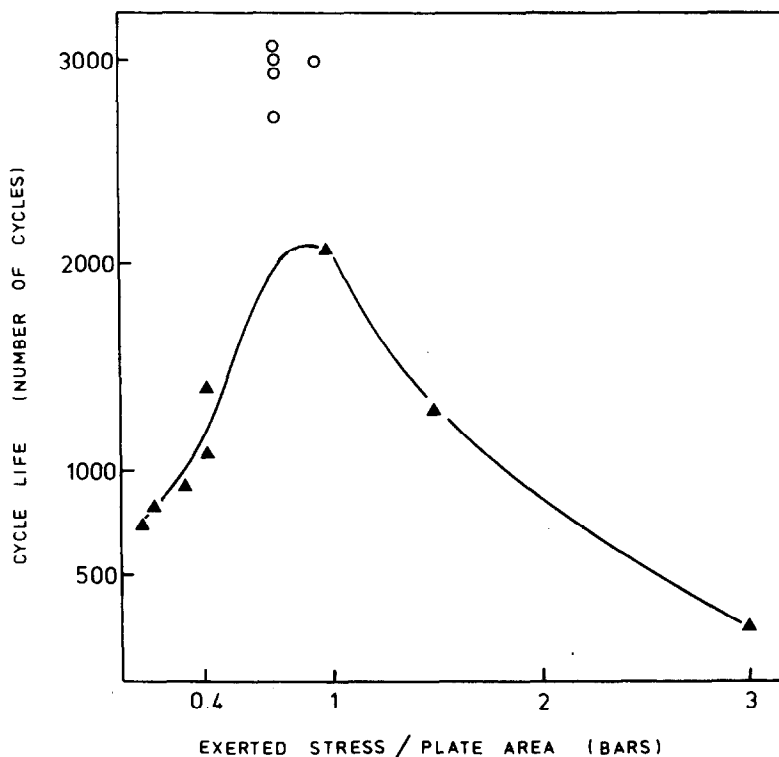
Fig. 4. Cycle life *vs.* exerted stress. ▲, First series of experiments; ○, experiments on modified structure fighting active material leakage (second series).

The results from the first series are plotted along the solid line and from the second series using open circles for individual points. We will discuss each of these separately.

First series of experiments

We initially studied the dependence of cell cycle life on pressure over a wide range of values (from 5×10^{-2} to 3 bar).

The continuous curve shows an optimum and can be considered in three parts:

(i) From 5×10^{-2} to 0.5 bar, the cycle life increased with pressure. Positive plates, in which the capacity had fallen to 0.8 C_c revealed neither shedding nor macroscopic change. Further, the depth of corrosion of the grids was insufficiently large to explain the ultimate failure. Loss of capacity may, therefore, be attributed to the breaking up of the grains of positive active material, which leads to a progressive increase in the electrical resistance.

(ii) At pressures above 1 bar the cycle life decreases with increasing pressure; the higher pressures accelerate the collapse of the internal structure. To be more precise, the separators soon collapse when subjected to

3 bar pressure and cell failure results from the decrease in the inter-electrode gap. At pressures up to 1.5 bar the separators bear the load, and cell failure is caused by the negative plates which are cut into vertical strips by the corrugations in the PVC sheet.

(iii) At about 1 bar, maximum lifetimes are achieved. Cells which had sustained 2000 cycles exhibited the following phenomenon:

(a) Spots where active material was lacking near the edges of the positive plates. In these places, the grid appeared to be deeply corroded, even to the extent of causing frame rupture (Fig. 5).
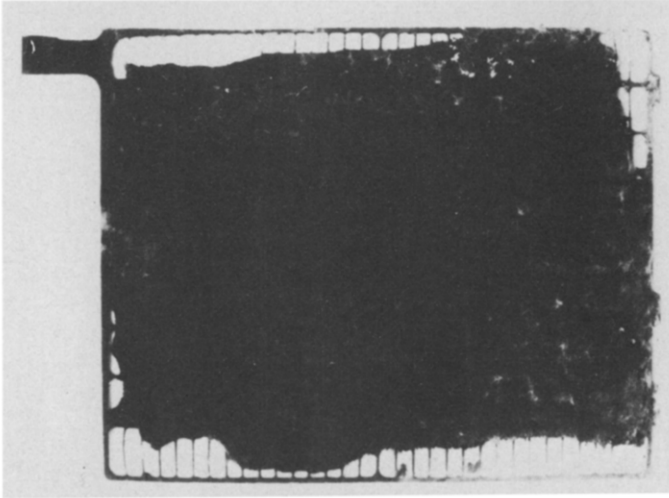
(a)
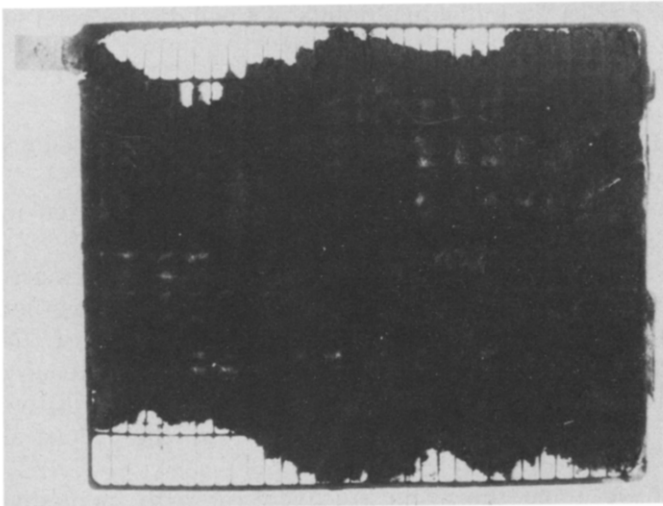
(b)

