IN THE FINAL ANALYSIS: POST MORTEM TESTS AND MEASUREMENTS ON A VRLA BATTERY

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ABSTRACT

The battery failed and is sent back to the laboratory. The laboratory technicians are asked to figure out what went wrong and why. What tests can be performed, and in what order should they be carried out? The following is a description of some of the tests one might conduct and what the test results might imply about the design and failure modes of the VRLA Battery.

INTRODUCTION

The Valve Regulated Lead Acid (VRLA) battery is the battery industry's response to the customers' demands for a simple, inexpensive, low maintenance, energy storage device. To a large degree, this has been accomplished in the VRLA product. By using absorbent glass mat separators, a limited volume of electrolyte, and a pressure release valve, the flooded lead acid battery has been transformed into the VRLA battery of today. With this metamorphosis, the VRLA battery has become considerably more difficult to analyze or diagnose. Gone are the days when you could look through the jar walls to see the extent of positive plate growth or dendrites sprouting on the negative plates. No longer can you drop a reference electrode into the cell to measure the plate polarizations or withdraw electrolyte to measure specific gravity.

VISUAL INSPECTION

The first thing in any battery post mortem or failure analysis is a visual inspection. Besides obvious physical damage, a visual check for acid venting around the vent plug, or acid weeping out from the jar to cover seal or terminals should always be performed. Acid vapor or stains around the vent usually indicate that something went wrong during float service. This leads one to suspect a high charging voltage or a thermal runaway problem. Taking this a step further, we might look to other parts of the battery plant, such as the rectifier or other cells as the root cause of the acid venting. Signs of acid, other than around the vent, indicate physical damage that might occur in shipping, installation or in the manufacturing process. Acid wicking through the post seal and up onto the terminal causes the terminal, as well as the interconnecting bus bar, to corrode. Terminal post seal failure occurs more frequently on the positive because of the chemistry involved. On the positive terminal, the lead is converted to lead dioxide, which is easily recognized by its dark black color. Although post corrosion is a maintenance headache, it rarely causes a major problem since it is easily recognized and corrected.

A leak or break in the jar-to-jar cover seal is a more serious problem for several reasons. There is a safety issue, in that the vent and spark arrester are circumvented. An electrostatic discharge near the opening can ignite the gases inside the cell with disastrous results. Any openings in the cell will allow external oxygen to enter the cell, which will cause the negative plate to selfdischarge or sulfate. Electrolyte weeping from anywhere on the cell is a serious problem, in that it can form a conducting path to ground or to another cell. Although an electrolyte path is a high resistance connection (compared to a metallic connection), it is sufficient to cause serious problem in any battery plant and should always be corrected immediately. A visual check for swelling or bulging of the jar wall should also be performed. Bulging of the jar wall can occur when the cell is exposed to elevated temperatures, which allows the internal pressure to deform the sidewalls. It can also occur when the plates buckle outwards due to positive plate growth.

VOLTAGE AND CURRENT MEASUREMENTS

The next step in the examination are voltage and current measurements. If the battery, or cell, has been on open circuit for a few days to a week, the open circuit voltage can be used to indicate the value of the Specific Gravity (S.G.). At the end of the manufacturing process, the S.G. of a VRLA cell's electrolyte is approximately 1.300 S.G. This corresponds to an open circuit voltage (Vo.c.) of 2.15 Volts (V). In service, the cell's electrolyte usually increases in concentration because water is driven off, or lost, from the electrolyte. Water is removed from the electrolyte through electrolysis, corrosion of the positive plate, and as vapor transmission through the jar walls. The Vo.c. increases by approximately 1mV per point increase in S.G. Therefore, there is correlation between the changes in a cell's Vo.c. and the amount of water lost. The water loss equates to ~0.24% of the original weight of electrolyte for ever 1mV change in Vo.c. For example, a cell that starts off with a kgm of 1.300 S.G. electrolyte and after several years of service has a Vo.c. equal to 2.18V, would imply that the cell lost approximately 72 gms (.0024 x 30 x 1000) of water.

Conversely, a Vo.c. of less that 2.15V implies that the cell's S.G. is less than nominal. This occurs during cell discharge when sulfate ions in the electrolyte form lead sulfate on both plates. This is also the case when a cell has an internal short. (A note here to the neophyte. An internal short is a metallic as opposed to an ionic (electrolyte) connection between the positive and negative element. Shorts in the range of 1 to 10 ohms are enough to cause the cell to self-discharge on float.) There are several other possible explanations that are unique to VRLA cells and involve only the negative plate. The first occurs when external oxygen enters the cell through some unintended opening and, upon reaching the negative plate, causes it to self-discharge. The second occurs when the net charging current to the negative plate (the float current minus the effective current of oxygen recombination) is insufficient to overcome the normal self –discharge.

Often a cell or battery is placed on charge, and the cell's voltage and current is measured after steady state is reached. Without some prior knowledge, a single reading of current and voltage is not very helpful. For example, 2.27V and 300mA doesn't mean very much. However, by comparing it to data from similar type cells as shown in Table 1, it can be very helpful. In this particular case, we conclude that current is rather high for the voltage setting and would look further for an explanation.

Tafel Data											
Vaverage	2.338	2.304	2.267	2.234	2.200	2.296	2.286	2.347	2.264	2.224	2.277
Icell (ma)	350	197	62	34.6	18.3	160	160	398	72	25	100

Table 1. Cell Float Data

When the data in Table 1 is displayed as a voltage vs. current plot, it is referred to as a "Tafel plot" (after J. Tafel) because it follows the Tafel relationship or equation. The unique feature of this plot is that, above open circuit, the voltage on the positive and negative plate increases as the log of the current. Another way to express this is that the current (and consequently the evolution of oxygen on the positive and hydrogen on the negative) increases exponentially with a linear increase in voltage. The slope of the line for the positive and negative plates is 80mV and 120mV per decade, respectively. The Tafel equations, together with measurement data, provide a fundamental understanding of the characteristics of the cell in float service.

