Capacity Loss in PV Batteries and Recovery Procedures

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Abstract. PV battery testing has been conducted to identify PV battery charging requirements and capacity loss mechanisms. To date, laboratory and system testing consistently identified the incomplete recharge of PV batteries as the predominant cause of premature capacity loss resulting in a lower than rated cycle-life. Incomplete battery recharge introduces battery degradation mechanisms such as electrolyte stratification, gas bubble entrapment, excessive sulfation, and degradation of the positive active mass. Recovery of the PV battery after extended periods in a deficit charge condition may or may not be possible depending on the extent of battery degradation and the resources available for recovery. This paper examines the causes of PV battery capacity loss and possible recovery methods.

INTRODUCTION

PV battery cost calculations by the author, the University of Cape Town, and Bopp et al. [1,2] indicate that optimistic battery life-cycle costs start at about 33% of overall initial photovoltaic (PV) system costs. The above costs were calculated for the lowest priced batteries using the most optimistic cycle-life predictions. Costs will increase accordingly if more expensive batteries are used or if they don't achieve their predicted cycle-life. The increased initial costs and lower cycle-life performance of valve regulated lead-acid (VRLA) batteries make proper charging and maintenance of these batteries even more important in controlling the PV system life-cycle costs. In most PV power systems with VRLA batteries, the battery is by far the single largest life-cycle cost factor. This is why it is so important to design the PV system with the battery in mind.

The information presented here is intended to help PV system integrators and consumers understand the reasons for lead-acid battery premature capacity loss in PV systems. The procedure for achieving optimal battery cycle-life begins with battery selection and requires identifying your battery charging, installation, and maintenance requirements. In support of the battery charging requirements, the Sandia PV Balance of Systems (BOS) program and the Florida Solar Energy Center are testing PV batteries to identify improvements in PV system design and battery charging. The results to date clearly show that significant capacity and cycle-life improvements are possible with relatively low cost PV system design and hardware modifications.

PV battery testing at Sandia National Laboratories and the Florida Solar Energy Center has been underway for more than nine years. During this time numerous PV battery tests were conducted in the laboratory and with fielded systems using various PV charge controllers, regulation voltages, and battery types. [3-6] In general, this work identified numerous preventable sources for premature battery capacity loss. The effects of battery regulation voltage, internal battery degradation mechanisms, and battery charging and recovery procedures will be examined in this report. A detailed summary of the above items follows.

PV BATTERY CAPACITY LOSS

Initial PV battery testing [3] using vented (flooded) thin plate deep-cycle lead/antimony batteries and PV charge controllers purchased using the charge controller manufacturer's recommended regulation voltage resulted in significant battery capacity losses, in most cases due to under charging. Figure 1 summarizes the results from this work and plots the charge controller array reconnect voltage (Vrr) vs. percent of initial battery capacity. The associated array disconnect voltage or regulation voltage (Vr) is also included for comparison purposes. The plot of Vrr vs. percent of initial battery capacity provides a much stronger relationship to battery capacity than Vr and battery capacity. When a constant voltage or pulse width modulated (PWM) charge controller is used, the Vrr and Vr are the same or nearly the same value. The best example of the strong effect that Vrr has on capacity is shown by the third data point from the top where Vr is 15.08 volts and Vrr is 14.08 volts. Even though this battery used the highest regulation voltage, it did not result in an improved battery capacity relative to the other Vrr values. Also the trendline projects that a Vrr voltage over 15.0 volts (2.50 vpc) is required for maintaining 100% of initial battery capacity. This is consistent with the manufacturer's (Trojan Battery) recommendation for a full charge or an equalizing charge. Trojan Battery recommends that 15.5 volts (2.58 vpc) for 2 to 4-hours be used for equalization. The full or equalization charge is usually not recommended in PV systems every cycle because of the dramatic increase in water consumption and resulting maintenance. Usually Trojan Battery will recommend an equalization charge about every 10th cycle in deep-cycle service to 80% depth of discharge. In PV systems a compromise between battery capacity and maintenance is reached by using a temperature compensated regulation voltage that maintains the battery to at least 80% of its initial capacity.

PV Battery Regulation Voltage
The Tramway [4] lighting systems using both on/off and constant voltage charge controllers with temperature compensation are an example of stand-alone PV system performance using the battery regulation voltages and array sizing specified below.

