Behaviour of lead–calcium alloys in positive plates of flooded and recombinant lead/acid batteries

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Abstract

FIAMM has been producing valve-regulated lead/acid batteries utilizing micro-fibre glass (AGM) separators since 1985 for float applications. Due to the success of the product line, FIAMM has been active in evaluating this technology in other areas, particularly consumer, automotive and traction applications. Flooded cells using lead–calcium grids do not perform as well as conventional lead–antimony grid cells but AGM valve-regulated cells exhibit very different behaviour. This paper briefly reviews some of the main differences in these characteristics.

Introduction

FIAMM introduced the MONOLITE series of valve-regulated recombinant lead/acid batteries into the standby market in 1985 after extensive laboratory and field testing. A detailed description of these batteries may be found in the literature [1–3]. The MONOLITE series has rapidly attained widespread market acceptance, particularly in telephone systems where it provides completely maintenance free and highly reliable standby power. At present, battery sizes range from 25 to 500 A h ($C/10$). This product line has been followed by the FIAMM-GS series FG units that are designed for general use in capacities from 1 to 40 A h ($C/20$). Both product lines utilize gravity-cast calcium alloy grids in both the positive and negative grids to ensure a long and reproducible service life. The positive grid alloy also includes tin to facilitate charge acceptance, particularly after extremely deep discharge. In addition, the batteries are assembled using 'dry charged' plates.

Prior to the MONOLITE batteries, FIAMM had relatively little experience in the characteristics of calcium grid lead/acid batteries, but it was very obvious that the MONOLITE batteries did not act like flooded batteries using calcium grids in several unanticipated respects, particularly deep-discharge cycle-life. Since then, considerable resources have been devoted towards investigating differences and similarities in the behaviour of batteries in flooded (PVC separator) and starved (AGM separator) conditions utilizing lead–calcium alloy grids. The purpose of these studies is to develop the data required to extend the recombinant technology into automotive and traction applications. Similar tests have been conducted to define the problems related to the use of lead–antimony (1.8 wt.%) positive grids. The aim of

0378-7753/91/$3.50

this latter work was to evaluate the advantages or disadvantages derived from the use of low-antimony positive grids in recombinant systems. The results confirmed the problems associated with the use of antimony. Research efforts in recombinant lead/acid batteries for automotive and traction applications are now directed exclusively towards the use of lead–calcium–tin positive alloys.

Standby batteries

Some preliminary results of gas-evolution tests on batteries and single cells made with calcium alloy grids in starved (AGM separator) and flooded (PVC separator) configurations under float conditions are presented in Fig. 1. The experiments were conducted at 2.27 or 2.40 V/cell at 40 °C for 80 days (2000 h). The positive grids in all cells were gravity cast and consisted of an alloy of calcium, tin, aluminium, and (remainder) lead. This is the standard MONOLITE battery grid alloy. Calcium binary alloy grids were used in the negatives. In all cases, the plates were tank formed, washed and dried. The separators in the 'starved' units were standard AGM, while the 'flooded' types used a sintered PVC material. The gas volume was measured by water displacement from a burette and measured at room temperature. Prior to commencement of the tests, the units were given a series of four cycles to insure reliable operation.

The gas volume reported in Fig. 1 is in terms of ml of gas per A h of cell capacity. For flooded designs, the gassing rate is practically constant during the duration of the test. The starved units behave similarly during the initial period of the test but then the gassing rate finally decreases to almost, but never quite, zero. The MONOLITE batteries are designed and fabricated to be operated at 2.27 V at 25 °C. Thus, the above procedure is a highly accelerated test and is designed to evaluate units in a limited time rather than over the ten-year design life. It should be mentioned that the float-current of the starved units at these voltages was about 2.5 times the float current of their flooded counterparts.

