Ageing Evaluation of Lead-Acid Battery Used in Off-Grid Photovoltaic System

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Abstract

Batteries are an indispensable component in off-grid photovoltaic (PV) systems, storing the excess energy produced during the day to provide electricity to the load during cloudy times and at night. The lead-acid battery is the technology frequently used in off-grid PV systems, mainly the automotive and deep cycle types. In Brazil, off-grid PV systems are located in remote areas with tough access, and the main problem is the battery's shorter than expected lifetime. The main degradation phenomena in lead-acid batteries used in PV systems are sulfation, stratification, corrosion, and active mass degradation. This paper presents laboratory tests that induce the main degradations, and the results of tests on OPzS lead-acid batteries from two manufacturers in 14 different groups. The objective of the laboratory tests is to provide data of the battery lifetime to an algorithm that will be developed in the future to estimate the State-of-Health of lead-acid batteries used in PV systems.

Introduction

In the last decade, the Brazilian Federal Government has created programs to obligate the utilities to provide electrical energy access to every household [1,2]. The objective of these programs is the universalization of electricity distribution in rural areas. Brazil is known by its continental dimension, and many people live in isolated areas, while the distribution networks are concentrated in urban and more populated regions. Therefore, utilities have two main options to provide electricity to isolated areas: build conventional electrical networks connected to the National Interconnected System, or use micro or mini generators. The implementation of a conventional electrical network involves high infrastructure costs, while micro or mini generators can represent a low cost and effective option. In addition, considering the Brazilian potential of renewable energy and its sustainable features, the use of Renewable Energy Sources (RES), such as solar and wind, as off-grid micro or mini generation, becomes an attractive and prominent solution for providing electricity access to isolated areas. Most of the RES installed in isolated areas consist of solar photovoltaic (PV) generators.

In spite of all the benefits RES can provide, solar energy sources are intermittent, requiring the use of energy storage systems, such as batteries, to store the energy excess when sunlight is abundant, enabling its use during periods of low or null irradiance. Because of the difficult access to the isolated areas, the batteries must have low maintenance requirements, great durability and reliability, and low environmental impact. To meet these requirements, batteries used in off-grid PV systems are stationary. However, due to the different operating conditions, these batteries must have specific design and features, compared to the ones applied in backup power system. In off-grid PV systems, the batteries operate with low current intensity, daily cycles with low State-of-Charge (SoC), and under uncontrolled temperature (usually above 25° C). On the other hand, the batteries used as backup operate with medium or high current intensity, on float voltage, small and sporadic cycles, and controlled temperature. Therefore, the battery design must be suitable for each type of application, and the main differences are thickness of the plates, composition of the alloy, amount of active material, electrolyte density, and additives.

Batteries are considered the most sensitive and expensive equipment in off-grid PV systems, representing up to 35% of the total system cost. Occasionally, inappropriate lead-acid batteries are used, resulting in a useful lifetime lower than expected and requiring periodic replacement. Even in situations where the durability of the battery is satisfactory, it was found that the battery capacity was lower than the recommended limit. Measurements[3] showed that batteries with 8 years of operation had a capacity between 3% and 50% of initial value, i.e., the capacity value was below the limit considered as the end-of-life (80% of initial capacity). In Brazil, one type of vented lead-acid automotive battery known as "maintenance free" remains the dominant solution for off-grid PV system applications, mainly due to its low initial cost. According to the Brazilian Standard NBR 14197[4], the lifetime of a battery applied in photovoltaic systems is 7 years at 25°C.

Despite all the new energy storage technologies, lead-acid batteries are the most recommended for use in off-grid PV systems because they have the best benefit-cost ratio. However, there is no consensus in the scientific community about the most suitable lead-acid battery type among the existing ones. Considering the adverse conditions to which the battery is submitted in off-grid PV system applications, a reasonable option is to adopt the Stationary Flooded Tubular Lead-acid Battery (OPzS battery), which is a vented stationary battery with tubular plates that offer a high cycling expectancy due to the protection of the positive mass (lead dioxide).

