

VRLA/AGM BATTERIES AND CYCLIC APPLICATIONS

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GENERAL

In this study, a collection of different experiments on VRLA/AGM monoblocs has led to a variety of data with favorable indications and conclusions about design factors and cycle performance of VRLA batteries. The active mass/Ah-ratio as well as the apparent mass density of the positive active mass has been found to be the overriding design factor. Knowledge of the different influences in the discharge regime helps additionally to dimension the battery according to the cyclic requirements.

INTRODUCTION

Lead acid batteries in their most recent design, the VRLA type, are used extensively in standby power applications, especially in telecommunication systems to power modern voice and data networks. In regions where power outages can frequently occur or regular capacity tests are performed, e.g. by remote-controlled battery diagnostic systems, the cyclic endurance of the installed battery can be a critical success factor of the whole installation.

These diagnostic systems are part of the rectifier/load management electronics. In such diagnostic systems, the charging voltage is lowered, and the available system load is used to partially discharge the battery. During this discharge, the voltage vs. time curve or the voltage at a fixed time is to make a judgment if the battery is “good-fair-bad”. An increasing interest from the telecom operating companies and Original Equipment Manufacturers (OEMs) in the specific skills of the different battery brands or battery models in charge/discharge cycles has become noticeable. Specific discharge regimes, especially those to a medium depth of discharge (d.o.d ~40%) and/or high rate discharges ($>1I_{10}$), could actually do more harm than good and push certain Lead Acid battery designs into a early capacity loss.

It is a well-known fact that charge and discharge cycles wear out the structure of the positive and negative mass and that this causes capacity losses. One of the key factors which affects the performance during charge/discharge cycles design of VRLA cells is the investment in positive active mass. In this study, a selection of charge/discharge test data shows the influences of different charge/discharge regimes to certain design as well as the behavior of different cell designs during specific charge/discharge tests.

For this purpose, different VRLA monobloc designs with AGM technology were chosen and repeatedly charged and discharged with a 24h round trip routine. The key parameters are listed in Table 1 below.

Table 1. Cell designs utilized in this study.

Design	VRLA monobloc type A	VRLA monobloc type B	VRLA monobloc type C
Parameter			
Unit nominal voltage	6 V	6 V	12 V
Positive active mass (PAM) / Ah ratio	13.5 g/Ah (C ₁₀)	16.5 g/Ah (C ₁₀)	13.0 g/Ah (C ₁₀)
Electrolyte (sulfuric acid) density at 20°C	1.30 g/cm ³	1.28 g/cm ³	1.30 g/cm ³
Electrolyte quantity	11 g/Ah (C ₁₀)	13 g/Ah (C ₁₀)	10 g/Ah (C ₁₀)
Float charge voltage	2.27Vpc	2.25Vpc	2.27Vpc

EXPERIMENTAL

The charge and discharge sequences were run using a programmable battery tester, type UBT 150-6, UBT 50-35 and UBT 30-6, manufactured by Digatron Germany. The discharge was always carried out at constant current, whereas the charge was carried out under limited constant voltage conditions with the voltage limited to the float voltage setting.

The end-of-discharge voltages were recorded and organized with a data logger HP 34970A by Hewlett Packard, USA and an Agilent BenchLink Software package.

Experimental set-up

The data in this paper has been collected from tests with 12V and 6V VRLA monoblocs. New, fully-charged monoblocs were used for each new test sequence. The monoblocs were always operated at a room temperature of 18° to 28°C.

For each test, two 6V monoblocs were serially-connected (as a 12V battery) to the cycling test circuit and subjected to the daily discharge routine. 12V monoblocs were connected directly to the test circuits. The cycle life achievable was defined as the number of discharges accumulated within the set discharge time before a final voltage of 1.80Vpc was reached or the available capacity was lower than 80% of the rated capacity.

The depth-of-discharge (d.o.d) was defined as the percentage of the rated 10h capacity. To study the effects of the discharge current, the units have been discharged at various discharge rates during a timed discharge or to a defined end of discharge (e.o.d) voltage.

RESULTS AND DISCUSSION

The data presented in this paper have been collected from several test series, some of which are still running. Data from these particular tests has also been included in our data analysis where necessary and where a first interpretation was already possible.

