

Performance of a VRLA battery in an arctic environment

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Abstract

The successful operation of stationary lead-acid batteries of the VRLA/AGM type at cold and extremely cold temperatures is a precondition for the further expansion of their application envelope. Application oriented tests and investigations show a surprisingly robust behavior of such batteries under temperature conditions as low as $-30\text{ }^{\circ}\text{C}$. The results obtained in these tests are presented and show data concerning available discharge energy at low temperatures, the behavior during charge and discharge cycles, the effect of freeze and thaw cycles and structural aspects of the “frozen” electrolyte at these temperatures.

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1. Introduction

VRLA batteries are extensively installed in data and voice transmission facilities, such as for example, transmission cells for mobile communication. In very remote locations these batteries store electrical energy for the power back-up in case of ac mains failures as well as the energy generated by diesel engines, wind or photovoltaic generating stations. The performances of these installations can be strongly impacted by severe weather conditions and their effects on battery behavior need to be assessed.

In this study the performance of different VRLA/AGM monobloc under cold weather conditions will be presented.

The following “cold” weather conditions have been simulated in these battery performance tests:

- A. Multiple electrolyte freeze and thaw cycles of a discharged battery at intermittent $-18\text{ }^{\circ}\text{C}$ cold weather conditions.
- B. Multiple discharge–charge cycles at permanent $-30\text{ }^{\circ}\text{C}$ cold weather conditions.
- C. Multiple discharge–charge cycles after battery compartment flooding and subsequent ice formation due to permanent $-18\text{ }^{\circ}\text{C}$ cold weather conditions.

2. Experimental

The tests have been carried out with 6 V/155 Ah (10 h discharge capacity, C_{10}) and 12 V/92 Ah (C_{10}) monoblocs of VRLA-AGM type manufactured by Oerlikon Stationary Batteries Ltd., Aesch, Switzerland.

The cold weather experiments have been carried out in a walk-in $-35\text{ }^{\circ}\text{C}$ climate chamber with recirculating air made by Frigorex AG, Switzerland.

The charge and discharge test were run with programmable battery testers of the type EW 200-24 and HEW 700-60 made by Digatron GmbH, Germany.

The temperatures, currents and voltages were recorded with a computer controlled datalogger of the type HP 34970A made by Hewlett Packard Ltd., USA.

3. Results and discussion

3.1. Freeze-thawing cycle test (cold weather condition A)

The 6 V/155 Ah and 12 V/92 Ah VRLA monoblocs and have been used for these tests. The test sequence is described in Table 1.

The monoblocs were tested in the following orientations as encountered in field installations:

- 6 V/155 Ah monoblocs: in vertical and horizontal (pancake) plate orientation mode as 18 V strings.
- 12 V/92 Ah monoblocs: in vertical plate orientation mode as 24 V strings.

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Table 1
Sequence of the freeze-thaw cycle test

Test step	Electrical test parameters	Duration (h)	Test temperature
(1) Discharge	I_{10} to 1.80 Vpc (15.5 A/9.2 A to 1.80 Vpc)	12	Room temperature (20–25 °C)
(2) Open circuit stand	No current flowing (open circuit)	72	Cool down to –18 °C
(3) Charge	Maximum current $2I_{10}$ voltage limit set to 2.25 Vpc	168	Warm-up from –18 to +25 °C

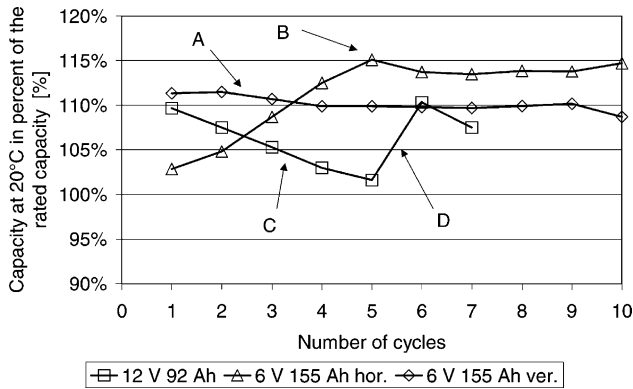


Fig. 1. Capacity (C_{10}) evolution during the multiple freezing, thawing cycle test.

