

Accelerated cycle-life testing of small sealed lead/acid batteries

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Abstract

An attempt has been made to devise methods for reducing the cycle-testing time of long-life sealed lead/acid batteries. In order for the accelerated test results to equate to the actual field operations, it is assumed that the failure modes under both normal and accelerated conditions must be the same. As a first step in the search for a reliable accelerated test, observations of the battery ageing process have been made under different daily duty cycles, viz., 1 (normal), 8 and 16 cycles/day at ambient temperature and 80% depth-of-discharge. It has been found that the main cause of failure is different for a given duty cycle. This complicates the task of applying accelerated test results to field operations. For the 8 cycles/day schedule, the main cause of failure is degradation of the positive active material. Positive grid corrosion is the main factor in the 16 cycles/day case. Under normal conditions, both grid corrosion and PbO_2 degradation appear to be equally significant.

Introduction

Secondary batteries used for energy-storage applications such as load-levelling of public utilities, spacecraft power supplies and photovoltaic power generation systems require a long cycle life, sometimes ranging from 10 to 20 years. This performance causes formidable problems for those engaged in the development and/or evaluation of the performance of such batteries. It is necessary to find a way to shorten the test time without introducing undesirable factors that cause serious errors in the results.

The irreversible stresses caused by the charge/discharge reaction in lead/acid batteries accumulate as cycling continues until the batteries eventually break down (fail). The type and the degree of these stresses depend upon both the internal and the external parameters of the battery under consideration. The former are related to the manufacturing conditions and involve such factors as the physical and chemical properties of the active material [1], acid concentration, grid alloy, and the characteristics of the separator. The external parameters are related to the operational conditions and include the effect of depth-of-discharge, discharge and charge rate, extent of overcharge, and temperature. These parameters are listed schematically in Fig. 1.

In an accelerated cycle-life test, one (or more) of the external parameters is applied to the testing battery in more severe conditions than might be experienced during normal operation. This serves to enhance the action of the irreversible stress [2-7]. The validity of the test results from such a procedure rests upon whether the battery failure mode for the accelerated treatment is the same as that usually encountered.

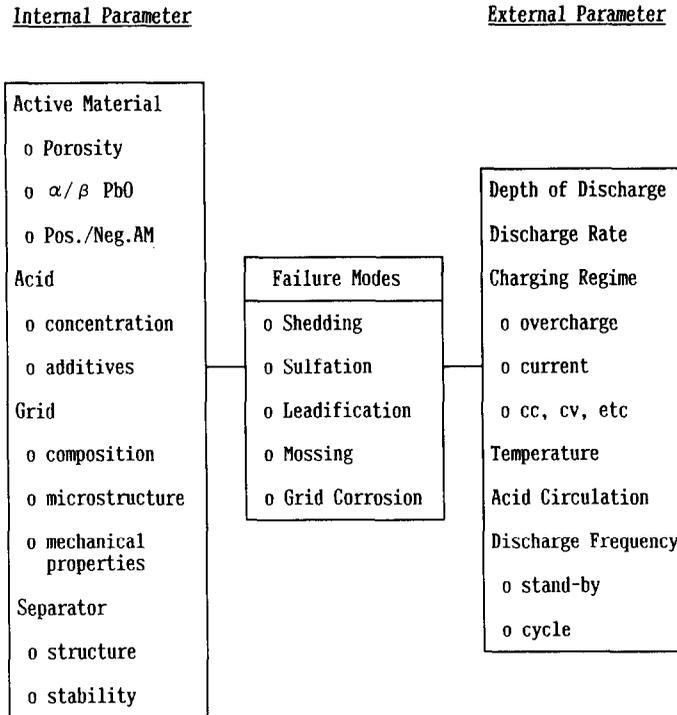


Fig. 1. Factors affecting lead/acid battery failure modes.

If this is the case, then it can be safely predicted that a superior performance observed from a given battery under one set of conditions will hold under another set.

One way of establishing the validity of the accelerated procedure is to examine the ageing sequence of the performance-limiting electrode — the positive electrode in this case [1] — during accumulation of the irreversible stresses. Figure 2 shows a schematic diagram of the accelerated cycle-life test chosen for the work reported here. In this study, an investigation was made of the effect of different daily duty cycles on the microstructure of the ageing electrode. Three different daily duty cycles of 1 (normal test), 8 and 16 cycles/day were applied at ambient temperature and at 80% depth-of-discharge (DOD).

Experimental

Test cell

The sealed lead/acid cells consisted of two positive electrodes and three negative electrodes with glass-mat separators. The grid was gravity-cast calcium alloy (Pb-0.09wt.%Ca-0.4wt.%Sn-0.03wt.%Al).