Float service with daily discharges according to IEC 60896-21:2004^[1]

Several series of monoblocs were run with this standardized test condition, which consists in a 2h discharge with $2I_{10}$ (40% d.o.d) followed immediately by a 22h of charge initiating with a constant current of $2I_{10}$ and terminating under constant voltage condition of 2.25V and 2.27Vpc respectively. The monoblocs have been oriented for a horizontal plate position. The test data is summarized in Table 2.

Table 2. IEC 60686-21 float service with daily discharge test, discharge for 2h at a current of $2 \cdot I_{10}$ – charge for 22h at a current of $2I_{10}$. The voltage limit was set according to the VRLA monobloc type (2.2xVpc).

Battery type	VRLA monobloc type A	VRLA monobloc type B
Test limit		
Average elapsed cycles to 1.80Vpc	61	> 400
Average cumulative discharged capacity	$24 \cdot C_{10}$	$> 160 \cdot C_{10}$

The unlikely behavior can be mitigated or prevented by appropriate design choices as visible from the above experiment.

The cycle performance differential of >400 cycles to ~60 cycles can be related to the amount of positive active material present per Ah of rated 10h capacity. In the >400 cycle design, 16.5g PbO₂/Ah are present on a positive plate, which is only about 16% thicker than in the ~60 cycle design where 13.5g PbO₂/Ah are present. Both active materials have the same apparent density. It is assumed that the difference in the H₂SO₄ concentration contributes to this cycle life deterioration. To quantify this additional influence of the electrolyte concentration, a test using different concentrations of sulfuric acid has been performed.

Float service with daily discharges at other rates with different concentrations of sulfuric acid.

As a next experiment, the influence of electrolyte density (1.28-1.30-1.36g/cm³), depth of discharge (40% vs. 80%) and discharge rate to 40% d.o.d ($0.66I_{10}$ vs. $1.33I_{10}$) was investigated with the VRLA model type A (13.5g PbO₂/Ah). The somewhat surprising test results are summarized in Table 3 below.

Table 3. Summary of the achieved numbers of cycles until the battery dropped below 1.80Vpc in relation to the depth of discharge and the electrolyte density.

Battery type A	40% d.o.d with a discharge current of $0.66 \cdot I_{10}$ for 6 h	80% d.o.d with a discharge current of $1.33 \cdot I_{10}$ for 6 h
Electrolyte density		
1.28 g/cm ³ (37.4 % sulfuric acid)	790 (=316·C ₁₀)	159 (= 127.2·C ₁₀)
1.30 g/cm ³ (40.0 % sulfuric acid)	666 (=266·C ₁₀)	75 (= 60·C ₁₀)
1.36 g/cm ³ (46.3 % sulfuric acid)	339 (= 135.6·C ₁₀)	54 (= 43.2·C ₁₀)

The data shows the possible impact of the intensity of the discharge current, as well as the d.o.d on the ultimate cycle life. Whereas with a discharge current of $2 \cdot I_{10}$, only ~60 cycles were achievable before the voltage drop set in. A significant difference in the two discharge regimes is noticeable. When discharging to the depth of discharge of 40% of 10h capacity and with a quite low discharge current, a much better cycle performance has been found.

As Figure 1 shows, the effect of electrolyte concentration, it confirms the expectation that high acid concentrations yield a generally shorter cycle life when looking at the discharge regime of $0.66 \cdot I_{10}$ to 40% d.o.d. However, in the present experiment, the abnormally high electrolyte concentration set “ 1.36g/cm^3 ” yielded, surprisingly, 339 discharge cycles before the voltage drop occurred.

The proportion of cumulative Ah extractable before the capacity loss or associated failure is as expected, not constant, when one compares the Ah out under 80% and under 40% d.o.d conditions. Here, a significant influence of the electrolyte is discernible and is confirmed with the 1.28 and 1.30g/cm^3 40% d.o.d set. A possible interpretation of the different dependence of the elapsed number of cycles when using a discharge regime at $1.33I_{10}$ to 80% d.o.d is that, in addition to the higher acid concentration, the higher discharge current has a negative effect on the total number of cycles.