Fig. 5. (a, b) First series of experiments: 2000 cycle positive plates.

(b) In the central area, the active material was hard and stuck to the grid. When denuded, the grid appeared to be corroded evenly and less deeply than near the edges of the plate.

Considering both the separator and the pressure exerted, any shedding came exclusively from the active material near the edges of the plates. Localized holes arose around which poorly maintained active material collapsed under stress, and soft zones spread into the active material from the initial shedding spot. Elsewhere the material remained hard. Lastly, corrosion was found to develop faster in the bare zones of the grid than in the central zone. Thus, failure of the positive plate resulted from two damaging processes:
- a deep and localized corrosion of the positive grid,
- a dislocation of the positive active material from the edges of the plate.

It has been pointed out that the central zone of the plate seemed to be in good condition. To corroborate this observation, we studied active material porosity with a mercury porosimeter. This measurement, taken at different stages of cycling, showed an initial increase in porosity followed by a stable period, as can be seen from Fig. 6 where the average radius of the pores is plotted against the number of cycles. A study of the positive active material non-stoichiometry by differential thermal analysis and thermogravimetric analysis showed a similar stable period [3].
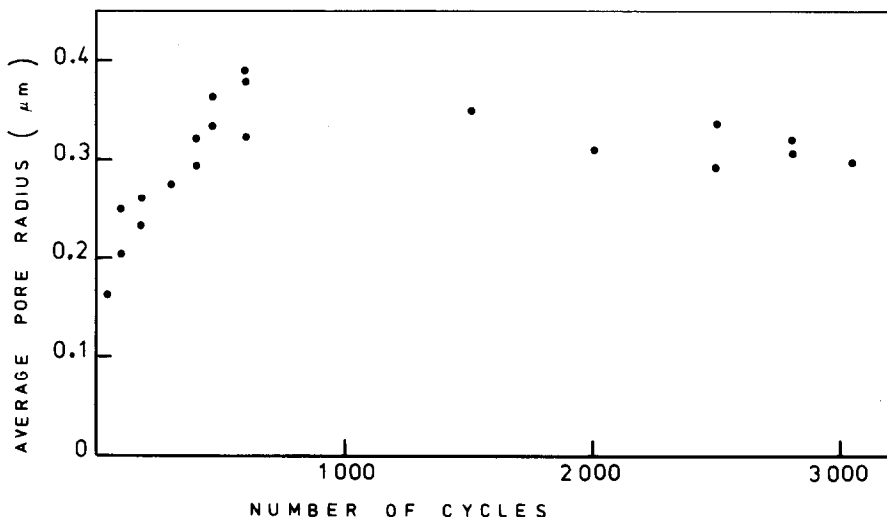

Fig. 6. Evolution of the average pore radius of the positive active material during cycling.

Second series of experiments

The aforementioned results suggest that the cycle life of the positive plates may be increased by suppressing the shedding process in the edge zones. To achieve this, we stopped active material leakage using a hot melt

polymer bond between the two microporous separators which were applied to each side of the positive plates.

The results of experiments carried out with this modified structure are shown by the open circles in Fig. 4. A significant increase in cycle life is demonstrated.

Post failure analysis showed that there were no PbO_2 deposits, although items of lead and lead sulfate came from the negative plates. On the positive plates, the active material remained hard and in good condition overall. We repeated the thermal analyses and porosity measurements on this material. The results are similar to the first ones, as may be seen in Fig. 6 which presents the average pore radius.

Finally, we observed a deep, evenly distributed corrosion of the whole of the positive grid. In the case of plates tested up to 3000 cycles, the depth of corrosion was 70% of the initial mass of the grid, and the horizontal bars, which were thinner than the vertical ones, had totally disappeared.

Conclusions

The lead–acid battery structure studied here can be characterized by the two following properties:
● the ability to withstand rapid charging (30 min);
● a long cycle life (3000 cycles) under this condition.

The potential applications of this battery structure are related to one or the other of these properties. We are now undertaking further experiments in two main directions:
● special applications for urban public transport, involving rapid charging;
● improvement in specific performance justified by the long cycle life.

Acknowledgements

References

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