Figure 1

Array Reconnect Voltage (Vrr) vs. Battery Capacity
Avg. of 4 and 8 Month Capacity Tests
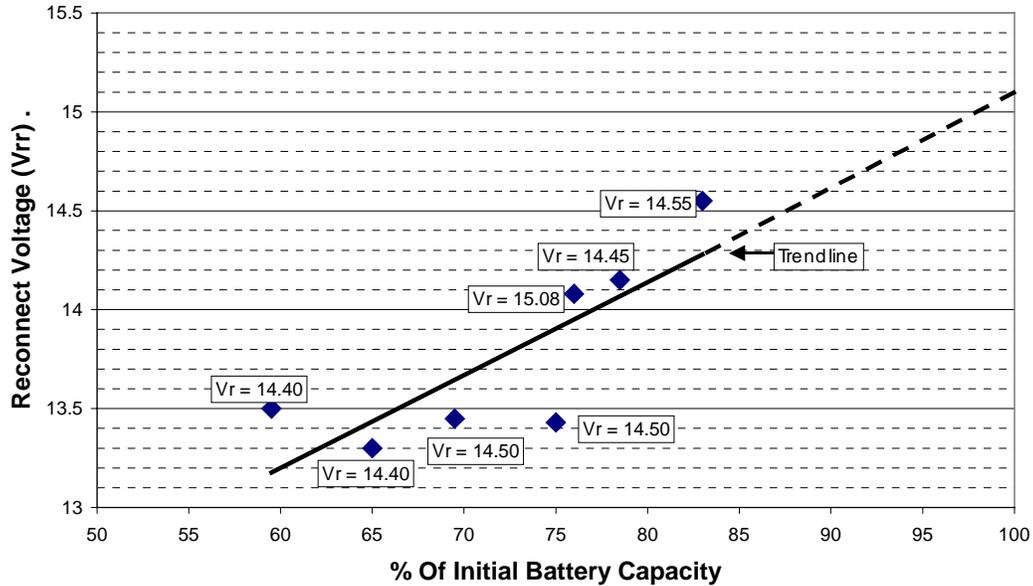
As suggested by Figure 1, a minimum vented lead/antimony battery regulation voltage of 14.4 volts (2.40 vpc) for constant voltage/PWM charging and 14.7 volts Vr (2.45 vpc) 13.7 volts Vrr (2.28 vpc) for on/off charging at 25°C is required to maintain the battery at about 80% of its initial capacity. In addition to the regulation voltages, batteries in stand-alone PV systems require adequate PV charging current measured in amp-hours (Ah) to ensure adequate battery recovery rates and overcharge. The Tramway PV systems used a minimum PV Ah to load Ah ratio of 1.27. The battery capacity from eight Tramway batteries after 2.5 years of operation indicated that battery capacity was 63 to 90% with an average capacity of 82% of the initial installed value. The batteries using constant voltage charge controllers exhibited slightly higher capacity values between 80 and 90% with an average value of 86% of their initial installed capacity. Additional field tests at the Venice, Florida lighting systems [5] with the same voltage setpoints and system design as the Tramway systems, resulted in batteries operating at 85 to 90% of their initial capacity after 1 year. The above golf cart batteries are expected to last over 5 years in PV systems before normal wear-out causes major capacity loss. In summary, the field results are very similar to the battery capacity values predicted in Figure 1 for the above voltage setpoints.
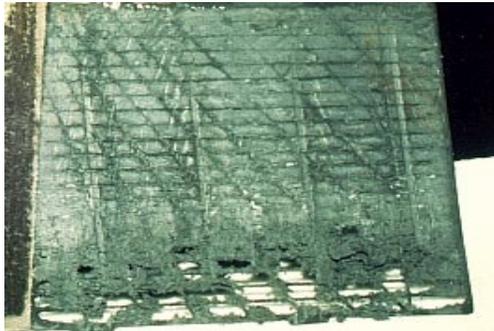
PV BATTERY CAPACITY LOSS MECHANISMS

PV battery post mortems from the above charge controller tests were conducted by cutting opening the battery cases and inspecting the internal battery components for

degradation. The post mortem results from the batteries used in Figure 1 have identified at least two obvious mechanisms for battery capacity loss in PV systems. In the most severe cases where battery capacity is in the 60% range, the battery will be suffering from electrolyte stratification and gas bubble entrapment. In intermediate cases where the battery capacity is around 80%, electrolyte gas bubble entrapment tends to block the electrolyte from circulating to the active material and this results in a temporary reduction in capacity. The other premature capacity loss mechanisms documented in numerous publications include excessive sulfation and degradation of the positive active mass (PAM). The less obvious internal capacity loss mechanisms such as excessive sulfation and degradation of PAM are usually not recoverable with a full recharge like stratification and gas bubble entrapment. It is important to understand that battery sulfation will only become excessive after weeks to months in a discharged condition.