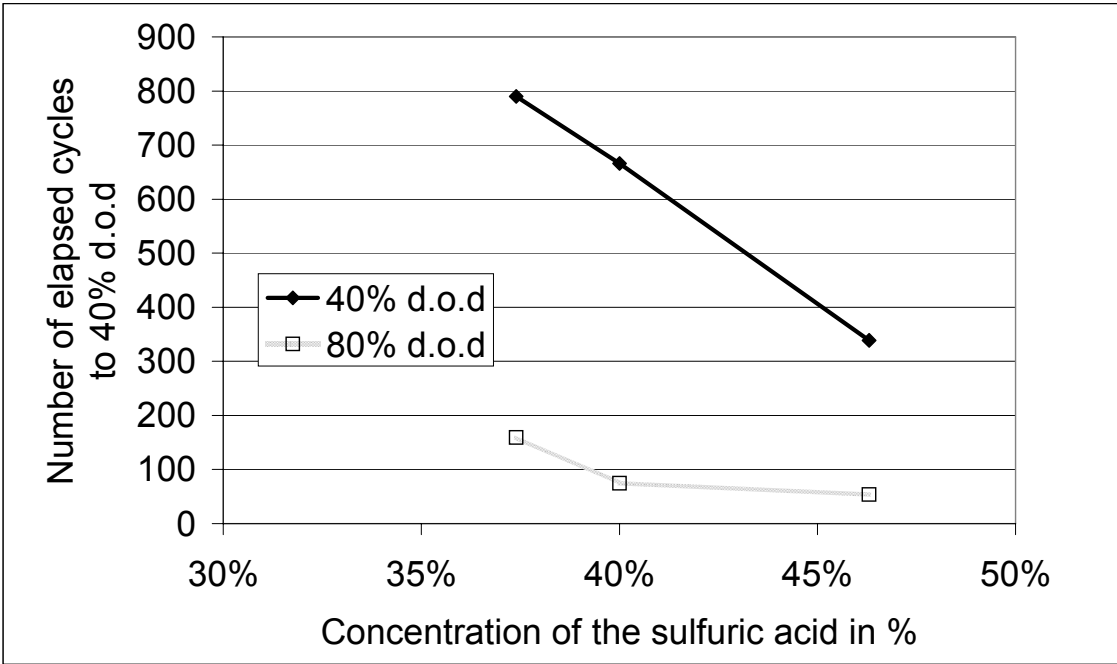


Figure 1: The concentration of sulfuric acid versus the number of elapsed cycles by cycling the VRLA model type A. The batteries have been discharged to 40% d.o.d with a discharge current of $0.66 \cdot I_{10}$.

In Figure 2, the evolution of the end-of-discharge voltage (E.O.D) during such a cycle regime is shown. It is typically characterized by an almost stable evolution over time for the major fraction (>95%) of the cycle life reducing by about 1 mVpc per cycle or even less.

With only little warning, this E.O.D voltage loss may then suddenly accelerate to about 20 to 50mVpc per cycle and announce the impending capacity reduction to less than 50% of the rated 10h capacity in about 10 cycles.

This “bolt from a blue sky”-like failure is very undesirable and raises doubts about the overall reliability of such power backup systems. A similar “surprising early capacity loss” can occur with Ni Oxide based secondary aqueous batteries, where it is often called “memory effect”, although, there, a different failure mechanism is operative.

