DEVELOPMENT OF A LONG LIVED, WIDE PLATE FORMAT VRLA CELL

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VRLA PERFORMANCE ISSUES

Since the widespread introduction of the absorbent glass mat (AGM) valve regulated lead acid battery in the 1980's, the battery industry has worked to extend the life and improve the reliability of the product. This effort has had mixed results. While life expectancy and predictability have improved since the product's introduction, the most popular commercially available VRLA products are not as predictable or long lived as traditional flooded battery designs. This unpredictability and shortfall in life is the key reason why flooded cells are still preferred over VRLA in many applications, despite VRLA's advantages in energy density and ease of installation and operation.

Initial versions of prismatic VRLA batteries (generally multi-cell monoblocks) were simply adaptations of calcium alloy flooded products, with changes to separators and internal structures to immobilize the electrolyte, and the use of higher strength sulfuric acid to offset the reduced electrolyte volume. "Ten year design" was a typical life claim, based on experience with equivalent thickness plates and alloys in flooded batteries.

Customer experience with the earliest prismatic VRLA product fell far short of expectations. Typically the batteries lasted less than half their claimed lives, and some failed in new and unexpected modes. These new failure modes included open circuits inside the battery cells, thermal runaway failures, and rupture of the plastic jars and covers – all of which were extremely disruptive to customer applications "20 year design life" VRLA cells (generally 2 V monoblocks) fared little better – with some customers having replacement policies at less than half the batteries claimed life. The continuing problems lead to customer demands that battery producers fully warranty their products for a substantial portion of their expected lives. These warranty requirements had not been necessary with flooded products, and caused considerable consternation among battery manufacturers.

The field experiences lead to intense research and development efforts on the part of battery producers. There was a vast body of knowledge available on the performance of flooded product – both under lab conditions and in the field. A natural inclination was to use this body of knowledge to compare the behavior of the VRLA product to flooded batteries, note the differences, and then work towards changes that would improve the life expectancy and eliminate the instances of catastrophic failure of VRLA cells. Naturally, different organizations approached the problem in different ways, each achieving varying degrees of success. These approaches can be categorized generally as follows:

1. Robust Design: Using the principles of flooded battery design, components (particularly the positive plates and active materials) were designed very conservatively. Plate thicknesses were increased, plate counts within cells were decreased, and internal grid members were enhanced. In response to problems with excessive plate growth, the alloys used for positive grids were screened and chosen to have the lowest feasible growth rates when polarized in sulfuric acid. Space around the plates was also increased, and plate support systems were introduced that allowed growth of the positive plate without interfering with the exterior plastic (jar/cover/terminal seals) or shorting to the negative plates. In some cases the active material was enhanced by introduction of tetrabasic lead sulfate (TTB) – a material shown to increase cycle capability in motive cells and a key ingredient in the 40 year warranty life Round Cell. This design approach was one element in the development of the C&D Liberty 2000 series of large format 2 V telecommunication cells.

2. Reduced Float Current: A major difference between VRLA and flooded cell behavior is float current acceptance. At the same charge voltage a flooded battery could have a float current that was an order of magnitude lower than a VRLA product. Under high temperature conditions this difference became greater – VRLA products were prone to a positive temperature feedback phenomenon known as thermal runaway that caused catastrophic field failure. In this design approach the goal was to reduce the float current in VRLA designs through changes in the design of the positive and negative active material, and the separator used to space and insulate the plates. Onoda, et al.,[1] describe this type of design effort in the development of the Panasonic MSE product line.

3. Catalysts: Another obvious difference between flooded and VRLA products is the limited quantity of water available over the life of the VRLA cell. Dry out of VRLA cells has been noted as a failure mode itself, and as a significant contributor to thermal runaway and excessive positive plate growth and corrosion. Any means of conserving water in the cell would naturally be desirable. This lead to the development of palladium and other precious metal catalysts, designed to scavenge hydrogen and oxygen in the cells and recombine the gases into water. A palladium based catalyst was a feature introduced first in the C&D Liberty 2000 product line, and is now offered commercially through other vendors. The behavior of the catalyst in the cell is subject to some debate, with differing views offered by Vaccaro et al.,[2] Jones and Feder,[3] among others.

