NEW INSIGHTS INTO THERMAL RUNAWAY OF VALVE REGULATED LEAD-ACID BATTERIES

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ABSTRACT

Valve regulated lead-acid batteries have been known to fall victim to thermal runaway. A number of factors can contribute to this problem, though most common is a combination of high temperature and high float voltage. Through a series of tests that were designed to induce thermal runaway, the effects of various combinations of external and internal battery conditions could be determined. As the tests progressed, it became more evident that battery health and manufacturer played a large part in the determining the batteries' susceptibility to thermal runaway. This paper outlines the basic theory of thermal runaway, describes a series of tests to induce thermal runaway, and suggests different methods of preventing it.

BACKGROUND THEORY OF THERMAL RUNAWAY

Thermal runaway is an ongoing concern with valve regulated lead-acid batteries. Anyone who has worked with batteries long enough can relate a story about the telltale sights and smells of a failed battery in the throes of thermal runaway. Figure 1 shows the visible signs of a battery that was subjected to this failure mechanism. The smell of hydrogen sulfide released during the latter stages of thermal runaway is one that humans can detect in several parts per billion and is nauseating in higher concentrations.

Figure 1. *"Bloated" battery showing thermal runaway conditions*

What happens to a battery to cause thermal runaway, and what can be done to prevent its occurrence? Without going too far into the electrochemical theory of operation, this paper attempts to explain the causes and symptoms of thermal runaway and some very basic ways to prevent its occurrence. Thermal runaway occurs when more heat is generated within the battery than can be dissipated through its case. Heat is generated internally by exothermic chemical reactions from excessive charge current pumped into the battery. This heat generation increases as the applied voltage and/or the battery's internal temperature increases. Power – in the form of heat transfer – is dissipated from the battery through its exterior case into the ambient environment. If the battery cannot reject as much heat as it generates, its internal temperature rises. As the battery's temperature rises, its internal power rises. This self-feeding mechanism can go out of control if the rate of increase of generated heat is greater than the rate of increase of dissipated heat. This heat/current cycle eventually causes the battery to bulge. At 90°C the plastic case becomes soft and, with just a little internal pressure, bulges out as seen in Figure 1. More seriously, during thermal runaway other side reactions can occur that cause hydrogen to be released through the safety vents, creating the possibility of an explosion. As we will see, the propensity for thermal runaway depends not only on the battery's applied charging voltage and its surrounding thermal environment (ambient temperature and air circulation), but also on other factors such as battery design, construction, and state of health.

So where does this internal heat come from? When the battery is nearly or fully charged, current entering the battery causes a number of electrochemical reactions to occur[1]. Some of these reactions are due simply to the normal process of self-discharging and recharging. Some are unintended and corrosive, causing irreversible damage to the battery's structure. The internal reactions that are most instrumental in thermal runaway are ones that are exothermal (heat-releasing). This internal heat is generated mostly at the negative plate, in which lead and sulfuric acid react with oxygen – which is generated at the positive plate – to form lead sulfate and water. Equations 1 and 2 represent these reactions.

$$2Pb + O_2 \Rightarrow 2PbO \qquad \text{(Eq. 1)}$$

$$2PbO + 2H_2SO_4 \Rightarrow 2PbSO_4 + H_2O \qquad \text{(Eq. 2)}$$

Exothermic
negative-plate
reactions

Since electrical current forces these electrochemical reactions to occur, the amount of heat generated inside the battery is proportional to the amount of current entering the battery on float charge. Electrical power is mostly converted to heat while the battery is on float charge, since most of the current [2,3,4] goes toward these oxygen-regeneration reactions. The equations that are used to determine a battery's internally generated heat (power-in) and dissipated heat (power-out) are the following:

$$P_{IN} = V_{FLOAT} k \, e^{\alpha(V_{FLOAT})} e^{\beta(T_{BATT})} \qquad \text{(Eq. 3)}$$

Internally generated heat[4]