The design of VRLA batteries is such that only a very limited amount of acid is left in the cell at the end of the manufacturing process. There is usually just enough to provide for the discharge reaction. The loss of water during float service causes the electrolyte to shrink away from the plates and lose surface contact. This process manifests itself as an increase in the internal resistance and a corresponding loss of capacity. Therefore, limiting water loss is of paramount importance. This is primarily accomplished through a process known as oxygen recombination. The oxygen generated on the positive plate diffuses over to the negative plate. At the negative plate, the current that would normally go towards evolving hydrogen (with a slope of 120mV/dec), instead now goes towards recombining the oxygen to form water. A cell that is recombining oxygen will have a slope of 80mV/dec (i.e. 80mV on the positive and zero on its negative), while one that is not will have a slope of 200mV/dec (i.e.80mV on the positive and zero on its negative), while one that is not will have a slope of 200mV/dec (i.e. 80mV on the positive and the slope of the curve falls somewhere between 80 and 200mV/dec. Figure 1 is an example of a cell Tafel plot using the data in Table 1; here, the slope in the float region is approximately 100mV. (Note: In Excel, the equation for the trend line is expressed in the natural log (Ln) rather than log to the base ten. Here we multiply the slope by 2.3 to convert to base 10; i.e. 2.3 x .0435V = .1V or 100mV/dec.)



Figure 1 Typical Cell Tafel

A catalytic converter is a device that recombines hydrogen and oxygen gas to form water. Some VRLA batteries are manufactured with a catalyst located inside the jar cover of each cell. Often they are incorporated in the vent cap. Since they can be put in or taken out of a cell with relative ease, they can be useful as a diagnostic tool in the laboratory. The effect of a catalyst on the positive and negative plate can be seen in the Tafel plot of the cell. Figures 2 & 3 are Tafel plots of two different (size and plate configuration) type cells. Each plot contains two sets of data, one with and one without the catalyst. In Figure 2, the data with the catalyst and without the catalyst are virtually the same. A slope of 100mV/decade indicates that there is reasonably good oxygen recombination occurring at the negative plate. The usefulness of the catalyst at recombining oxygen cannot be determined from the data. The effectiveness of the catalyst in the cells can be assessed by comparing weight loss over time, both with and without the catalyst.



Figure 2. Cell Tafel plot with and without Catalyst

In Figure 3, the slope of the initial (without the catalyst) Tafel line is 117mV/decade. This implies that not all of the oxygen is making its way over to the negative plate to be recombined. There is a distinct shift in the Tafel line after placing the catalysts inside the cells. Here it is obvious that the catalyst is actively recombining oxygen and hydrogen. For the same current, the cells have higher voltages with the catalysts installed. This implies that even less oxygen reaches the negative plates and that the catalysts are recombining oxygen in the headspaces that would have otherwise made its way back to the negative plates. To determine the quantity of oxygen the catalyst is recombining in each cell that would have otherwise been lost through the vent, we again need to revert to weight loss measurements over an extended period of time.



Figure 3. Cell Tafel plot with and without catalyst

MULTIPLE CELL UNITS

Because of the size and the number of cells used in a battery plant, economic often dictates the packaging of several cells into one unit. Most often, this takes the form of six cells in series to form a 12V module. In such cases, there is only access to the end terminals and, therefore, the voltage and the impedance readings are the sum of six cells. Reading the voltage or impedance of six cells at a time greatly reduces the sensitivity of the measurement. The difference between a cell that is recombining and one that isn't may only be 40 mV. The same is true for the impedance measurements. Has the impedance increased by 5% on all six cells or has one cell increased by 30%? A 5% increase in each of six cells will give a much better capacity performance than a battery with a 30% increase in just one cell. The capacity of one weak cell can have a drastic effect on the capacity of the battery.

One of the practices used in the laboratory is to drive a nail through the cover and into the intercell connector. The nails act as external tabs to read each of individual cells in a 12 V battery. To demonstrate how helpful this can be, Figure 4 is a discharge profile of a 12 V battery at the end of life. The discharge shows each of the cells and their numerical average. From the plot, it is obvious that one cell is much worse that the others. The vent cap was removed at the end of discharge and a reference electrode was used to measure both the positive and negative plates. From the plate measurements, it was determined that the negative plate caused the premature voltage decay during the discharge. In most lead acid battery designs, the negative plate has more capacity than the positive and normally retains its capacity throughout its service life. Our suspicion was that the negative plate had self-discharged. On examining the cell's vent plug, it was noted that the oring was damaged. It was therefore concluded that the defective o-ring allowed oxygen to enter the cell and discharge (i.e. sulfate) the negative plate.





Often, only one plate or one cell in a 12 V battery is drastically weaker than the others. This can often be detected in the discharge curve by extending the discharge beyond the normal cut off voltage of 10.5V. When one of the plates (such as the negative plate in the previous example) is weak, there will be a sharp drop of 1V in the voltage plot. If one cell is weak, as when a cell is shorted, there will be a 2V drop. An example of this is shown in Figure 5. At 100 minutes into the discharge, there is a sharp drop of 2V. The battery then stays relatively flat for another 100 minutes before its final decay. Here we would conclude that the battery contained one weak cell that drastically reduced the performance of the battery.



Figure 5. 12V Battery Discharge

CONCLUSION

The VRLA battery is a much more complicated battery to design, manufacture and diagnose than the flooded design. Over the years, designers and manufacturers have had to develop new techniques and measurements to diagnose the various failures that are unique to this product.

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