In addition to the general design approaches, there have been improvements made in the design and production of VRLA battery systems across the industry. These have included better plastics, better battery systems (thermal management in rack systems), front access termination for small multi-cell monoblocks, and continued expansion of product offerings to higher and lower capacities.

DEVELOPMENT OF WIDE FORMAT ADVANCED TECHNOLOGY (AT) PRODUCT LINE

In 2003 C&D Technologies entered into an agreement to purchase the production facilities and license the technology for the Panasonic MSE battery line. This provided a unique opportunity to study the effectiveness of two different approaches to VRLA product development. More importantly, it allowed the opportunity to see if the two design approaches could be combined synergistically to create a product with an improved life and improved float behavior.

Product Design

On completion of the transaction it was quickly apparent that it may be feasible to produce cells that combined the characteristics of the Liberty 2000 and MSE line. Some choices had to be made between product characteristics – these in general were dictated by production requirements:

Design Feature Selection – Advanced Technology Product

Design Feature	Liberty 2000	MSE	Advanced Technology (AT)
Positive Alloy	Low calcium – tin	Higher calcium – High Tin	Liberty 2000 Low calcium – Low tin
Positive grid thickness	0.260” (6.6 mm)	0.230” (5.8 mm)	Liberty 2000
Plate width	7.9” (203 mm)	5.75” (145 mm)	Liberty 2000
Active Material	Synthetic TTB added	No TTB added	MSE
Plate Suspension	Top and bottom – plastic support	Top only – strap/post support	Liberty 2000
Jar/Cover material	PVC	FR Polypropylene	PC-ABS (See note)

Design Feature Selection – Advanced Technology Product			
Design Feature	Liberty 2000	MSE	Advanced Technology (AT)
Formation method	Dry charged plate/ vacuum fill/ activation	Gravity fill, jar formation	Gravity Fill-Jar formed
Jar design	Self supporting (<120°F)	Self supporting	Self supporting
Vent release set point	2 PSI	2 PSI	2 PSI
Catalyst	Present	None	None

NOTE: Neither PVC or FR polypropylenes were suitable for the new format product – peak temperatures in jar formation would prevent use of PVC; and FR polypropylene was not compatible with the Liberty jar/cover molds. A flame retardant PC-ABS polymer alloy material had been in qualification testing for the Liberty 2000 and was adopted for the new design.

All other aspects of initial production were handled by running Liberty 2000 components on the MSE pasting equipment, and cell assembly on Liberty 2000 assembly equipment. As the initial test was simply to validate whether an 8" wide plate could be handled on the new battery production equipment the qualification goals were modest – capacity equivalent to or better than the Liberty, and a fast life test indicating that the resulting cell could survive 60-90 days at 71°C.

AT Prototype Production

On completion of the design evaluation two sets of prototypes (460 and 1500 AH/cell) were produced using combinations of MSE and Liberty equipment. In all cases MSE production methods were used for plate production, while Liberty assembly equipment was used for physical cell assembly. The cells were formed using MSE processes, adapted for the larger Liberty 8" plate format. No significant problems occurred during prototype production.

Cell Testing - Procedures

Accelerated life testing of the new product was performed according to Bellcore Standard TR-NWT-001200 at 71°C (160°F). Capacity tests were performed at 30 day intervals, from 2.26 VPC float. Cell weights, impedances, and other measurements were also taken during these capacity test pulls. The data from the testing were compared to previously tested MSE and Liberty 2000 cells, as well as data from standard telecommunication grade flooded product. It should be noted that the Liberty cells were run without catalysts – the high temperatures and expected gassing rates were found to result in unacceptably high catalyst temperatures, which could deform or damage nearby plastic parts. The only anomaly that occurred during testing was an equipment error that caused over-discharge and reversal of one battery set. This set was at the 230 day point in testing, and the test had to be halted due to product damage.

Initial Results – Capacity

Initial capacity of the new products exceeded expectations – the Liberty 2000 was designed to provide a industry standard minimum of 95% capacity on delivery, and the new products (designated AT-9 and AT-27 for the 460 and 1500 AH cells respectively) delivered more than 100% capacity on delivery. The increase in capacity was found to carry through from the one hour to eight hour discharge rates.