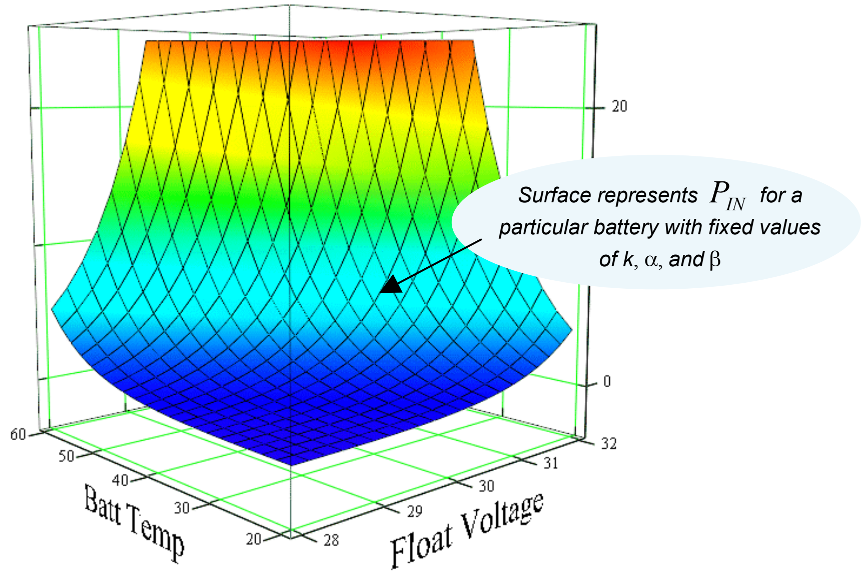
$$P_{OUT} = G_{THERMAL}\left(T_{BATT} - T_{AMBIENT}\right) \qquad \text{(Eq. 4)}$$

Dissipated heat

where $G_{THERMAL}$ is the thermal conductance of the outer casing of the battery and k, α, and β are constants which characterize how each unique battery responds to voltage and temperature. V_{FLOAT} is the float voltage at which the battery is charging. Using Equations 3 and 4, it would theoretically be possible to predict whether or not thermal runaway will occur for any given set of conditions.

Power In

In Equation 3 above, P_{IN} can be graphically represented by a three-dimensional surface. Figure 2 shows what this surface looks like for a representative battery with fixed internal characteristics k, α, and β. This surface shows that the power (rate of heat rise) generated inside the battery increases exponentially with applied voltage *and* internal battery temperature – if either rises, internal heat generation goes up.



Surface represents P_{IN} for a particular battery with fixed values of k, α, and β

Figure 2. *Graphic representation of Equation 3 – Power-in model for one representative battery*

Various electrochemical battery characteristics cause this curve to look different for each battery type, make, and condition, but the general shape of the curve remains the same for any valve regulated lead-acid battery. Figure 3 shows the modeled power-generation curve for four batteries (called G2, C3, C4, and Y3) having the same size and shape, and similar electrical rating. These curves approximate the actual battery characteristics exhibited during the testing for this report. Note that even though the batteries' ratings are nominally similar, their behavior under float conditions is dramatically different.

Power Out

Equation 4 shows that the amount of power that can be dissipated by the battery depends on its thermal conductivity and how hot it is relative to its surroundings. Thermal conductivity is the measure of the ability of the battery to shed its internal heat through its case into the ambient air around it, which depends on the properties of the plastic walls and the physical contact between the battery's internal active material and the external case. Since this relationship rises linearly with battery temperature and does not depend on float voltage, it is represented by a flat plane in the 3D voltage-temperature-power space. Figure 4 compares a typical power-out plane of Equation 4 with a typical power-in surface of Equation 3.