In this context, CPqD is conducting a Research and Development (R&D) project supervised by the National Electrical Energy Agency (ANEEL - Brazil) and sponsored by Dresser-Rand Guascor, with the main objective being the development of an algorithm that estimates the State-of-Health (SoH) of OPzS lead-acid batteries for off-grid PV system application. This algorithm is based on the results obtained with computer simulations and laboratory tests on OPzS batteries from two different manufacturers, and its development will be finalized in the next stage of the project. The algorithm will be implemented in a battery monitoring system in order to identify early failures in the batteries; therefore, preventive and corrective maintenance can be adopted and replacement can be planned in advance.

Types of Lead-Acid Batteries Used in Photovoltaic Systems

Although there are lead-acid batteries designed specifically to operate in off-grid PV systems, in practice, the cost and availability of the market cause the user to utilize other types of batteries. The most commonly used battery types in PV systems are:

- **Starting, Lighting and Ignition (SLI) or Automotive Batteries**: These are widely used due to market availability and low cost compared to other technologies. This battery has thin plates in order to withstand high peak currents during a short time period. In photovoltaic operations, the battery is submitted to daily recharge and discharge cycles, requiring a thick grid to support this condition. This battery type, when used in PV systems, suffers strong corrosion and degrades quickly, making the system unreliable. Some manufacturers make minor changes in this battery technology to use it in PV systems by reducing the amount of antimony to decrease water loss and increase the thickness of the plate and improving the cyclic operation. The SLI battery is not recommended to use in photovoltaic systems.
- **Deep-Cycle Batteries**: These are stationary lead-acid batteries designed to discharge up to 80% of the Depth of Discharge (DoD) and have thick plates composed of a high-purity lead alloy, with less surface area. This battery is designed specifically for photovoltaic applications, so is the most suitable for this use.

The main subclasses of lead-acid batteries for the application in PV systems are:

a) **Absorbed Glass Mat (AGM) Valve Regulated Lead-Acid (VRLA)**: This is the most sensitive to environmental conditions of PV operation because, at high temperatures, the degradation processes are accentuated and can cause the case “bulging” and even explosion of the battery due to thermal runaway. It has the advantage of not needing to add distilled or deionized water.

b) **Gel VRLA**: This has the advantage of not needing to add distilled or deionized water, has a lower susceptibility to stratification of the acid, which means a longer life, and is less prone to thermal runaway than AGM batteries. However, it is very sensitive to high temperatures.

c) **Vented**: This has low initial cost and longer lifetime compared to other lead-acid battery technologies. Although this battery type requires periodic maintenance (addition of distilled or deionized water), if maintenance is done correctly, this battery will offer longer life than the VRLA battery. Stratification of the electrolyte is a major problem in PV system application.

Degradations of lead-acid batteries in PV systems

The main causes of degradation of the battery in isolated PVs systems are described below.

Stratification

Stratification occurs due to the lack of uniformity of the electrolyte concentration (sulfuric acid) in the vertical direction of battery plates, causing the formation of regions or layers of different density in the electrolyte[5]. Depending on this density difference, the current distribution over the plate also becomes inhomogeneous, the capacity is reduced, and the voltage and current characteristics change. The stratification of the electrolyte is not a degradation process itself but accelerates other ageing mechanisms, such as sulfation and corrosion in the top and bottom of the plates, being most common in the positive plate. Equalization charges can prevent stratification because the gassing mixes the electrolyte.

Vented batteries are more prone to electrolyte stratification. The damage caused by this phenomenon can be avoided by using air pumps and the natural evolution of gasses during charging at a higher voltage. VRLA batteries are also subject to stratification of the electrolyte, but significantly lower than vented batteries. In Gel VRLA batteries, this effect is negligible, while in AGM batteries, the electrolyte stratification effect depends on the quality of the glass fiber.

Sulfation

During the discharging process, the active mass becomes lead sulfate. If the recharge does not occur in sequence, depending on the solubility of sulfate ions, lead sulfate crystals form and accumulate at the plates. In subsequent recharge, small lead sulfate crystals dissolve but large crystals are not totally removed and grow, reducing the surface area of the electrodes and, hence, the battery capacity over time, since there is less active mass available to charge and discharge reactions[6]. Depending on the degree of sulfation, the battery may reach a state of partial or totally irreversible degradation. In PV systems, sulfation is mainly accentuated by battery operation for a long period at low SoC.

