ACCELERATED LIFE CYCLE TEST. ADVANCED LEAD–ACID CELLS AT ELEVATED TEMPERATURE

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Summary

Optimized designs for advanced lead–acid, load-leveling batteries were selected in a limited time period by means of an accelerated life cycle test combining two 80% D.O.D. cycles per day with a target mean test temperature of 71 °C. Preprototype load-leveling cell designs were selected from 60 cell design variations in three fractional factorial test plans. Some of the successes and limitations of this accelerated test are discussed.

Test objectives and methods

EXIDE recognized the possibility of a 12-fold acceleration in time, compared with the time required for one 80% D.O.D. cycle per day, 5 days per week load-leveling cycle, by combining a 2 cycle per day 80% D.O.D. and an operating mean temperature of 71 °C (160 °F) [1]. A demonstration of 4000 cycles at 25 °C would be possible in 333 days' minimum time for cells cycling at 71 °C for seven days per week.

The cycling regime selected consisted of 2 cycles per day, 4.4 h discharge delivering 80% of the rated 5 h cell capacity, coupled with a 7.6 h 2-step constant current charge which comprised a 24% overcharge each cycle. Full size 33 × 44 cm industrial battery plates were used in all test cells so as to reduce the scale-up factor; however, 17 plate, 3 kW h cells were evaluated as a prediction of performance of a 35 plate, prototype 6 kW h cell, rated at the 5 h rate to 1.67 V per cell (25 °C). At intervals of 50 - 100 cycles, capacity measuring cycles were performed on each test cell by cooling the cells to room temperature (generally from Friday afternoon to Monday morning) and then discharging the cells at constant current (5 h rate capacity divided by 5) to 1.60 V per cell.

Automatic equipment recorded individual cell voltages during all cycling, currents, times, acid temperature; stored the data on tape, and later computer capacity and energy outputs *versus* operating time during both discharge and charge. Condensed summaries of these data became the basis for characterization of cell designs and comparisons by statistical analysis.

Three fractional factorial tests were run simultaneously. Each test was on 20 each of 17 plate cells in a variety of designs. Two factorials were on cells designed to be positive limited. One factorial was on cells designed to be negative limited.

Cycling began with characterization cycles at 25 °C at a number of discharge rates from the 3 h to the 20 h rate. The temperature of the cells was increased stepwise, with 5 - 10 cycles at 40 °C, then 5 - 10 cycles at 50 °C until the target temperature of 71 ± 3 °C was achieved.

For cycling, each 17 plate cell was supported on a plywood rack. The jar end-walls parallel to the plane of the plates were compressed to zero jar bulge using plywood clamps. One layer of glass-wool insulation (8 cm thick) was wrapped around the clamped cell to retain internal and externally applied heat. Two 50 W pad heaters were found to be necessary to achieve the 71 °C acid temperature goal. These were installed on the walls of each cell, opposite the plate edges, before the insulation wrap was applied.

During the two cycle per day regime, acid temperature was monitored and recorded. A thermocouple was mounted in a polycarbonate test tube filled with silicone oil. The test tube dipped about 6 in. into the acid electrolyte in one corner of the cell. Automatic equipment recorded and printed out the acid temperature before and after each discharge and before and after each charge. Full temperature profiles were thus available to verify temperature control. From cycle 200 - 900, an operating temperature range of 71 ± 3 °C was successfully maintained.

Cycling was continued until a cell failed to deliver 80% of the rated 5 h energy output to 1.60 V per cell on two successive capacity measuring cycles at 25 °C, or failed to deliver the discharge capacity required during the 4.4 h discharge of the 2 cycles per day test at 71 °C.

Limitations of the accelerated high temperature test

Any cell subjected to the accelerated 71 °C cycling test must be made with materials (jar and covers, separator system, adhesives, insulators, etc.) which can withstand long-term exposure to sulfuric acid at 71 °C. If materials survive such exposure, room temperature exposure during real-time tests should be possible for the long lives of a utility load-leveling battery. The failure modes of test cells would then be restricted to the failure modes of the positive and negative plates alone!

In the EXIDE test cells, component materials were selected, on the basis of the best available information, to be capable of surviving 71 °C exposure while immersed in acid with a test gravity range of 1.260 - 1.310 (top-of-charge). No life limiting problems were observed for microporous rubber separators, glass fiber absorber wraps (random or slyver mat), perforated polyvinyl chloride retainers, or high impact styrene insulators.

During 2 years of elevated temperature cycling, interactions were observed between the heater pads and the jar walls in the areas of immediate contact. In some cases, heater pad failures resulted in 110 V a.c. electrical shorts with burn damage on the jar walls. In most cases we were able to rejar and recover the damaged cells *without* damage to the element assembly. Thus, reported cycle life is based on element assembly failure. In the future, glass jars or more temperature resistant plastic jar materials (perhaps polysulfone) will be likely candidates for the high temperature accelerated test cells.

Near the end of the test (after real time cycle 965) the 50 W heater pads on each cell were removed and the glass wool insulation thickness doubled. Without heaters, a stable cycling range of 60 - 65 °C was maintained using heat generated from within the cell, largely during the 24% overcharge.