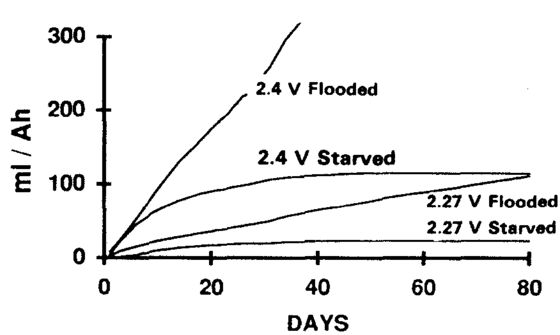

Fig. 1. Cumulative gas vented from recombinant and flooded Pb–Ca batteries during float at 2.27 and 2.40 V/cell at 40 °C.

The expected gassing rate, calculated from the float current, reveals that all of the units exhibit some recombination. Chromatographic analysis of the gas released from starved batteries and single cells detected only hydrogen (after the initial stabilization period). The use of the AGM separator facilitates oxygen recombination, but does not completely eliminate all of the battery gassing. The batteries must use a pressure-relief valve in order to prevent build-up of the excessive internal pressures, particularly in the event of battery abuse or charge failure.

Units made with antimonial grids in the starved configuration exhibit an initial gas evolution that is higher than the analogous calcium configurations; this finding is demonstrated in Fig. 2. After a longer period of time, the antimony system also achieved a drastic reduction of gas emissions to an almost zero rate. It should also be noted that the float current of the antimonial units at 2.27 V/cell was fairly stable over the test period, but about twice the float current of the calcium types. At 2.4 V/cell, the float current of the antimonial designs continued to increase with testing and reached a final float current which was about four times that of the calcium versions.

A comparison was made of the cycle-life of MONOLITE batteries made with calcium grids and other batteries using low-antimony positive grids. The test procedure comprised 2 cycles per day with 4 h discharge at $C/5$ and 8 h charge at 2.4 V/cell (with a current limit of $C/5$). Figure 3 represents data obtained on both the performance (as a percent of the nominal capacity) and the weight loss of the batteries. The results were considered to be encouraging and stimulated further experimentation with recombinant batteries for different applications, using the same lead–calcium–tin alloys for the positive grid.

Automotive batteries

The use of recombinant batteries for automotive applications is of great interest, particularly since such units could be placed in a wide variety of locations — even outside the engine compartment. The higher initial voltage

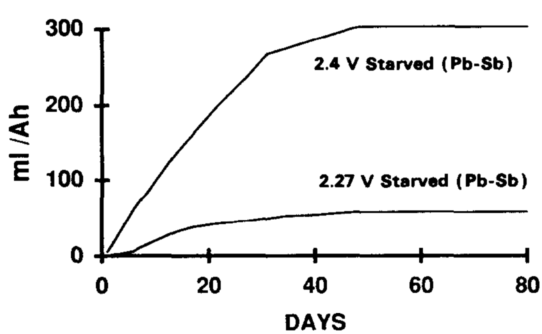

Fig. 2. Cumulative gas vented from recombinant Pb–Sb batteries during float at 2.27 and 2.40 V/cell at 40 °C.

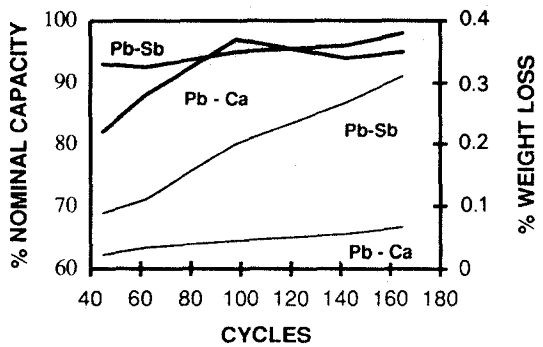

Fig. 3. Performance (—) and weight loss (—) from recombinant Pb–Sb and Pb–Ca batteries during cycling at 2 cycles per day; 80% DOD.

under high-rate conditions, as compared to standard flooded types of battery, would compensate for the additional *IR* drop due to the increased distance from the starting motor.