Electrolyte Stratification
Figure 2 is a photograph of a PV battery that was damaged due to long term stratification causing negative plate deterioration. Note that only the bottom of the plate experienced loss of grid and active material from stratification. The top half of the plate contributed very little capacity to the battery because the electrolyte was at a very low specific gravity. At the bottom of the plate the electrolyte was at an excessively high specific gravity causing the loss of active material. The high acid concentration consumes the bottom of the grid resulting in the loss of active plate material. The operating capacity for this battery was probably about 60% of its initial capacity over most of its life. In a healthy battery, normal wear-out occurs from uniform positive plate grid corrosion and the negative plate remains intact.

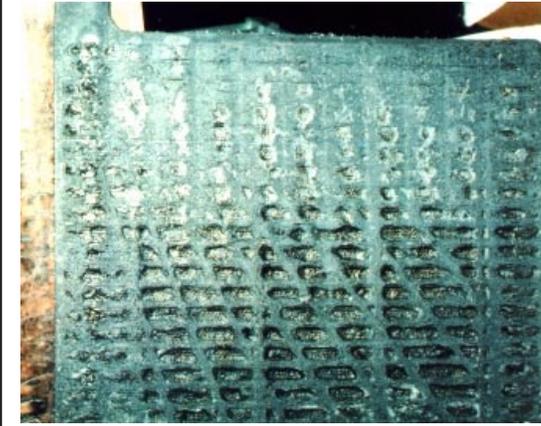**Figure 2: Electrolyte Stratification Causing Negative Plate Grid Deterioration**

Electrolyte stratification is caused when the heavier acid/water mixture falls to the bottom of the battery and the lighter water floats to the top of the battery during recharge. If the gassing rate on recharge is limited by a low regulation voltage and/or is cut short because of cloudy weather, then the required mixing of the electrolyte will not occur. Recovery requires extended heavy gassing of the battery for hours at voltages at or above 14.4 volts (2.40 vpc).

Gas Pockets

Figure 3 is a photograph of a negative plate that shows signs of gas bubbles for an extended period. The oval looking pox marks are left in the negative active material because of the differences in plate activity between areas with and without gas bubbles. The battery capacity is usually in the 60 to 80% range and can be easily recovered with heavy gassing. Gas bubble removal requires some vibration or motion of the battery case and/or heavy gassing.

Figure 3: Gas Pocket Marks On Negative Plate

Excessive Sulfation

Excessive sulfation as defined by Vinal [7] in deep-cycle lead-antimony batteries occurs primarily because of 1) incomplete recharge over an extended time usually weeks to months, 2) filling cells with electrolyte instead of water, and 3) operating the battery at excessive temperatures. The excessive sulfation is also referred to as "hard" sulfation because the sulfate crystals grow larger than normal, have a gritty feel, and become difficult to reduce by charging current. The degree to which capacity is lost depends on the regulation voltage, depth of discharge, temperature, and time spent in a deficit charge condition. "Hard" sulfation as a capacity loss mechanism can be identified by a long history of under charging (usually months) and a low specific gravity (<1.250) after heavy gassing for several hours during a full recharge to the equalization voltage.

Degradation of The Positive Active Mass

According to the most recent research on 'premature capacity loss' (PCL) [8-13] there are at least three possible degradation processes that occur in the positive active mass (PAM). The PAM degradation mechanisms include the following: 1) the positive active material interparticle contact zones increase in internal resistance, 2) a passivation layer of lead-oxide (PbO) and barrier layer of lead-sulfate ($PbSO_4$) are formed on the grid, and 3) the active material expansion and contraction results in an electrical contact loss with the grid. The net effect is a loss in capacity due to a loss in available positive active material. In the case of deep-cycle vented batteries with high antimony content grids (~5% Sb), the non-conductive passivated grid oxides ($PbO_{<1.5}$) are converted back to conductive ($PbO_{>1.5}$) oxide by charge voltages at or above 14.7 volts (2.45 vpc) as shown by Pavlov. [12]