Corrosion

In normal battery operation, the lead grid of the positive plate corrodes slowly, reducing the cross section of the lead grids, increasing its internal resistance. Then, a layer of oxide and lead sulfate is formed between the bars and the active material, which also increases the contact resistance. Factors influencing the corrosion rate are the density of the electrolyte, float voltage, temperature, the alloy used in the grid, and the quality of the manufacturing process[5]. Corrosion occurs more intensely when the element voltage is below 2.0V or above 2.4V[6]. Batteries used for photovoltaic systems have thicker plates to prevent the complete disintegration of the grid.

Active Mass Degradation

During operation of the lead-acid battery, the electrodes suffer from strong mechanical stress. Throughout the discharging process, more than 50% of the active material is transformed into lead sulfate. It is known that lead sulfate has a volume per mol 1.89 times greater than lead dioxide[6]. This large variation in volume causes the loss of the active material because it becomes loose and the drag of the acid can separate it from the electrode. This effect is stressed by the increase in the depth-of-discharge during the daily cycles of PV systems.

High Temperature

In general, any chemical or electrochemical process is accelerated by an increase in temperature. The same happens with batteries, accelerating the degradation processes, mainly corrosion, sulfation, excessive generation of gasses, and self-discharge. It is estimated that for every increase of 10°C in temperature, the battery life is reduced by half, and it is suggested to keep the operating temperature between 10°C and 25°C[6].

Laboratory Tests

To evaluate the battery's behavior throughout its life, and thus to estimate the end of life, accelerated ageing tests are performed in the laboratory. This study is based on reproducing real operating conditions such as temperature, depth of discharge, and state-of-charge in cyclic operation.

In the elaboration of standards and testing procedures for batteries used in off-grid PV systems, one of the main goals is to simulate the actual operating conditions of these batteries, i.e., the state-of-charge, voltage, current, temperature, etc. The reproduction of these conditions is a complex task because many factors can affect them, such as:

- Variation of solar radiation, as well as the weather, the seasons, etc.;
- Battery project sizing (DoD, autonomy, etc.);
- Installation configuration (only PV, hybrid with diesel generator, etc.);
- Variation of power consumption according to each user.

For example, the battery may, in summer, operate at high temperatures and undergo cycles at a high-level SoC, and may even suffer from overcharging. But in rainy periods, the battery has few periods of recharge cycles and is subjected to a low-level SoC. In other words, a battery used in PV systems rarely has a constant and determined operating profile. Therefore, it is not possible to state that the battery will operate according to the design conditions. It is important to note that charge controllers generally limit the battery recharge (voltage and current), as well as the depth of discharge by disconnecting from the system when it reaches a preset voltage value.

Studies[7,8] based on actual operating data indicate the factors that most affect the life of the lead-acid battery. These factors were obtained by statistical parameters (voltage, current, temperature, and SoC) from actual PV installations, which identify the operating conditions that are relevant for the estimation of the state of lead-acid battery degradation. These factors are:

- **Charge Factor**: The ratio of the energy recharged and discharged. This factor identifies the operating conditions of the battery and, closer to 1, the ratio indicates that the battery operates in partial cycling with limited recharge. On the other hand, the longer the time that the battery operates on floating, the greater the charge factor. This factor may particularly indicate the amount of water loss that may occur in the operation as well as the degradation of the active mass.

- **Ampere-hour (Ah) Throughput**: This represents the cumulative value of the amount of energy that the battery has provided, and its normalized value is obtained by dividing the annual amount of energy discharged by the nominal capacity of the battery. This factor can differentiate a battery that operates as a backup and in cyclic operation, and the higher its value is, the more pronounced is the degradation of the active mass and the stratification of the electrolyte.

- **Highest Discharge Rate**: This factor represents the maximum discharge current responsible for discharging at least 1% of the amount of energy discharged. In PV systems, this rate is generally low, although this factor is more significant in PV systems that have electric motors (for example, for pumping water) or in systems that have large variations in energy demand. High flow rates cause stratification. In the systems studied, the maximum discharge was C_{10} rate.