Figure 4 compares the performance of recombinant and flooded batteries during a modified SAE cycling test. In both situations, the plates are the same but in the case of the flooded batteries, positive polyethylene envelope separators were substituted for the AGM. Figure 4 is the discharge time(s) above 7.2 V at the cold-cranking current measured periodically during the test. The electrolyte specific gravity was the same in all cases. The cycle-life of batteries made with AGM was about twice that of flooded batteries. In addition, the discharge plateau voltage was somewhat higher for the AGM batteries. Other tests on these batteries are still in progress and will be reported in future papers.

Traction batteries

Work on valve-regulated recombinant batteries for traction applications was started a few years ago with comparative testing of elements made

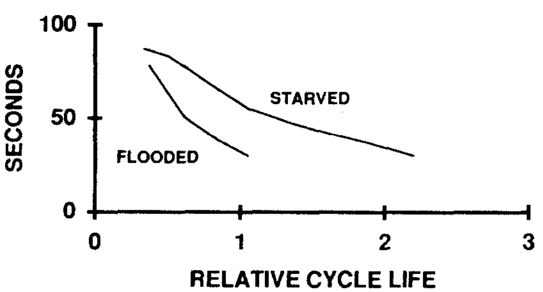

Fig. 4. Performance of flooded and starved automotive batteries during SAE cycling test.

with round-section tubular positive plates. The alloys were low antimony and lead–calcium–tin, while the separator was AGM. The initial results with low-antimony grids confirmed the anticipated problems associated with antimony transfer to the negatives. Thus, only tests on batteries having lead–calcium–tin alloy grids were continued. In the next step, an attempt was made to establish the effects of using square-section tubular positive plates. During these tests, considerable data was collected, viz., profile of the potential during charging and discharging, final charging current, weight loss, acid stratification, internal pressure, gas evolution. Some units were disassembled for X-ray diffraction and porosimetic analysis of the positive and negative active materials, as well as for determination of the electrolyte concentration. The efficiency of the acid-stratification detectors was also checked.

The cycling performance of the above batteries was poor: only a few cycles were achieved. Analysis indicated the presence of considerable electrolyte stratification, especially in the cells made with round-section tubes. Remembering that with the MONOLITE batteries (of course with flat plates) stratification problems did not occur and the batteries cycled quite well, it was decided to verify the effect of pasted flat-positive traction plates. Another series of units was made and, to give comparative evaluation, both flat pasted and tubular positive plates were used. In some units, a small amount of fumed-silica was added to minimize the acid stratification. Some units were also constructed with a traditional separator in a flooded condition. After initial characterization, all the units were subjected to two cycles per day with 3 h of discharge at $C/5$ and recharge for 9 h at a constant voltage of 2.4 V (with current limitation of $C/5$). The temperature during the test was regulated at 25 ± 1 °C. All the batteries had a nominal capacity of 110 A h ($C/5$ rate). Starved types were filled with 1.290 sp. gr. electrolyte. Figure 5 compares the percent of the nominal capacity during the cycle test of recombinant tubular designs with and without silica. The results are not very good and silica is found to exact little beneficial effect. Figure 6 compares the first 580 cycles with pasted-plate units utilizing AGM, with and without silica. These tests are still in progress. The performance has been very good

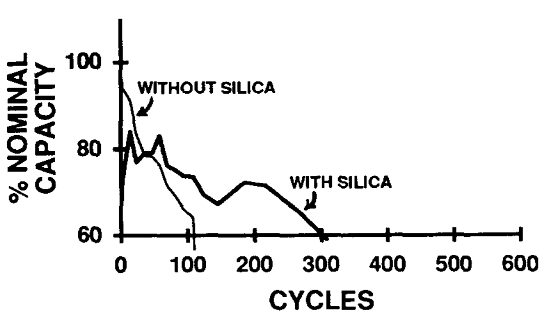

Fig. 5. Capacity loss from tubular recombinant traction batteries during cycling at 2 cycles per day; 60% DOD.