The fully charged monoblocs have a rated electrolyte density (d^{20}) of 1.28 g cm^{-3} . During the discharge step (Table 1) the density of the sulfuric acid is decreased to an average density of $\sim 1.06 \text{ g cm}^{-3}$, freezing at $-5 \text{ }^\circ\text{C}$.

The evolution of the capacities during the above sequence of freeze and thaw cycles is shown in Fig. 1 and a slightly differentiated behavior of the monoblocs can be observed.

The 6 V/155 Ah monoblocs in vertical plate orientation (data curve A) showed an essentially stable capacity evolution, at 110% of rated, during the entire 10 cycles. In each cycle the dilute electrolyte, present at the end of discharge, was frozen solid in the OC period. The 6 V/155 Ah monobloc with plates in horizontal or pancake orientation (data curve B) showed a lower initial capacity which evolved to

115% of rated during the first 5 cycles and then stayed also constant.

The 12 V/92 Ah monoblocs, with plates in vertical position, showed a small linear decrease of capacity of about 2% per cycle during this freeze-thaw cycle sequence. This decrease (data curve C) is related to a slight acid stratification and associated “undercharging” of the positive plate. This undercharging occurs because some of the charging current is prematurely shunted, in areas of lower acid density, away from PbSO_4 oxidation and toward oxygen evolution.

This decay mode hypothesis was confirmed by the observed capacity increase (D) to 110% of rated after a 3 week continued charge at the float voltage.

The investigation of the cells after the completed test showed no obvious damage due to the multiple freezing and thawing at the plates. Neither an active mass spalling nor a significant pull out of mass during peeling-off of the AGM absorber could be observed (Fig. 2).

3.2. Discharge and charge test at $-30 \text{ }^\circ\text{C}$ (cold weather condition B)

12 V/92 Ah monoblocs were used in this test as a 24 V string and with a vertical plate orientation mode.

This test simulated an operation with a permanent low battery temperature of $-30 \text{ }^\circ\text{C}$ during both discharge and charge. The charge voltage was increased to 2.35 Vpc and the discharged monoblocs accepted, at $-30 \text{ }^\circ\text{C}$, an initial charging current of $\sim 6 \text{ A}$ ($\sim 0.6I_{10}$).

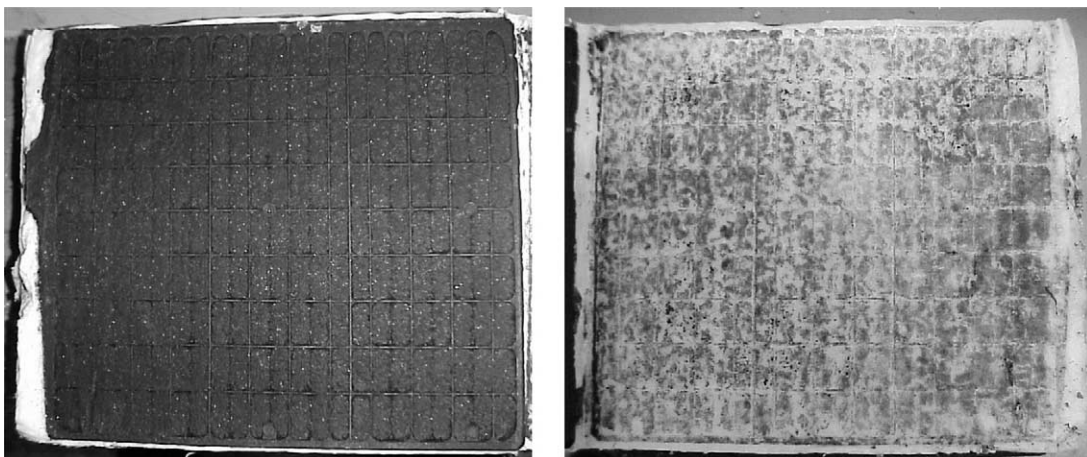


Fig. 2. Positive plate (left) and AGM absorber (right) of a 6 V/155 Ah monobloc as inspected after 10 freezing-thawing cycles.