- **Cycling Partial**: This is related to cycling in different SoC levels that the battery can operate in PV systems. These can be separated into different operating ranges with minimum and maximum SoC values. The smaller the SoC level during the cycles, the greater its weight in normalized value because it accelerates the sulfation and stratification.

- **Time in Low SoC:** The period that the battery stays in a SoC below 35%. In this case, the lead-acid battery suffers an accelerated sulfation.

- **Temperature**: For every increase of 10°C at operating temperature referenced at 25°C, the corrosion rate doubles in the lead-acid battery and, therefore, has a loss of about 50% of its useful lifetime[5].

Studies[7,8] show that the corrosion is caused mainly by the recharge process, as it appears more intense in systems where batteries are recharged more often or with greater intensity. The sulfation and stratification are intense in batteries that remain for long periods in low SoC and are not recharged frequently. The active mass degradation is strongly influenced by cycling with high DoD.

For laboratory tests, lead-acid batteries of OPzS technology from two manufacturers were selected. Table 1 presents the selected tests and degradation expected for the respective group[9], composed of three elements connected in series.

Table 1. Groups of laboratory tests that are being carried out in the project

Group	Test	Expected degradation
1	Discharge Profile	Not Applicable.
	Recharge Profile	Not Applicable.
2	CAR INMETRO at 40°C	Sulfation, stratification and corrosion.
3	CAR INMETRO at 50°C	Sulfation, stratification and corrosion.
4	Cycling test around 10% SoC	Sulfation and stratification.
5	Cycling test around 40% SoC	Sulfation and stratification.
6	DRE Cycling	Sulfation, stratification active mass degradation.
7	Partial cycling between 85% and 100% SoC at 40°C	Corrosion.
8	Partial cycling between 70% and 85% SoC at 40°C	Sulfation.
9	Partial cycling between 55% and 70% SoC at 40°C	Sulfation and stratification.
10	Partial cycling between 40% and 55% SoC at 40°C	Sulfation and stratification.
11	Partial cycling between 85% and 100% SoC at 50°C	Corrosion.
12	Partial cycling between 70% and 85% SoC at 50°C	Sulfation.
13	Partial cycling between 55% and 70% SoC at 50°C	Sulfation and stratification.
14	Partial cycling between 40% and 55% SoC at 50°C	Sulfation and stratification.
15	Cycling based on hybrid system deployed by Dresser-Rand Guascor in Brazil	Sulfation.
16	SoC estimation	Not Applicable.

The corrosion process did not occur with high impact on any of the tests, and the test of Conformity Assessment Regulation (CAR) from INMETRO is the one with the highest corrosion intensity. Another interesting point to observe is that most tests cause a medium to high intensity of sulfation.

None of the test procedures can cause the four main degradation phenomena in lead-acid batteries for PV system application. Therefore, it was necessary to select different groups of tests to simulate the main degradations in the laboratory and thereby observe the battery behavior in each one.

Following are the tests selected to carry out the project, with the main results presented.

Initial Capacity

The capacity of a battery is the amount of electricity, in Ah, at the reference temperature, supplied by the battery at a determined discharge rate, until the final discharge voltage. The lead-acid battery, especially the vented type, is not completely formed after its production and, to reach its actual initial capacity, should undergo recharge / discharge cycles. To determine the actual initial capacity, C_{10} tests are performed and the recharge is according to the manufacturer's recommendation. The test is finished when two successive capacity values are obtained that differ by less than 2%. According to the Conformity Assessment Regulation (CAR) for system and equipment for photovoltaic application in Brazil[10], a nominal capacity of batteries for off-grid PV systems is determined at 120-hour rate of discharge (C_{120}). Also, the capacity of the battery in C_{10} was obtained because this value will be used to assess the capacity loss during the ageing tests.