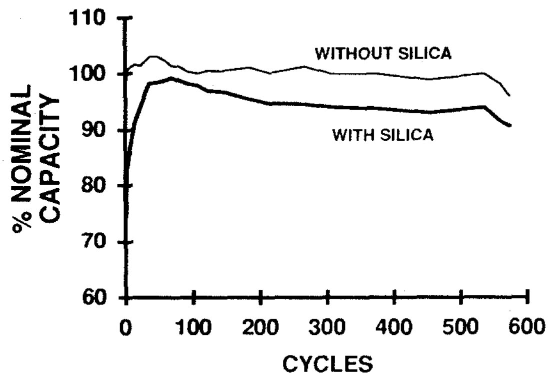

Fig. 6. Capacity loss from flat recombinant traction batteries during cycling at 2 cycles per day; 60% DOD.

with little loss of capacity. The addition of silica results in a decrease in capacity. To date, these units have delivered more than 700 cycles and are still in good condition.

For flooded cells, the electrolyte was calculated to provide the same total amount of sulphate as in starved cells; in practice, the specific gravity was 1.25. The cycle-life of the flooded elements is shown in Fig. 7 and is much shorter for both the tubular and, particularly, the flat plates. In fact, the tubular versions give about twice the cycle-life of their flat-plate counterparts. This can be explained by greater retention of active material due to the gauntlet construction. Autopsy of the cells confirmed this assumption: shorts due to positive active material shedding were observed in flat-plate cells while the tubular-plate designs contained less sludge and thus retarded the formation of shorts.

Figure 8 summarizes the behaviour of the tubular and pasted positive plates under starved and flooded conditions. The definitive difference between the flat starved elements and all the others is rather obvious. The tubular elements exhibit slightly better behaviour in the flooded than in the

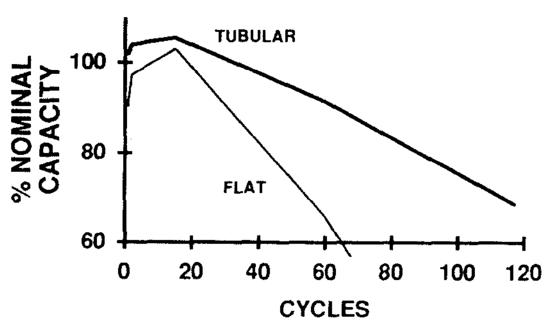

Fig. 7. Capacity loss from flooded traction batteries during cycling at 2 cycles per day; 60% DOD.

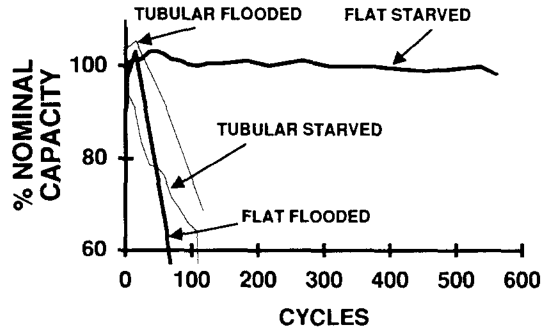

Fig. 8. Capacity loss from Pb–Ca traction batteries with flat (—) and tubular (—) plates in starved and flooded condition during cycling at 2 cycles per day at 60% DOD.

starved condition. Other data have been obtained during the course of these experiments and will be presented at a later data when the results are complete.

Conclusions

This work has reconfirmed the 'antimony-free effect' for calcium grid cells and batteries of flooded design: very little cycle-life is obtained due to softening and shedding of the positive active material. When cells are designed with the glass mat separator normally used for oxygen recombination, the antimony-free effect no longer appears to be present. Autopsy of batteries at the end of the life and analysis of the results suggests that the AGM separator contains effectively the positive active material. Indeed, it appears that there is sufficient interparticle and particle-to-grid electrical contact to maintain excellent performance in both automotive and traction units.

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