Deep-cycle tests on pure lead grids, lead grids with a low percentage of antimony (~1.5%), and especially grids alloyed with calcium show a strong tendency to form a non-conductive passivation layer on the positive grid even when charged properly. In the case of the calcium grids this is known as the 'antimony free effect' and in general this phenomenon is termed 'premature capacity loss' because it occurs after deep cycles and complete recharges. Many VRLA batteries use lead-calcium grids; and to minimize the PCL they will add small amounts of tin and other elements to the grid alloy. In some cases phosphoric acid is added to the electrolyte as shown by Dimitrov, Pavlov, Hollenkamp, et al. and Bullock. [8,9,12,13,15]

The batteries most resistant to PCL are those using high antimony (~5%) alloyed grids and those that have a high content of tetrabasic lead sulfate ($4PbO \cdot PbSO4$) crystals in the positive active material produced during the positive plate curing and formation. The tetrabasic lead sulfate crystals as stated by Lam, et al. [14], "…produce a robust, crystalline network that serves to increase the mechanical strength of the plate material (i.e., in a manner similar to the action of steel rods or wires in reinforced concrete)." Most deep-cycle batteries will use the above process because it imparts a longer cycle-life and a stable capacity over the cycle-life.

"Hard" Sulfation Battery Recovery
Lead-acid batteries left discharged for a long period of time (months) will suffer from "hard" sulfation and may or may not be recoverable. Desulfation tests based on the battery manufacturer's recommended recovery procedures have demonstrated that vented deep-cycle lead-antimony golf cart batteries could be recovered after approximately 6 months of cycling in a deep discharge state between 20 and 30% capacity.

Additional tests on deep-cycle gel VRLA batteries discharged for months also indicated that recovery was possible. The deep-cycle gel batteries had phosphoric acid additions to the electrolyte, which is believed to enhance deep-cycle performance by minimizing "hard" sulfation and PCL. In this case full recovery was accomplished with repeated deep cycles using an extended charge time of 24 hours at a regulation voltage of 14.1 (2.35 vpc) or 14.4 volts (2.40 vpc).

The best indicator that a vented battery is suffering from "hard" sulfation is a battery history of being undercharged and a low specific gravity (<1.250) after a full recharge to at least 15.3 volts (2.55 vpc) for a minimum of 3 hours. Figure 4 shows electrolyte specific gravity plotted vs. the number of Ah recharged into the 6-volt battery at a 20-amp, 10-hour (C/10) rate as per manufacturer's recovery recommendations. In this case the battery is clearly suffering from "hard" sulfation as indicated by the low battery specific gravity of 1.230 after an equalization charge to 7.65 volts (2.55 vpc) for 3 hours. Each data point after the initial charge to 7.65

volts is a constant current charge at 20-amps terminated when the battery reaches 45°C. After battery cool down to room temperature, another 20-amp charge is initiated until the specific gravity reached the manufacturers recommended value of 1.277. The result after nearly 600 Ah recharged into the battery was a recovery to normal specific gravity (~1.277) and 80% of the battery's initial capacity after 2 years of normal PV service and 6 months of cycling between 20 and 30% capacity. As indicated in the above section on the Tramway PV lighting systems, 80% of initial capacity is typical of batteries that were cycled under Tramway PV conditions for 2.5 years.

Figure 4

Desulfation Charge For Tramway Golf Cart Battery
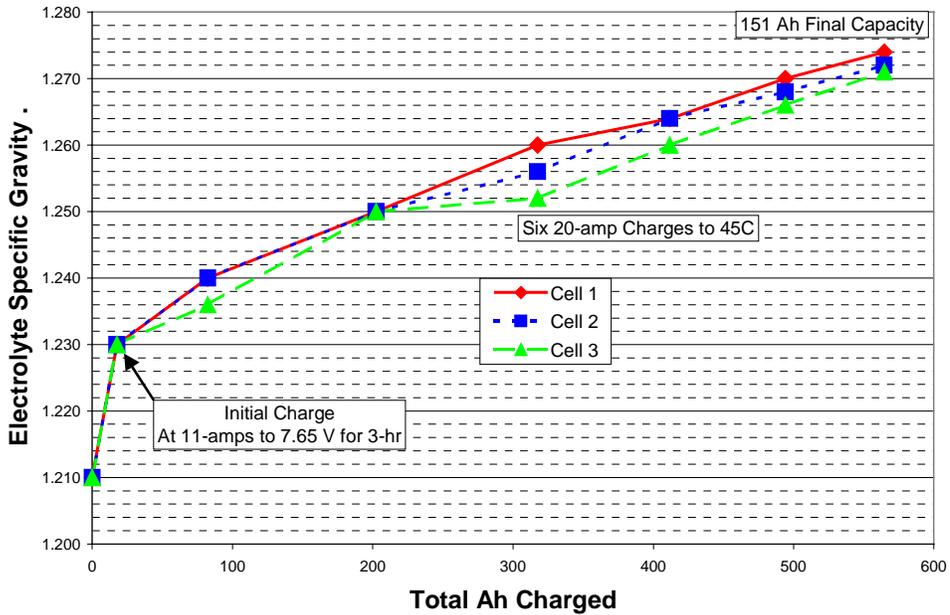
PULSE CHARGING