Initial Results – Float current

Float current in the new cells were measured after a minimum of seven days on float at 2.26 VPC, at room temperature. The values measured were compared to MSE and Liberty 2000 cells – see Figure 1. The 6 mA/100 A-hr found in the new product and in the MSE were comparable to typical flooded battery float current values.

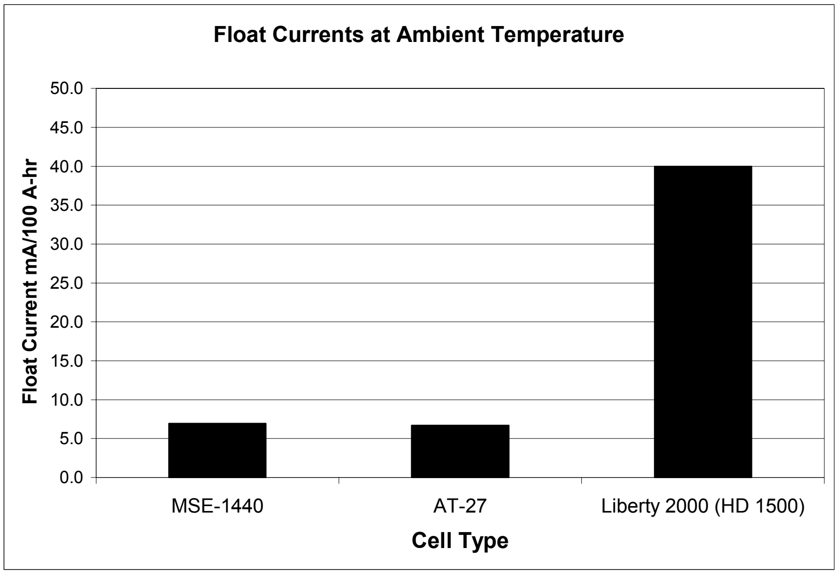

Figure 1

Accelerated testing – Float current

Monitoring of float currents continued daily during high temperature exposure. Figure 2 shows float currents at 71 C for the three products types being evaluated – a Liberty 1500 AH system, an MSE 1440 AH system and the new AT 460 and 1500 AH systems. The data has been normalized to mA/100 Ah capacity to ease comparison. All systems were maintained at 2.26 VPC – the recommended room temperature float voltage. These data show that the MSE active material design maintains its low float current characteristics at high temperatures, and that this behavior was transferred to the AT product. The Liberty design (run without catalyst), on the other hand, showed evidence of exponentially rising current acceptance – a possible indicator of thermal runaway. This phenomena was not unexpected at the high test temperatures (30°C higher than the maximum recommended operating temperature), especially when the catalyst was removed for the test. The two designs with MSE active material, however, showed **no** signs of rapidly increasing float current, even without catalysts.