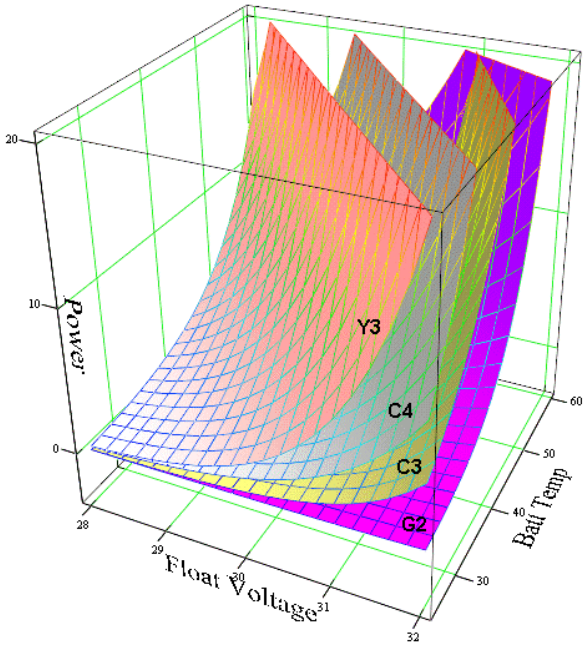


__Figure 3.__ Power-in model for four batteries of different make, model, and age

The hatched plane in Figure 4 depicts Equation 4 – the power that can be dissipated from a representative battery – for a particular ambient temperature (25°C in this example) as a function of the internal temperature of the battery. Notice that power out rises linearly with internal temperature but is constant relative to float voltage. The curved surface is the power generated within the battery by the exothermic reactions of over-current – the same general surface shape that was introduced in Figures 2 and 3. The black line in the foreground shows actual data recorded for a lead-acid battery at a fixed float voltage of 28 V, which corresponds nicely with the model.

For every different ambient temperature, a different power-out plane exists with a different intersection with the curved power-in surface (dotted yellow line). The higher the ambient temperature, the less temperature difference there is between it and the battery and so the less heat dissipation possible – therefore, the power-out plane is lower and has a lower intersection with power-in with respect to float voltage and battery temperature. Qualitatively, this means that the higher the ambient temperature, the lower the combination of float voltage and battery temperature that will cause thermal runaway to occur. In addition, other factors such as battery chemistry and the battery's thermal conductivity (G_{TH}) will affect the relationship between these two surfaces. Figure 5 shows how ambient temperature and G_{TH} move the power-out plane relative to the power-in surface.

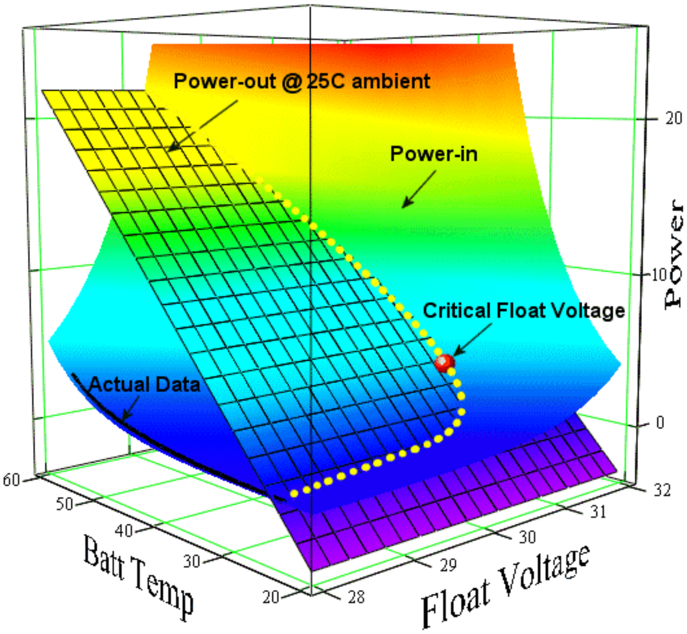


__Figure 4:__ Power-in surface and power-out plane, and the intersection between them

Stable Condition

In Figure 4, for any given combination of battery temperature and float voltage where the power-out plane is above the power-in surface, power-out capability is greater than power-in – a stable condition. For example, with 28 V applied to the battery at 25°C ambient temperature, power-in is temporarily greater than power-out, so the internal battery temperature will rise. The battery's internal temperature will rise to the point where the power-in curve intersects the power-out surface. At this point power-out equals power-in, so there is a balance in the system and battery temperature stays at this level. The battery will continue to operate indefinitely with a temperature slightly above ambient.