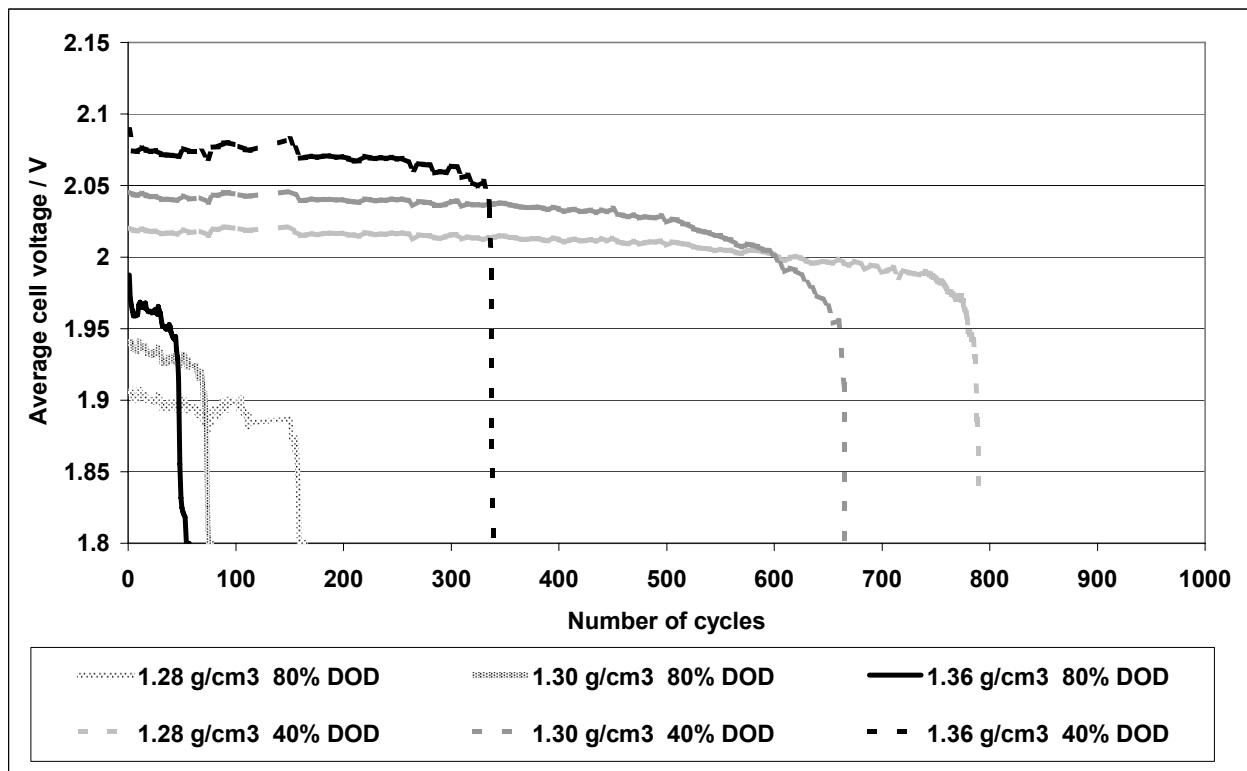


Figure 2: Typical transients of the E.O.D voltage evolution versus the number of cycles, by cycling the VRLA model type A. The batteries have been discharged to 40% d.o.d with a current of $0.66 \cdot I_{10}$ and to 80% d.o.d with a current of $1.33 \cdot I_{10}$ both in 6 hours and have been CC_CV-charged (constant current_constant voltage charge) for 18h before a new discharge was initiated. The d^{20} density of the used electrolyte (diluted sulfuric acid) is indicated in the index.

The influence of the discharge current level on the onset or completion of the capacity loss is quite obvious when the data from Table 2 is used for comparison. Whereas, with a discharge current of $2 \cdot I_{10}$ to 40% d.o.d only 61 cycles were achievable, a discharge to the same depth but at a lower current yielded a cycle life of 666 elapsed cycles. In the test with a discharge to 80% d.o.d, a certain recovery of the capacity was possible after the first time the 1.80Vpc was reached. For this recovery, the voltage was raised to 2.30Vpc and another 35 cycles to the renewed and definitive 1.80Vpc limit were achieved. It is quite possible that at the 80% d.o.d level and only 18h of recharge time (CC-CV $2I_{10} - 2.27Vpc$), a charge deficit accumulated.

The wish for more detailed information about the influence of the used discharged current and the d.o.d to the cycle performance led to the following set of tests:

Float service with daily discharges at other rates and depths as per IEC 60896-21:2004 [1]

A test matrix has been defined to narrow down the “danger zone” for discharges in gravimetrically optimized VRLA cells and monoblocs, and a further series of cycle tests was initiated. In this test sequence, the VRLA model type A has been used. For each test circuit, a 12V string of two 6V monoblocs was assembled. The monoblocs have been operated with a horizontal plate orientation.