The active material was prepared from a conventional leady oxide formulation. After formation, the electrodes were dried and assembled in a polyethylene container.

The nominal capacity of the cells was ~1 A h. Fifteen and ten cells were used in the normal and accelerated tests, respectively.

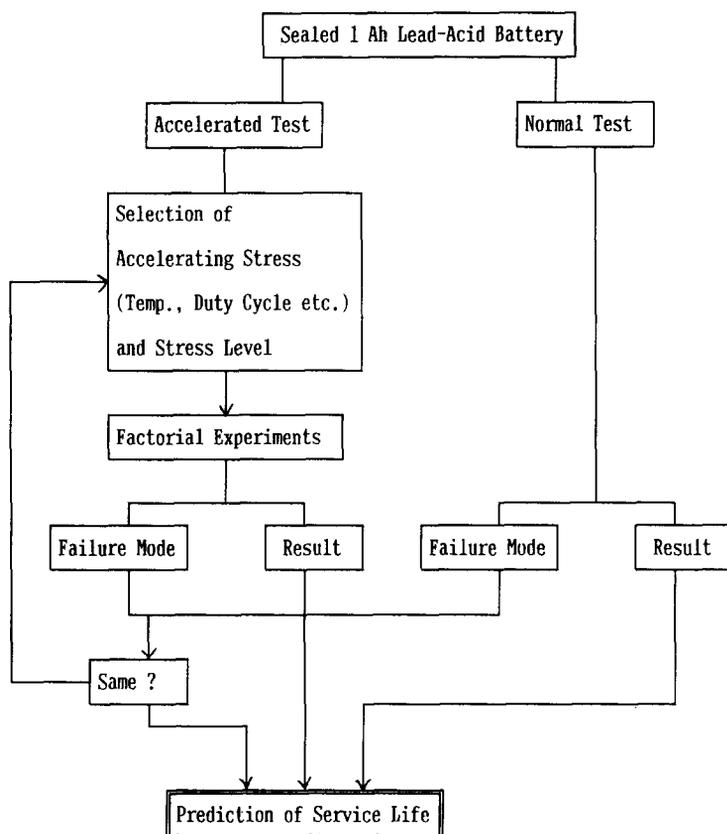


Fig. 2. Schematic diagram of accelerated cycle-life test.

Normal test

This method involves conditions that are closest to those of the intended application.

The test conditions are as follows:

- (i) duty cycle: 1 cycle/day
- (ii) charge time: 8 h
- (iii) discharge time: 16 h
- (iv) DOD: 80%
- (v) overcharge: 10%
- (vi) failure: 80% of initial capacity.

Accelerated cycle test

The duty profile comprised 8 or 16 cycles/day at room temperature. The ratio of the charge-to-discharge time, DOD, and the amount of overcharge were the same as those used in the normal test schedule. The normal and accelerated test conditions are given in Table 1.

Metallographic specimen preparation

The ageing sequence under the 8 cycles/day test was investigated in detail and taken as a representative case. The test was interrupted at 5, 60 and 120 cycles and

TABLE 1

Normal and accelerated test conditions at ambient temperature

Duty cycle (cycles/day)	1	8	16
Discharge time (h)	8	1	0.5
Discharge current (mA)	116	740	1375
Charge time (h)	16	2	1
Charge current (mA)	64	408	756
Rated capacity (mA h)	1160	926	857

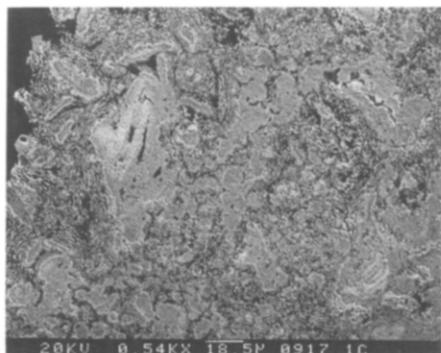


Fig. 3. Fresh positive active material.

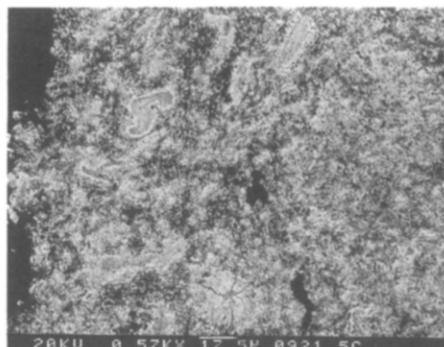


Fig. 4. Positive active material after 5 cycles (duty cycle = 8 cycles/day).

the microstructure of the positive electrode was examined by scanning electron (SEM) and optical microscopy. Metallographic specimens were prepared by impregnating the electrode with epoxy resin under vacuum. After the epoxy had hardened, the specimen was polished with alumina powder. In other tests (viz., 1 and 16 cycles/day), only failed positive electrodes were examined by this method.