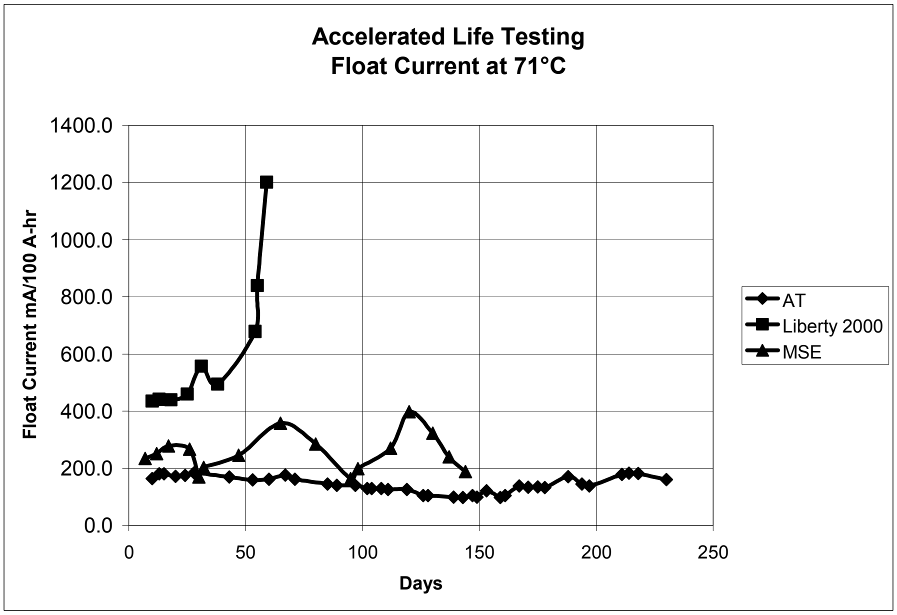

Figure 2

Accelerated testing – Capacity results

As noted, the battery systems were removed at regular intervals for capacity testing at the 8 hour rate. The data are shown in Figure 3. The results achieved were unexpected. The Liberty 2000 cells (without catalysts) dropped steadily in capacity with time, reaching 80% capacity in roughly 58 days. The MSE product showed far better behavior – a more gradual decrease in capacity with time, crossing the 80% limit in ~145 days, better than twice the Liberty performance. The best performance was found in the two AT systems – no significant decline in capacity over the course of testing – 200 days for the 1500 Ah product and 180 days (and continuing) for the 460 Ah product.

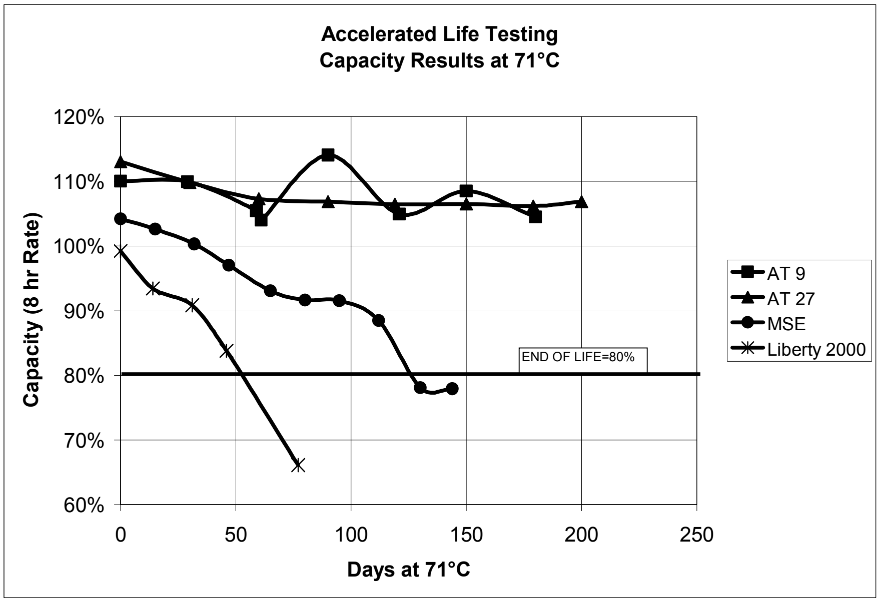

Figure 3

Weight measurements taken during the course of the testing confirm that the extended life on test was associated with lower water loss (Figure 4). This appears to be a direct effect of the low float current technology. The rate of water loss between the MSE and AT designs was roughly similar, however, the more robust design of the AT results in a greater initial reservoir, and extended time before harmful effects occur.

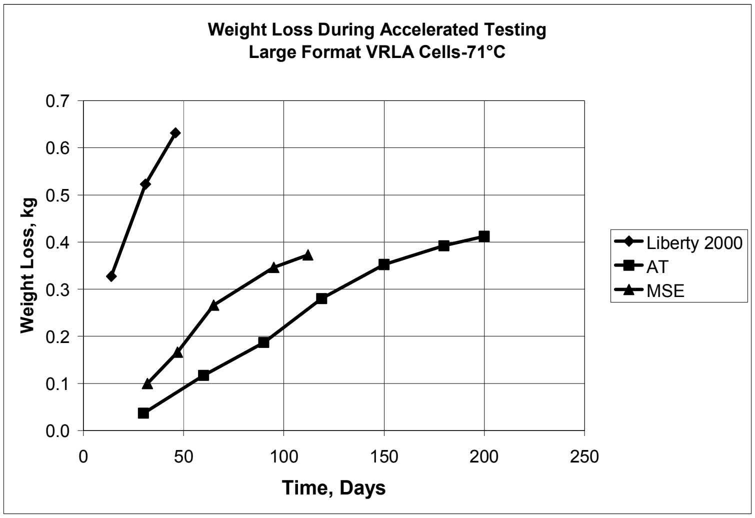

Figure 4

The long life on the 71°C point leads to a natural question – can a VRLA product match flooded battery performance when tested under similar conditions. While complete testing is not available, Figure 5 shows that this is indeed a possibility.