The greatest challenge that faces PV battery charging is providing the lead-acid battery with the last 5 to 20% of charge. Continued cycling without completely recharging the battery will result in a steady decline of capacity due to the incomplete charge and the resulting capacity loss mechanisms of stratification, gas bubble entrapment, "hard" sulfation, and degradation of the PAM. In some cases the time required to recharge the last 5 to 10% of capacity is beyond the capabilities of the PV system. Battery recharge in stand-alone PV systems must occur within the time that the sun is shining. Even in PV/hybrid power systems where there is an engine generator for battery charging, the cost of running the engine generator to complete the battery finish-charge may be beyond the economic limits of the

system. As a result of the need for more efficient battery charging in PV systems, high current pulse charging is being examined as a means of accelerating the battery charging process. Fast, efficient lead-acid battery charging research has its roots in the electric vehicle industry. The initial research goes back over 28 years and the results have been mixed.

Literature Survey
The earliest work reviewed here was by Mas and Sparks in 1971-72 when the concept of high current pulse charging was first introduced for electric vehicle (EV) battery charging. [16,17] At the time claims were made that indicated a high rate (~300 amps), short duration (~4 milliseconds) discharge pulse at predetermined intervals could dramatically reduce the time required to charge the battery with the associated high charge rates (100 amps). Tests were conducted on 6- and 12-Ah batteries at the above high rates. In addition to the tests on small batteries, a 190-Ah traction battery using a charge rate of ten times the capacity (1900 amps) and the associated >1900 amp depolarization discharge pulses was also tested. Recharge times in both cases were claimed to be 5 to 10 minutes. In contrast, Smithrick [18,19] found that high current pulse charge or discharge provided no reduction in recharge time for lead-acid batteries. The most recent work in 1993 and 1995 by Lam, et al. [14,20] claimed medium current (30 amp, 0.2 sec) pulse charging alone was responsible for dramatic improvements in positive plate formation efficiency, reduction in recharge time, and increased cycle-life through reduced premature capacity loss. It should be noted that in the earlier pulse charging work a depolarization discharge pulse was included and considered essential to the success of the fast charge process. No depolarization discharge pulse was used in Lam's work.

Depolarization Discharge Pulse Testing
It is important to emphasize that all of the previous research was conducted in support of the EV battery charging market where utility power is available for rapid high rate recharges. In PV systems, both stand-alone and hybrids, the recharge rate is limited by the PV and engine generator. Most PV recharge currents are in the 10 to 40-hour range because of the hardware and economic limitations. The specific testing reported on here was limited to medium current (10 to 40 amp) pulse discharge testing only because of the fundamental charge rate limitation using PV, specific interest in depolarization current pulses for VRLA battery charging, and the limitations of the laboratory test equipment.

An absorbed glass mat valve regulated lead-acid (AGM VRLA) battery was chosen because similar batteries had been well characterized in previous testing. Valve regulated batteries in general require longer finish-charge periods than vented (flooded) batteries and are difficult to finish-charge in PV-cycle conditions. If VRLA batteries can be charged in less time in PV systems, then that could significantly enhance their performance. It was hoped that depolarization current

pulses would shorten this finish-charge time by increasing the charge acceptance. The performance parameters in this test procedure were percent overcharge (charge acceptance) based on amp-hours (Ah in/Ah out) and battery capacity in Ah.