Results and discussion

Ageing of the positive electrode

Duty cycle: 8 cycles/day

Figure 3 shows the microstructure of fresh positive active material (PAM). This structure has a dense and compact form. After 5 cycles, voids were formed near the electrode surface, as shown in Fig. 4. With further deep-discharge cycling, the voids increased in size and grew into the inner part of the electrode (Fig. 5). Finally, large voids developed throughout the whole area of the material (Fig. 6). The structure is shown at higher magnification in Fig. 7. This ageing sequence can be explained by the disintegration and the rearrangement of the PAM [1]. The difference in the molar volume between PbO_2 ($25 \text{ cm}^3 \text{ mol}^{-1}$) and PbSO_4 ($48.2 \text{ cm}^3 \text{ mol}^{-1}$) can easily cause the agglomerated active material to loosen into fine particles as deep-discharge cycling proceeds. The fine particles will be rearranged by the oxygen evolved during the charging period to form the so-called 'coraloid' structure. Once this structure develops, the PAM loses its charge/discharge capability.

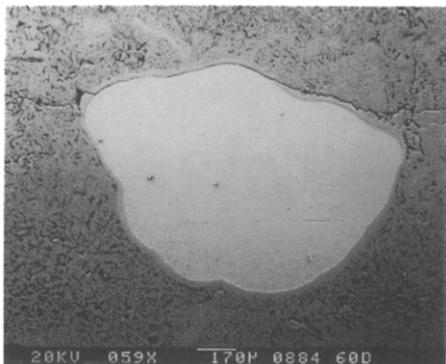


Fig. 5. Positive active material after 60 cycles (duty cycle=8 cycles/day).

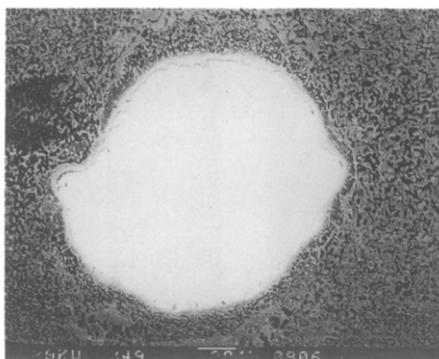


Fig. 6. Failed positive active material (duty cycle=8 cycles/day).

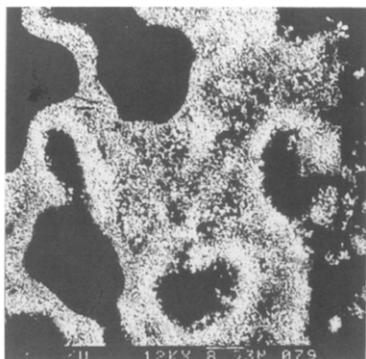


Fig. 7. Material of Fig. 6 at higher magnification.

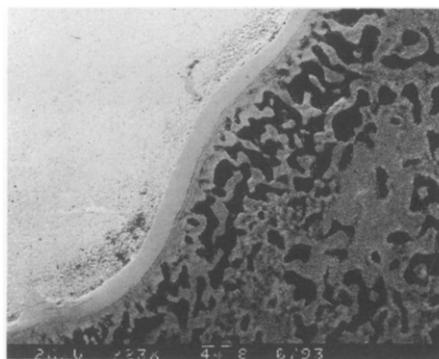
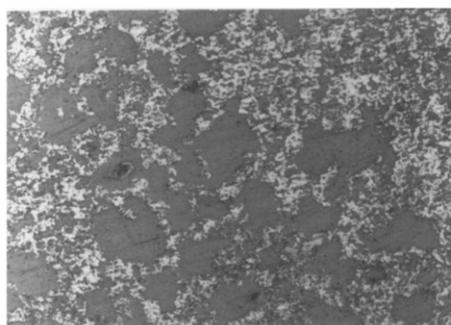


Fig. 8. Interface structure.



(a)



(b)

Fig. 9. (a) Failed positive material; (b) interface structure. Normal test conditions.