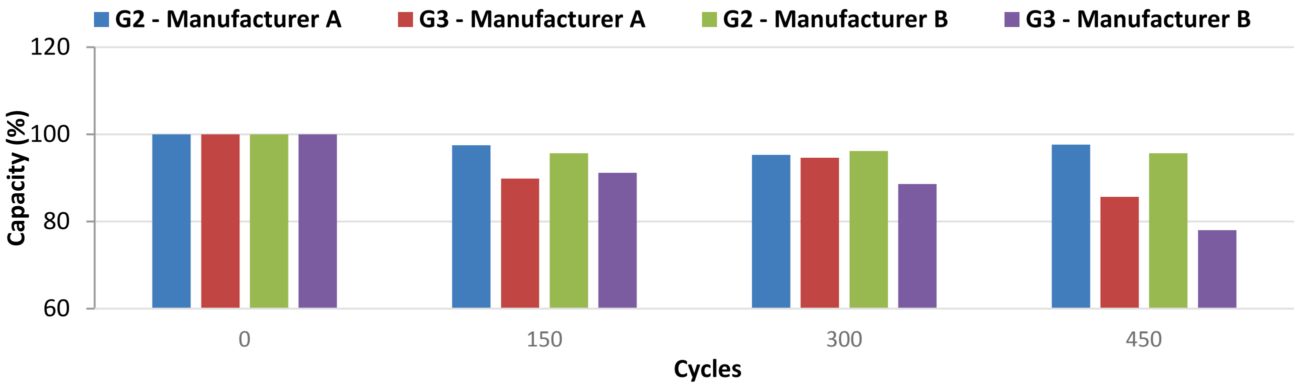
For Manufacturer A, an average value of 126% from the nominal capacity in the 10-hour rate of discharge (C_{10}) and an average of 122% for C_{120} was obtained. For Manufacturer B, an average of 106% and 109%, respectively, was obtained for the C_{10} and C_{120} rate.

CAR INMETRO for PV Systems (Based on IEC 61427)

The CAR for system and equipment for photovoltaic application was created by INMETRO (National Institute of Metrology, Quality and Technology), aimed at energy efficiency and security of PV systems components (battery, inverter, charge controller and PV module). The cycling test (endurance) in lead-acid batteries is based on IEC 61427[11]. The test has two phases. In Phase A, the battery performs 50 cycles with the SoC level limited between 25% and 55%, followed by Phase B, in which the battery performs 100 cycles with new boundaries of the SoC that are 75% and 100%. After the end of Phase B, a capacity test (C10) is performed to evaluate the capacity loss of the samples during the cycles.

This test was selected to simulate cycling at different levels of SoC, which is a condition usually found in isolated PV systems. In periods of good sunlight, the battery performs shallow cycles (high SoC). However, in rainy periods, the battery will supply power to most of the load and will have less recharge, operating at partial cycling with low SoC. Figure 1 presents the results obtained in G2 (40°C) and G3 (50°C) for both manufacturers.

Figure 1. Capacity C_{10} - G2 e G3



The results show that Manufacturer B is ageing faster than A. Another important point is that the battery is ageing faster at 50°C, as expected.

Cycling Test Around 10% SoC

Cycling in low SoC, proposed by CEA-GENEC (French Alternative Energies and Atomic Energy Commission) when there were no specific standards for the PV application, in order to evaluate batteries in systems that are undersized or operating in areas where there may be little sunlight for long periods.

The test is performed on a battery cycling between 0% and 20% of SoC at 40°C. This test emphasizes the sulfation and stratification process, which are the most significant and common degradations for lead-acid batteries of the OPzS technology in PV application. It is noteworthy that this cycling is similar to Phase A of IEC 61427.

Figure 2. Capacity C_{10} - G4 - Manufacturer A

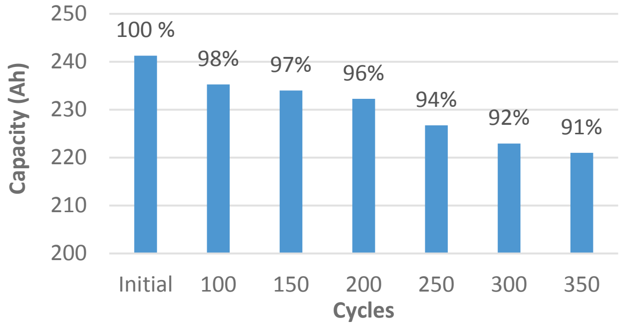
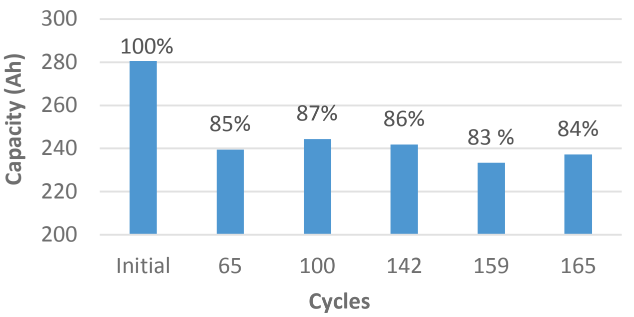