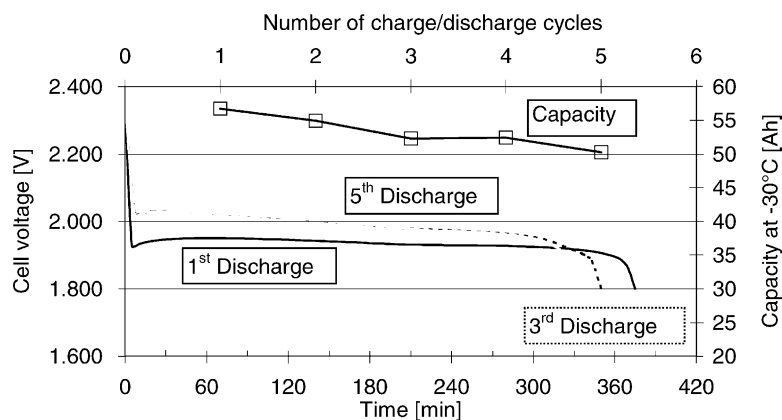


Fig. 3. Evolution of capacity and cell voltage during five sequential discharges at $-30\text{ }^{\circ}\text{C}$ (9.2 A to 1.80 V per cell).

During the discharge, the water formed on the positive plate dilutes locally the electrolyte. As soon as this mixture reaches a composition which freezing point is equivalent to that of the actual local temperature in the plates, ice crystals precipitate. This ice formation then increases the resistance within the plate pores and terminates the discharge process.

The first discharge at $-30\text{ }^{\circ}\text{C}$ yielded an actual capacity of 56.7 Ah or $\sim 62\%$ of the rated capacity of 92 Ah at $20\text{ }^{\circ}\text{C}$ and showed the discharge voltage vs. time trace marked “first discharge” in Fig. 3. The fast voltage decrease at the end of the discharge can be related to the formation of ice at the electrode/electrolyte interface.

The calculation of the electrolyte density after the discharge of 56 Ah gives a value of $\sim 1.16\text{ g cm}^{-3}$ freezing at $-19\text{ }^{\circ}\text{C}$.

This temperature is above the $-30\text{ }^{\circ}\text{C}$ to which the monobloc was cooled down and would indicate that the actual reaction site temperature was, at $-19\text{ }^{\circ}\text{C}$, significantly warmer thus allowing to discharge more ampere hours before ice formation sets in. As in VRLA cells and monoblocs, with immobilized electrolyte, the heat exchange is mostly given by conductivity and less through fluid flow heat transfer, it is assumed that increased internal resistance causes “self heating” and therefore yields better discharge capacity values.

In the subsequent discharges again a $\sim 2\%$ capacity decrease per cycle was noticeable and the discharge voltage versus time trace (third discharge–fifth discharge) showed an evident change.

The change consisted in an increase of the average discharge voltage by about 50 mVpc during the entire duration of the discharge when compared to the discharge voltage at cycle 1.

This higher average voltage could tentatively be associated with a higher local electrolyte concentration. The elevated voltage signal corresponds to a theoretical approximate density of the sulfuric acid of $\sim 1.33\text{ g cm}^{-3}$ at the beginning of the discharge.

At the conclusion of the $-30\text{ }^{\circ}\text{C}$ cycle test a capacity determination at room temperature was carried out which

gave 108% of the rated capacity thus confirming the absence of low temperature related permanent damage to the battery (Tables 2 and 3).