Temperature changes during the accelerated test were integrated over 25 °C characterization cycles, the stepwise approach to 71 °C, and the final reduction upon removal of the heater pads, giving a weighted average test temperature of 66 °C. This was accomplished by using the acceleration factors, F, relating cycles at any temperature, t_E °C, to the equivalent cycles at 25 °C. The equation is [2]:

$$\ln F = \alpha(t_E - 25\ ^\circ\mathrm{C}) \quad (1)$$

where α has the value 0.039. In this relation, $F = 6.0$ at 71 °C and 1.0 at 25 °C, and 4000 cycles at 25 °C are equivalent to 667 cycles at 71 °C. The cumulative value of t_E reached 66.0 °C on the 493 real-time cycle and remained within the range 66.0 ± 0.5 °C through the last real-time cycle (1673), equivalent to 8470 cycles at 25 °C, achieved by the longest life cell in the test program.

This equation presumes a linear relationship for cycles delivered in the range 25 - 71 °C. Practical experience in cycling batteries at controlled temperatures from frigid to hot extremes predicts a maximum cycle life in the range 25 - 45 °C, with cycle life declining from this maximum at cooler or hotter temperatures [3]. The maximum is likely to be system and design dependent. The best hope is that as operating temperature increases, degradation processes at the positive and negative plates will have similar activation energies. EXIDE anticipated that positive grid corrosion would limit positive life, and negative active material sulfation would limit negative plate life. In fact, all 60 cells failed by energy decay with both processes contributing. The longest lived cells of optimized design failed by energy decay with the negative plates limiting output (monitored by PbO_2 reference electrodes during 100% depth capacity measuring cycles).

Successes on the accelerated test

EXIDE/Argonne National Laboratory/Sandia National Laboratory, who jointly funded the cell development and testing program, agreed to have Battelle, Columbus Laboratories perform a critical analysis of the fractional factorial test data. Battelle's analysis revealed the following relationships between cell design variables and cycle life [3]:

TABLE 1

Multi-temperature cycle life on 6 kW h prototype cells (6-30-85)

Test temperature target (°C)	Life mean (°C)	Cell sample size (ea.)	Cycles to date or to failure (F) (ea.)	Cycle life goal (ea.)	Percent of goal	Equivalent 25 °C cycles (Calc.) (ea.)
40	39	6	2324	2220	105	4190
50	50	6	1582	1495	106	4430
60	54	3	916	1250	73	2965
70	66	4	1012 (F)	775	130	5220

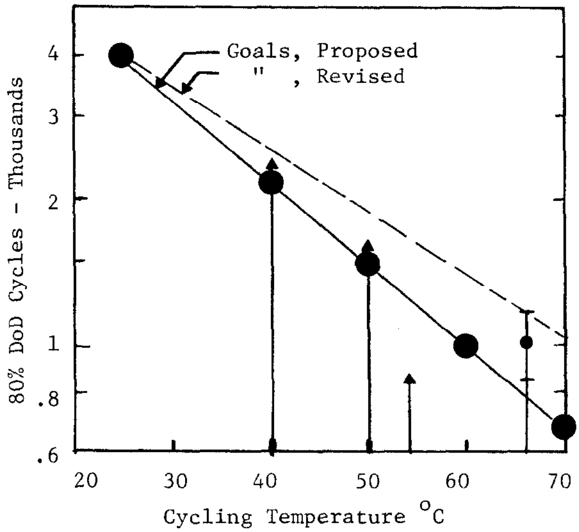

Fig. 1. Cycling status (6/30/85).

Equivalents of acid between plates (and in the pores of plates) were directly proportional to real-time cycles at 66 °C.

Negative plate depth of discharge was indirectly proportional to log real-time cycles at 66 °C and to equivalent 25 °C cycles.

In the range 1.260 - 1.310 specific gravity, lower specific gravity increases the cycle life at 66 °C of both positive and negative limiting cells.

There were no significant differences in extending cycle life between random mat and parallel glass mat fibers in positive plate wraps.

A perforated PVC outer wrap on the positive plates had a beneficial effect on cycle life.

Prototype 6 kW h cells were made with a design selected from those evaluated on the accelerated high temperature test. Single cells were tested at EXIDE, and 18 and 36 kW h modules are on test at ANL/National Battery Test Laboratory [4]. Test results to date (6/30/85) are summarized in Table 1. Battelle suggested that the value of α in the relationship

$$\ln F = \alpha(t_E - 25\ ^\circ\mathrm{C}) \tag{2}$$

be decreased from 0.04 to 0.03. Figure 1 shows a plot of the relation with $\alpha = 0.04$ as a solid line, and $\alpha = 0.03$ as a dotted line. Cycle life achieved to date from Table 1 is plotted as vertical bars. These tests are continuing with no cell failures to date. Only the tests at 66 °C have been completed.

Conclusions

(i) The original goals for cycle life of prototype cells at 40, 50 and 70 °C have been reached or exceeded. Tests are continuing.

(ii) An optimized prototype cell design was selected based on an accelerated, high temperature, deep cycle test conducted in the temperature range 70 ± 5 °C, assuming temperature acceleration factors F governed by the expression $\ln F = \alpha(t_E - 25\ ^\circ\mathrm{C})$, where

$$F = \left(\frac{\text{Cycles at 25 °C}}{\text{Cycles at } t_E}\right) \tag{3}$$

(iii) Best projections now suggest decreasing the presumed value of α from 0.039 to 0.030, based on tests completed at 70 °C.

(iv) Longest life cells were negative limited.

(v) Positive grid corrosion, while contributing to energy loss, has not been life limiting in these industrial cells.

(vi) While many questions remain unanswered, the accelerated cycle test at elevated temperature for long life lead–acid batteries appears to be a viable alternative to the very long, expensive room temperature test. More data are needed to establish experimentally the relationship between the acceleration factor (F) and the cell operating temperature (t_E).

References

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