In Table 4, the number of elapsed cycles versus the applied discharge condition is listed. The recharge condition is standardized to a CC-CV condition with $2I_{10}$ and to voltage maximum of 2.27Vpc (average). Depending on the discharge time, the recharge time was set to the time difference to complete the 24 hours cycle.

Table 4: Total elapsed cycles and accumulated capacity (C_{10}) before failure during cycling of Type A batteries with a variation of the D.O.D and the discharge current. (Test in gray fields are terminated)

d.o.d Discharge Current	20% d.o.d of C_{10}	30% d.o.d of C_{10}	40% d.o.d of C_{10}	60% d.o.d of C_{10}	80% d.o.d of C_{10}
0.75*I₁₀	431 (86*C ₁₀)	520 (156*C ₁₀)	450 (180*C ₁₀)		
1*I₁₀	393 (79*C ₁₀)	440 (132*C ₁₀)	512 (204*C ₁₀)	850 (510*C ₁₀)	
1.5*I₁₀	333 (67*C ₁₀)		284 (114*C ₁₀)	440 (264*C ₁₀)	75 (60*C ₁₀)
2*I₁₀		220 (66*C ₁₀)	62 (25*C ₁₀)	107 (64*C ₁₀)	
3*I₁₀	342 (68*C ₁₀)	163 (49*C ₁₀)	50 (20*C ₁₀)	117 (70*C ₁₀)	105 (84*C ₁₀)

These results confirm that especially high discharge currents risk provoking a faster decrease of the available capacity in cyclic applications. The lowest capacity turnover pops up at 40% d.o.d and at the highest measured discharge current of 3*I₁₀. Cycle regimes to 40% d.o.d and with a discharge current of 3I₁₀, yielded even less cycle life (50) than when the same d.o.d is reached with 2I₁₀ currents.

Once the 50% rest capacity level was reached, several of the affected monoblocs were submitted to several “recovery” routines consisting in long duration CV charges (168h), charges at higher voltages (2.35Vpc to 2.34Vpc) or forced over-discharges. None of these “recoveries” had any lasting effect, and the minor capacity recoveries lost their effect within a few cycles

Capacity optimized formulation of the active mass seems to be sensitive in these kinds of discharge regimes. This risk has been recognized also by the latest International Standard for Stationary Lead Acid Batteries of the VRLA type (IEC 60896-21:2004), in which the achievable cycle life is required to be quantified under the “danger zone” conditions.

Float service with daily discharge until the E.O.D voltage is reached.

As it was already obvious that the use of more active mass is of benefit to charge/discharge behavior, two different positive plate variations have been produced to verify the influence of an additional amount of active mass. In this test, VRLA monoblocs of the model C have been used. These monoblocs have a nominal voltage of 12V and a lead/Ah-ratio of 13g/Ah. In Figure 3, the evolution of the discharged capacity is displayed. The variation (VN) represents a construction with the same apparent mass density as has been used in all previous experiments. (VN) has been installed in vertical plate orientation for the test procedure.

The variations (VH) and (HH) have been produced with a 5% higher apparent mass density than (VN) but the thickness of the plates has not been changed. This results in an investment in about 5% more lead in the positive active mass. The monobloc with (VH) indication has been installed with a vertical plate orientation, while the monobloc with the (HH) indication has been tested with a horizontal plate orientation. While these experiments are still running, it is already possible to see the difference.