3.3. Charge and discharge test with battery encased in ice (cold weather condition C)

In decentralized outdoor installations it may be advantageous, for space or thermal management reasons, to install the battery below ground level. Such installations are however prone to flooding and special protective features have to be applied to the battery monobloc. These features prevent short circuits of the terminals and allow a directed escape of the gas vented from the units.

In the present investigation of the behavior of the VRLA battery in an arctic environment, the combined effects of water around the monobloc and associated freezing of this water to solid ice was investigated.

Table 2
Sequence of the cycle test at $-30\text{ }^{\circ}\text{C}$

Test step	Electrical test parameters	Duration (h)	Test temperature ($^{\circ}\text{C}$)
(1) Discharge	9.2 A (I_{10}) to 1.80 Vpc	12	-30
(2) Open circuit stand	No current flowing (open circuit)	72	-30
(3) Charge	Maximum current $2I_{10}$ voltage limit set to 2.35 Vpc	168	-30

Table 3
Evolution of the available capacity (C_{10}) at $-30\text{ }^{\circ}\text{C}$

Cycle number	Discharged capacity at $-30\text{ }^{\circ}\text{C}$ to 1.80 Vpc in (Ah)	Capacity in percent of the rated capacity at $20\text{ }^{\circ}\text{C}$ (%)
1	56.7	62
2	54.9	60
3	52.3	57
4	52.4	57
5	50.3	55

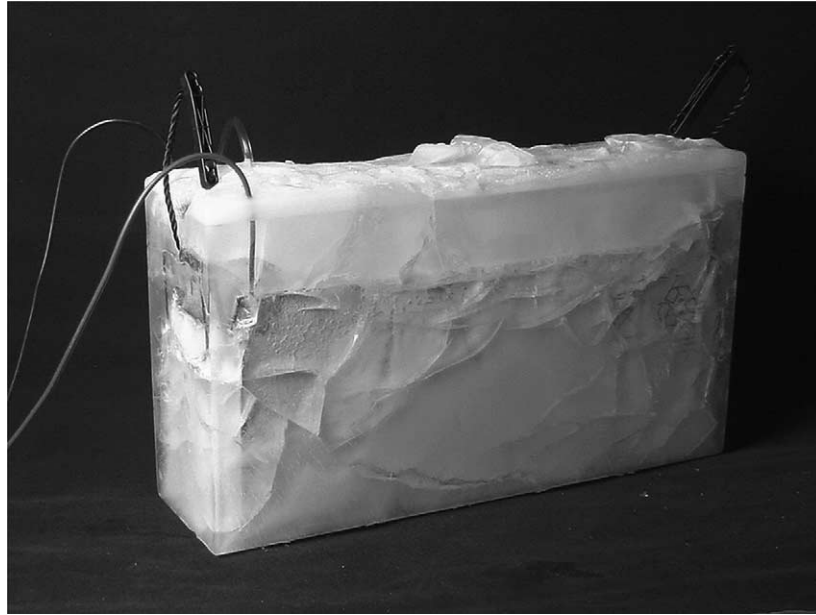


Fig. 4. A 12 V/92 Ah VRLA monobloc encased in ice.

For this test a 12 V/92 Ah monobloc, equipped with sealed terminal cables to prevent shunt currents and a central gas collection manifold, was immersed in water.

After cooling down the assembly to the test temperature of $-18\text{ }^{\circ}\text{C}$, the water froze and the monobloc resulted encased by solid ice of 20 mm thickness at the sides and at the bottom and of about 100 mm thick ice on the top (Fig. 4).

The ice-encased monobloc was then operated at $-18\text{ }^{\circ}\text{C}$ with the test sequence described in Table 4 later.