Figure 3. Capacity C_{10} - G4 - Manufacturer B



The results show that this is one of the most severe tests. Again, battery Manufacturer A has a better performance because it lost 9% of capacity after 350 cycles, while Manufacturer B lost 17% after 159 cycles. Manufacturer B has a lower number of cycles because, during the cycles, the samples are reaching the lower limit voltage established for the tests (1,5 Vpc) in order to not cause irreversible damage to the battery, so it is necessary to stop the test and to check if the battery has reached end of life.

Cycling Test Around 40% SoC

Just like the previous cycling, this procedure was developed by the CEA-GENEC. The objective is to evaluate the battery performance in cycles with the state-of-charge between 30% and 50%, running at 40ºC. It also emphasizes the sulfation and stratification.

Figure 4. Capacity C_{10} - G5 - Manufacturer A

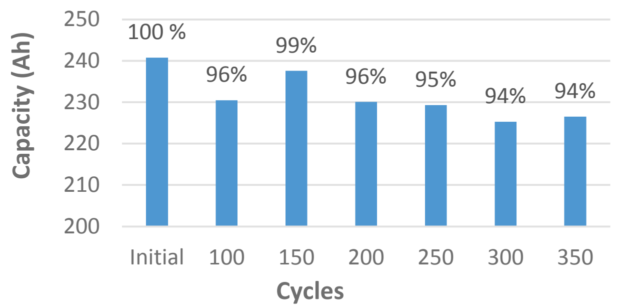
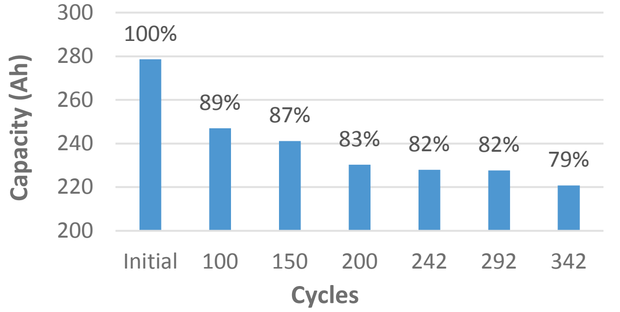


Figure 5. Capacity C_{10} - G5 - Manufacturer B



In theory, this test is supposed to be less severe than the previous test. However, it was observed that the battery from Manufacturer B had a greater degradation.

Decentralized Rural Electrification (DRE) Cycling Test

This procedure was also prepared by the CEA-GENEC to meet the characteristics of Decentralized Rural Electrification (DER). Cycling with high DoD is carried out to cause sulfation and stratification and, in order to mitigate these phenomena, cycles are then performed to overcharge the battery. The test is performed at 40°C with two steps of cycling: (i) 5 cycles with discharge up to 1.75 Vpc, followed by 3-hours rest, and a recharge limited by 2.35 Vpc, also followed by 3-hours rest; (ii) 5 cycles with discharge up to 1.75 Vpc, followed by 3-hours rest, and recharge coefficient of 1.2 C_{10} (i.e., 120% of capacity), and 3-hours rest. This behavior can be found in installations having sporadic use.

The tests were not severe. As a result, after 70 cycles, the samples of Manufacturers A and B lost 3% and 4.5%, respectively. Therefore, the overcharging had proven to be a good method to prevent sulfation and stratification.

Partial Cycling at Different Levels of SoC

Charging and discharging cycles occur daily in batteries for PV system application, and it is important to simulate different conditions to identify the influence of the SoC and temperature in the degradation. This test aims to identify the life curve of the battery in different conditions of cyclic operation, such as DoD, SoC and temperature. High temperatures are used (40°C and 50°C) to accelerate the ageing process and to compare the influence of this factor. The recharge during the cycles is performed at constant current of 1.03 x C_{10} (A) to compensate for losses.