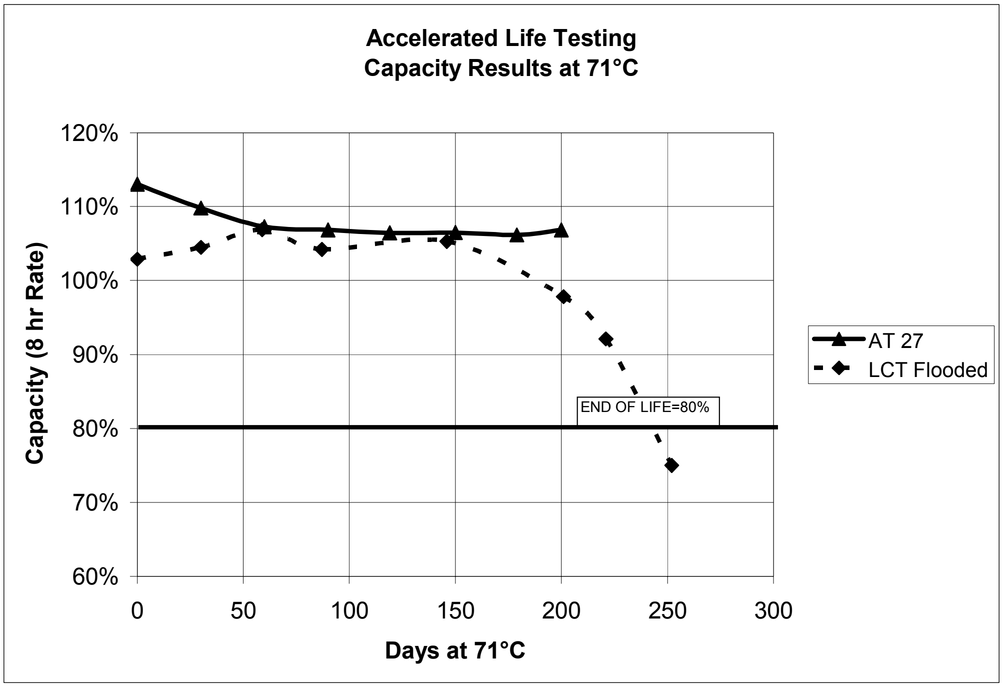

Figure 5

CONCLUSIONS AND FURTHER WORK

The results of the life testing to date indicate that low float current active material design is the key to achieving stable performance in large format VRLA cells. It also shows that combining this active material design with a robust structural design – thicker grids, greater liquid reservoirs, and internal support elements - can result in a VRLA product that approaches, and may exceed, flooded battery performance on standard accelerated tests. This behavior is likely to result in more reliable performance at ambient and elevated temperature customer applications, with the ultimate goal to provide customers VRLA reliability expectations equal to that of a flooded design.

Further work is underway to characterize the performance of the new product – at other accelerated temperatures, at ambient temperatures, and under cycling conditions. Work is also proceeding to see if the performance of the product is correlated with internal resistance measurements.

REFERENCES

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[1] Y. Onoda, M. Noda, H. Hori, H. Jimbo, Y. Tanabe "*Development of a Large Sized VRLA Long Life Battery for Telecommunication*" Proceedings of the Twentieth INTELEC, San Francisco, CA 1998

[2] F. Vaccaro, J. Rhoades, B. Le, J. Timmons "*A Catalyst In A VRLA Cell: A Tafel Look, Etc*" Proceedings of the Twenty-Third INTELEC, Edinburgh, Scotland, 2001

[3] WEM Jones, DO Feder "*Behavior of VRLA Cells On Long-Term Float; Part 2*" Proceedings of the Eighteenth INTELEC, 1996