The battery exhibited a quite stable capacity evolution as reported in Table 5 and displayed in Fig. 5. The charge

Table 4
Sequence of the cycle test of the ice-encased VRLA monobloc

Test step	Electrical test parameters	Time (h)	Test temperature ($^{\circ}\text{C}$)
(1) Discharge	9.2 A (I_{10}) to 1.80 Vpc	12	-18
(2) Open circuit standing	No current flowing (open circuit)	72	-18
(3) Charge	Maximum current $2I_{10}$ voltage limit set to 2.35 Vpc	168	-18

Table 5
Capacity evolution of a VRLA battery completely packed in ice

Cycle number	Discharged capacity at $-30\text{ }^{\circ}\text{C}$ to 1.80 Vpc in (Ah)	Capacity in percent of the rated capacity at $20\text{ }^{\circ}\text{C}$ (%)
1	63.3	69
2	65.3	71
3	63.5	69
4	62.0	67

acceptance is much better than that observed with the same monobloc at $-30\text{ }^{\circ}\text{C}$ (Chapter 4.2) and resulted in an inrush current of $\sim 11\text{ A}$ ($1.2I_{10}$) at the start of the constant current/constant voltage charging phase.

The discharge voltage versus time trace showed also in this experiment a trend to higher initial discharge voltages as cycling proceeded.

A room temperature capacity test and thorough inspection of the battery case and cover at the conclusion of this test showed no permanent damage either from the $-18\text{ }^{\circ}\text{C}$ cycling, nor from ice pressure.

3.4. Ex situ investigations of the electrodes and electrolyte at $-30\text{ }^{\circ}\text{C}$

One of the key tenets of operating lead-acid batteries at low temperature has been the strict avoidance of any incipient or complete electrolyte freezing. Such an electrolyte ice formation was considered extremely deleterious for the integrity of the battery container and the active material.

The insensitivity of the above tested VRLA monoblocs thus required additional information to be gathered about “electrolyte freezing” phenomena.

For this purpose samples of 3.5 mm thick, formed positive plates were completely submerged in plastic beakers containing sulfuric acid of different densities and in pure water. The different samples were then placed in a test chamber at $-30\text{ }^{\circ}\text{C}$ and the electrolyte thus frozen.

Another experiment consisted in freezing, at $-30\text{ }^{\circ}\text{C}$, the same electrolytes and water in laboratory glass test tubing.

The tests showed, as experienced and reported above with fully assembled monoblocs, that the formation of ice from

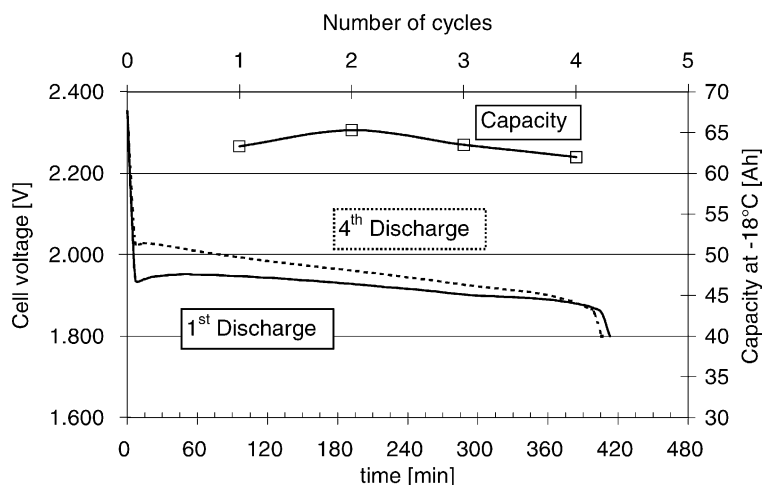


Fig. 5. Capacity evolution and cell voltage during four sequential discharge cycles.

dilute sulfuric–water mixtures (1.040 g cm^{-3}) and also pure water does not result in significant active mass disruption. The stresses imposed by the +7% volume increase of frozen electrolyte, were without consequences on the mechanical integrity and the low (10 h) or high rate (15 m) performance of the VRLA monobloc. In parallel experiments this behavior was also verified with VRLA cells of 1600 Ah C_{10} capacity.