Cycling tests at high SoC do not result in much degradation. Figure 6 shows only the results of the tests performed in groups 10 and 14 of Manufacturer B, because the samples of Manufacturer A had a capacity loss of only between 3 to 4%. It is possible to note that temperature does not influence in this case. For Manufacturer B, it is possible to affirm that the lower the DoD during the cycles, the greater the degradation.

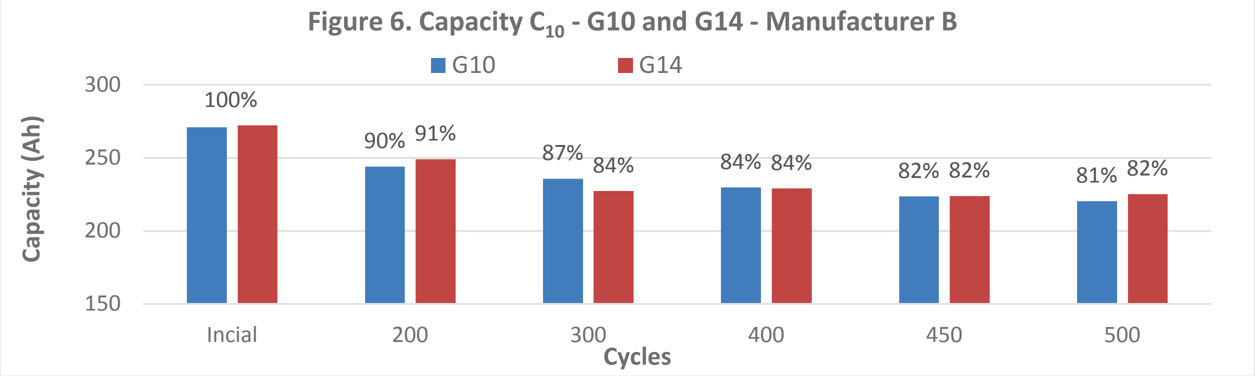


Figure 6. Capacity C_{10} - G10 and G14 - Manufacturer B

Cycling Based on a Real PV System of Dresser-Rand Guascor

This test was based on operating conditions of the batteries in a PV system installed by the Dresser-Rand Guascor company in the northeast of Brazil. Cycling is performed varying the SoC of the battery between 50% and 90% at 40°C, with a 3 hour rest period between the discharge and recharge. The rest period simulates a period when the battery can remain discharged due to the absence of sun.

Figure 7 shows the test results on samples of Manufacturers A and B. The battery in this cycling test operates at a medium SoC, and it is a severe test in terms of sulfation and stratification.