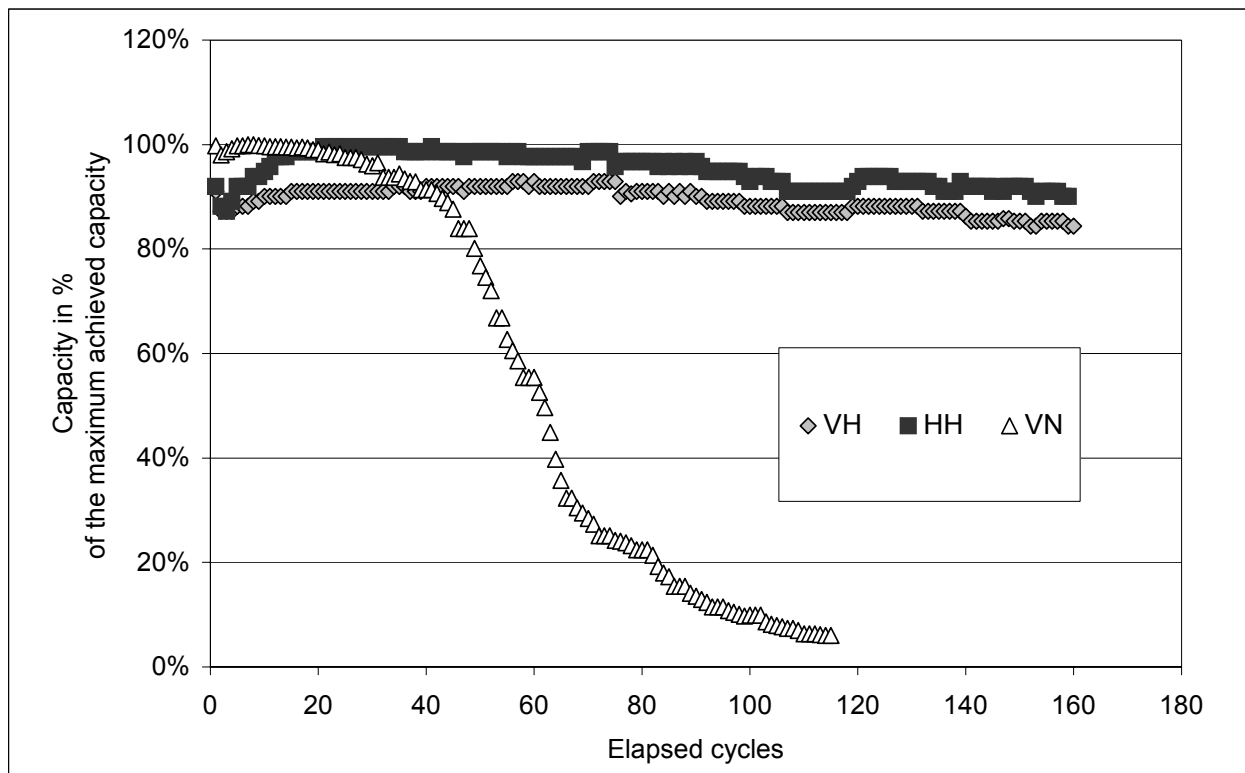


Figure 3: The evolution of the discharged capacity during a discharge test with $4 \cdot I_{10}$ to about 70% d.o.d (at the maximum capacity) of VRLA model type C.

While the monoblocs with the (VN) setup showed more or less the expected behavior, based on the discussed data, the monoblocs (VH) and (HH) show a significantly improved behavior under this discharge situation. A major influence from the orientation was not noticeable.

SUMMARY

Frequent or daily discharges with high currents ($>2I_{10}$) to average depths of discharge ($\sim 40\%$ d.o.d of C_{10}) can induce a surprisingly faster loss of capacity than discharges with lower rates to the same depths or with the similar rates to larger depths.

This “danger zone,” especially at high discharge rates, may exist in certain gravimetrically optimized VRLA designs and has to be taken in account when decisions are to be taken for certain applications.

The appearance and eventual severity of this condition can, however, be mitigated by choosing the appropriate VRLA design and the right discharge parameter selection as a result of the battery dimension. The overriding key factor is the active mass/Ah-relation as well as a paste formulation with a resulting high apparent density.

Besides this, there has been found a clear influence of the concentration of the sulfuric acid, so that a general rule can be established that high concentration decreases the potential cycle life.

Strategies for capacity recovery after failure, such as charging for a longer time, higher charging voltages during cycling, or a therapy with a few discharges to 100% depth of discharge resulted only in marginal and short-term benefits. These results are based on a VRLA/AGM design with a thick plate construction.

ACKNOWLEDGEMENTS

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REFERENCES

[1] International Standard IEC 60896-21, Stationary lead-acid batteries, Part 21: Valve regulated types – Methods of test, February 2004.