The test procedure consisted of cycling an 80 Ah absorbed glass mat (AGM) valve regulated lead-acid (VRLA) battery in a PV battery cycle program designed to simulate a stand-alone PV system with an array Ah-to-load Ah ratio of 1.3 for 25-cycles. The battery was discharged and charged at the 35-hour rate to 20% depth of discharge. The charge was limited by time so that the battery reached regulation voltage (14.1 volt, 2.35 vpc) for 2.6 hour every cycle. Base-line performance data using constant voltage, current limited charge was measured using this test procedure at the beginning, middle, and end of the 7-month test period. The base-line percent overcharge data was used to track changes in charge acceptance over time and used to compare to the charge acceptance or overcharge using the 20 and 40-amp depolarization discharge pulse during the voltage regulated recharge period. The depolarization discharge pulse was programmed to occur 159 times over the 2.6 hours at regulation voltage. The discharge pulse was programmed to occur once every minute for 1 second. Discharged amp-hours were precisely calculated by the battery tester, then subtracted from the charged Ah to provide accurate net Ah measurements for percent overcharge and battery initial and final Ah capacities.

The results in Figure 5 show that 0.16 to 0.32 additional Ah were charged into the battery every cycle over the 2.6-hour charge at regulation voltage. The additional charged Ah translate into a 1 to 2% increase in overcharge during initial testing from about 105%, to 106% and 107% due to the depolarization discharge pulse. The battery manufacturer usually recommends about 110% overcharge for a full charge. Near the end of the test sequence in Figure 6, after about 100 cycles, significant changes occurred in the battery resulting in overcharge increases to 114% from about 107% initially. The overcharge increase also occurred in the baseline constant voltage charge, which again was slightly lower by 1 to 3%. Battery capacity measurements after a complete 12-hour finish-charge and the end of each test sequence do not show a clear trend toward improvement. Only the initial tests using both constant voltage and discharge-pulse charging show small increases of 2 to 6 Ah in battery capacity. At the end of the 7-month test sequence and 175 cycles, battery capacity was clearly dropping from 80 Ah to about 67 Ah in both constant voltage and discharge-pulse charging. The capacity loss in Figure 6 began to occur after 100 cycles. At this time it is not known if the increase in overcharge to 114% from 107% is due to the depolarization discharge pulses or to battery aging characteristics. Historically this battery did not demonstrate an increase in overcharge unless it was left in a discharged condition. No deficit charge cycling was conducted on this battery. More testing would be required to better establish the cause of the increase in overcharge over time and establish the value of this charge algorithm in life-cycle battery tests and fielded PV systems.
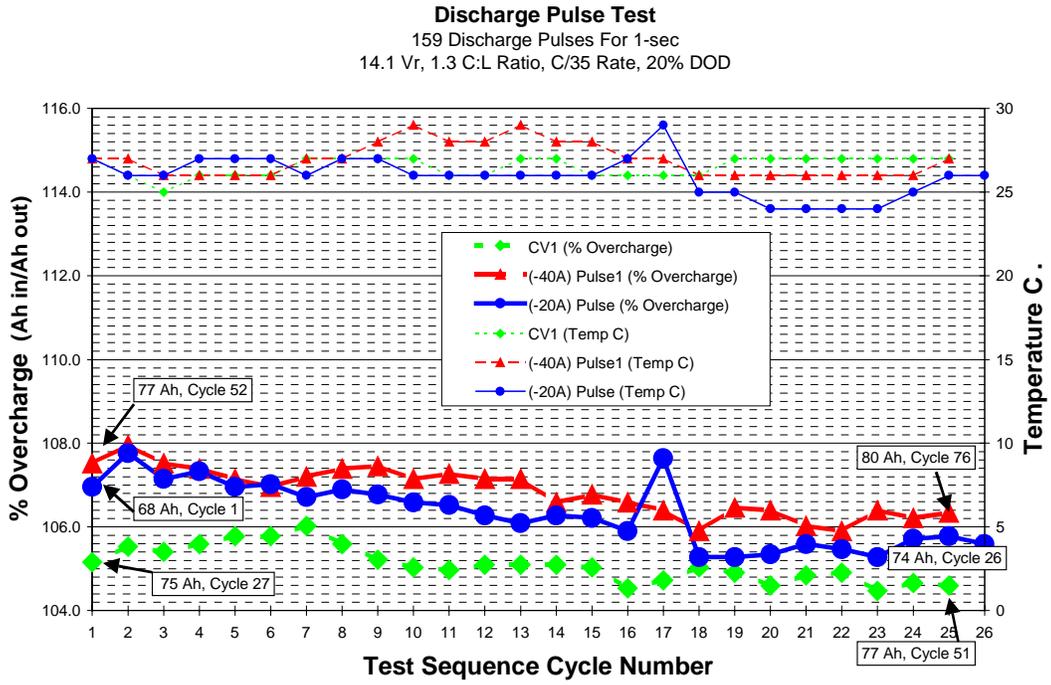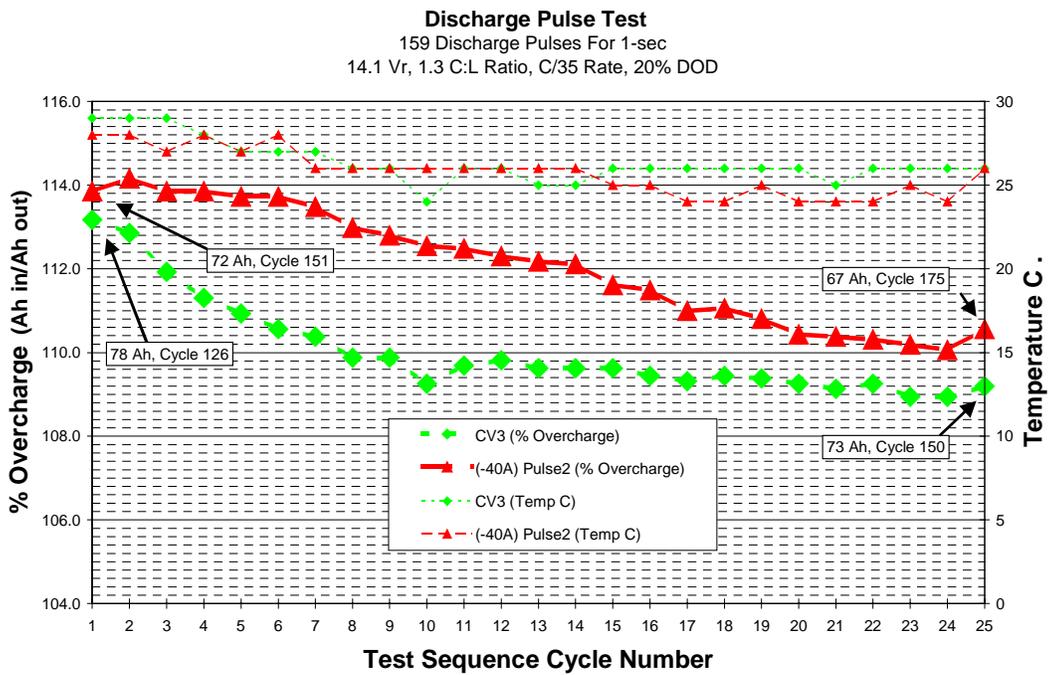
Figure 5