Under normal battery operating conditions and functioning final voltage limits, a final electrolyte density of 1.05–1.06 g cm^{-3} can be expected.

The presence of differentiated electrolyte freezing related stresses has been established in the above-described simple glass test tube experiment.

Whereas the test tubes with 1.180–1.040 g cm^{-3} acid survived unbroken the freezing of the electrolyte at $-30 \text{ }^\circ\text{C}$, the test tube containing pure water shattered indicating that the dilute sulfuric acid electrolyte results in less ice stress generation. This reduced stress generation can be probably ascribed to a minimum quantity of surviving liquid phase consisting, at $-30 \text{ }^\circ\text{C}$, of a sulfuric acid electrolyte with about 1.20 g cm^{-3} density (Fig. 6).

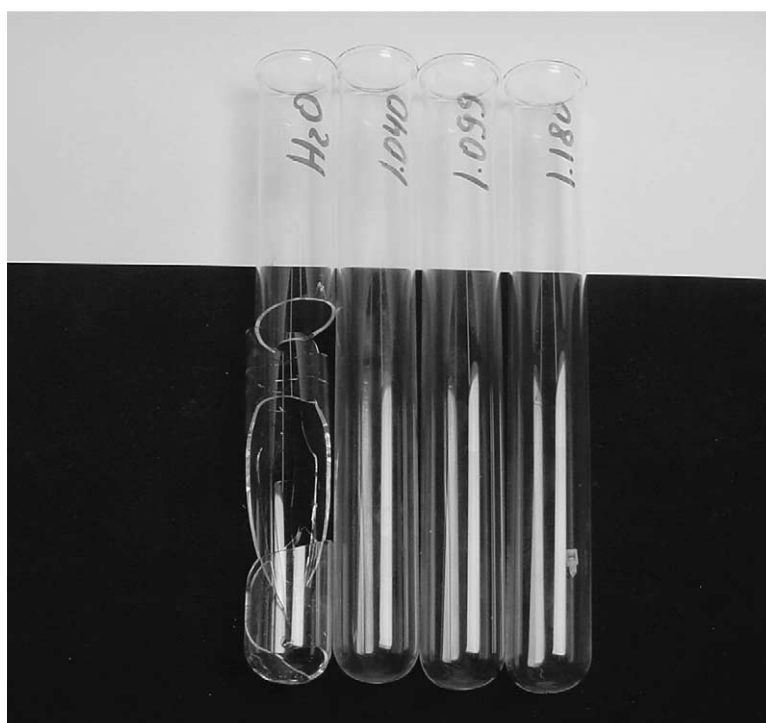


Fig. 6. Electrolyte freezing test showing shattered glass tubing of the pure water sample.

4. Conclusions

This investigation of VRLA monobloc operated under simulated arctic conditions leads to the following conclusions:

- The observed available capacity during 10 h rate discharges at low temperatures is surprisingly high with $\sim 62\%$ of the $20\text{ }^{\circ}\text{C}$ rated capacity available at $-30\text{ }^{\circ}\text{C}$ and $\sim 71\%$ available at $-18\text{ }^{\circ}\text{C}$.
- No damage or failures related to mechanical stresses in the plates could be observed when the electrolyte was allowed to freeze at the end of a discharge. The absence of such damage can be related to the particular freezing structure of dilute electrolyte.
- The recharge of the cells at low temperatures or with frozen electrolyte is feasible also at $-30\text{ }^{\circ}\text{C}$ due, in the latter case, to the existence of a residual amount of conductive liquid electrolyte which, for example at $-30\text{ }^{\circ}\text{C}$, has a density of $\sim 1.20\text{ g cm}^{-3}$.

- The capacity recovery at low temperature is, as shown, quite slow requiring up to approximately 168 h to recover to more than 98% of the previous capacity. Such a behavior has been reported by previous authors [1,2].

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