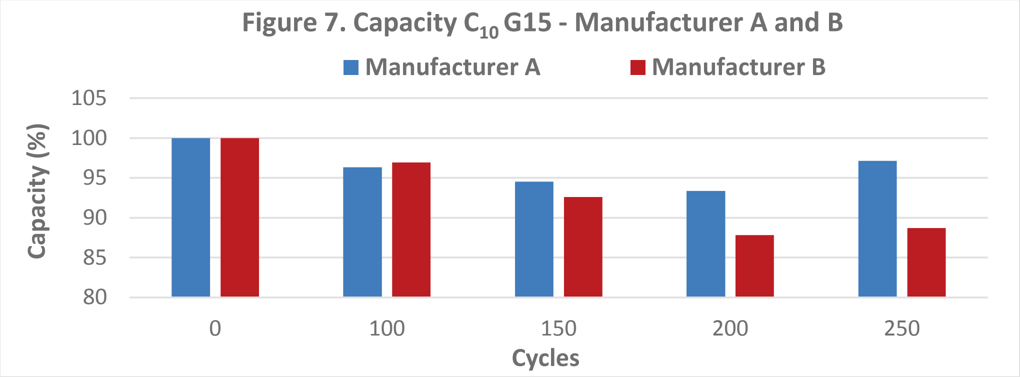
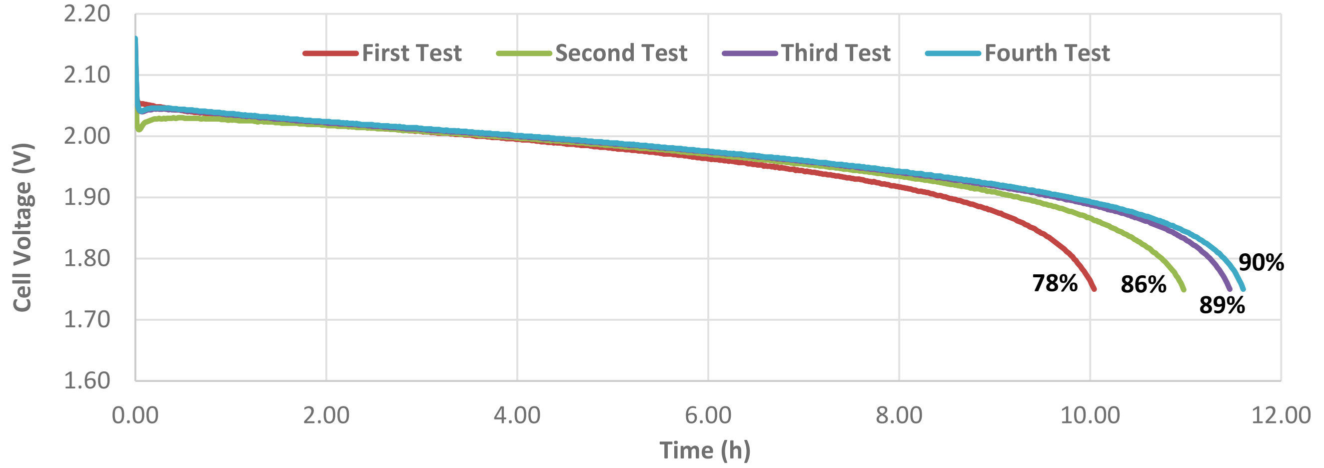


Figure 7. Capacity C_{10} G15 - Manufacturer A and B

Impact of the Overcharging in the Effect of Sulfation

After 450 cycles, one of the cells of Group 3 from Manufacturer B had achieved the capacity of 78%. It was observed that after each capacity test (C_{10}), the cell recovers an amount of energy. Figure 8 presents the sequence of capacity tests and, next to each curve, the percentage of capacity obtained is shown, increasing from 78% (first test) up to 90% (fourth test).

Figure 8. Sequence of capacity tests in one cell of the G3 - Manufacturer B



The increase of capacity, with the sequence of tests, may be occurring due to the breakdown of lead sulfate crystals during the recharge, causing an increase in the active material in the plate. In order to fully recharge the batteries used for the tests, the manufacturer recommended recharging 120% of nominal capacity, thus requiring the application of constant current at the end of recharge. Therefore, this overcharging may be reducing the sulfation. On the other hand, it is important to remember that overcharge causes corrosion.

Summary

The use of appropriate lead-acid batteries for off-grid PV systems is crucial to maintaining the durability and reliability of PV generation. The four main degradations that can affect a lead-acid battery in this application are sulfation, stratification, corrosion, and active mass degradation. The lead-acid battery of OPzS technology was considered the best one because it is more resistant to corrosion and active mass degradation.

It is difficult to predict the operating condition of a battery in off-grid PV systems because there are several variables. Consequently, to reproduce the behavior of the battery during its life, it is necessary to incorporate different laboratory test procedures, as each one has to cause a distinct type of degradation. The main conclusions of the laboratory tests are:

- The real capacity of the batteries was oversized, compared to the nominal value stated by the manufacturer.
- Different performance was observed in batteries of the same technology (OPzS). This can be explained by the different designs from the manufacturers (manufacturing process, grid alloy, etc.).
- The OPzS batteries proved to be resistant in the tests that accentuate the corrosion phenomenon.
- The tests that induce stratification and sulfation are more aggressive to OPzS batteries.
- Overcharge can avoid the sulfation and stratification effect.
- Projects that involve degradation of batteries should plan for long periods of testing, because is difficult to estimate the duration of tests that can vary for each battery technology.

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