Discharge Pulse Test
159 Discharge Pulses For 1-sec
14.1 Vr, 1.3 C:L Ratio, C/35 Rate, 20% DOD

Figure 6

Discharge Pulse Test
159 Discharge Pulses For 1-sec
14.1 Vr, 1.3 C:L Ratio, C/35 Rate, 20% DOD

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SUMMARY

Work here has clearly shown that significant improvements in vented (flooded) lead-acid PV battery charging are possible with minimal additional costs. The most significant improvement can occur by using appropriate regulation voltages with temperature compensation in conjunction with adequate PV array sizing. This was found to eliminate most premature battery failures.

PV system tests have demonstrated that vented lead-antimony batteries require a minimum regulation voltage of about 14.4 volts (2.40 vpc) for constant voltage charging and about 14.7/13.7 volts (2.45/2.28 vpc) for on/off charging with a minimum array amp-hour to load amp-hour ratio of about 1.3. In areas where battery temperatures deviate by more than 5°C above or below 25°C, temperature compensation of the regulation voltage was required for effective battery charging.

The charging limitations with VRLA batteries are more challenging. Because these batteries have strict charge voltage requirements due to the limited available water in the battery and the oxygen recombination cycle, they require longer finish-charge times. More efficient charge controllers with precise voltage regulation (14.1 or 14.4 volts) are required; and use of VRLA batteries more tolerant to deficit charge cycling is critical to good PV battery cycle-life. With this in mind, the PV system designer needs to understand the cost, maintenance, cycle-life, and operational limitations between vented lead-antimony batteries and available VRLA batteries. In the end, the most cost-effective system will be the one that utilizes its batteries most effectively. To do this requires a solid understanding of battery performance and battery requirements.

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