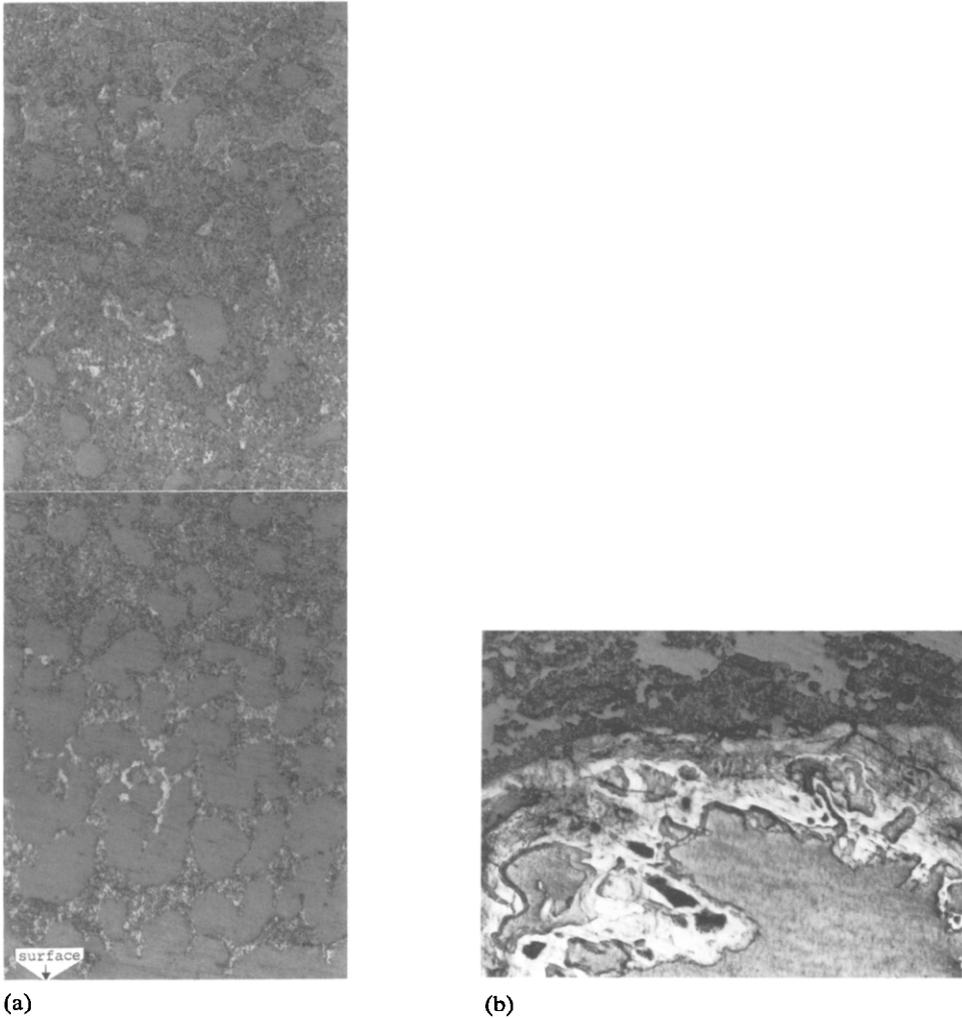


Fig. 10. (a) Failed PAM; (b) interface structure (duty cycle = 16 cycles/day).

The corrosion layer of the grid has a thickness of $\sim 20 \mu\text{m}$ (Fig. 8). The layer is considered to cause only a minor degradation of capacity [1]. Thus, the principal cause of battery failure is disintegration of the PAM rather than grid corrosion.

Normal test: 1 cycle/day

The microstructure of the PAM and the corroded grid of a failed positive electrode under normal conditions are shown in Fig. 9. The coralloid structure, shown in Fig. 9(a), was observed over the whole area of the PAM and the corrosion layer had a thickness of $\sim 100 \mu\text{m}$ (see Fig. 9(b)). Thus, both degradation of the PAM and grid corrosion appear to be responsible for failure of the electrode.

Duty cycle: 16 cycles/day

The microstructure of the PAM and the corroded grid of a failed positive electrode are presented in Fig. 10. A well-developed coralloid structure is present near the

TABLE 2
Analysis of battery failure modes

Test (cycles/day)	PAM		Grid corrosion
1 (normal)	dispersed 'coralloid' (whole area of electrode)	>	uniform ~100 μm
8	'coralloid' (whole area of electrode)	≥	uniform ~20 μm
16	'coralloid' (surface of electrode)	≤	non-uniform, severe

electrode surface. In addition, some parts of the inner area of the PAM remain intact (see Fig. 10(a)). Severe grid corrosion has occurred, as seen in Fig. 10(b). It is therefore concluded that grid corrosion, rather than degradation of the PAM, is the main cause of electrode failure. This is probably due to the high discharge/charge rate which causes the irreversible stress on the electrode to concentrate at the electrode surface and the PAM/grid interfacial boundary.

Conclusions

1. The different duty cycles promote different battery failure modes. A summary of the findings is given in Table 2.

2. Further studies are required to understand fully the relationship between the failure mode and external parameters such as duty cycle, temperature, and DOD.

References

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