Unstable Condition

For thermal runaway to occur, the battery would have to continuously generate more heat than it can dissipate, making its temperature rise indefinitely. In Figure 4, if 32 V were to be applied to this example battery at a temperature starting at 25°C ambient, its power-in would be greater than its power-out and its internal temperature would rise. As the battery's temperature rises along the 32 V line, the power-in curve is always greater than the power-out plane. This means that the battery's internal temperature would constantly rise, indicating thermal runaway.

Float Voltage vs. Ambient Temperature

For a given set of battery characteristics that determine the shape of the curves seen above, there is a relationship between the ambient temperature and the maximum charging voltage above which thermal runaway will occur. To determine this relationship, take a closer look at Figure 4. A critical point on the 3D power plot is where the intersection between power-in and power-out bends around (the red dot marked "Critical Float Voltage" in Figure 4). This is where, for a given ambient temperature and battery characteristics, there is no higher float voltage where thermal equilibrium is attainable. Mathematically, this is where the slopes of each of these surfaces are the same at an intersecting point between the two surfaces. The derivation of this relationship is beyond the scope of this paper, but the results are fairly simple. Taking the partial derivative with respect to T_{BATT} of Equations 3 and 4, and combining with the equality: $P_{IN} = P_{OUT}$ results in:

$$T_{BATT} = T_{AMB} + \frac{1}{\beta} \qquad \text{(Eq. 5)}$$

This is true at the critical point where V_{FLOAT} is the maximum allowable for a given ambient temperature. Substituting this back into $P_{IN} = P_{OUT}$, results in an expression for V_{MAX}, the maximum float voltage for any given ambient temperature.

$$V_{MAX} = \left(K - \frac{\beta}{\alpha} \cdot T_{AMB} \right), \qquad \text{(Eq. 6)}$$

$$\text{where: } K = \frac{1 + \ln \frac{G_{TH}}{V_{MAX}}}{\alpha} \qquad \text{(Eq. 7)}$$

Since K is approximately a constant over the voltage range of interest, Equation 6 is approximately a straight line on a typical V_{FLOAT} vs. T_{AMB} plot in Figure 6. The area to the right and above this line represents conditions conducive to thermal runaway (the thermal runaway zone).

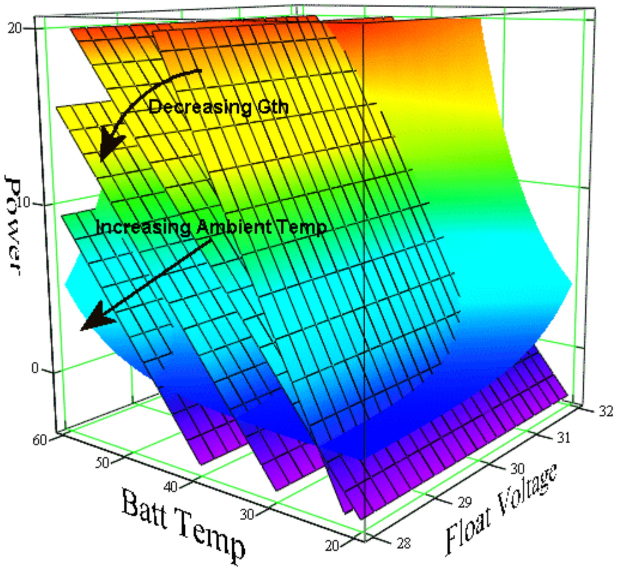


Figure 5. Effect of increasing ambient temperature and decreasing thermal conductivity on the power-out plane

The lower the power-out plane, the less heat the battery can dissipate for any given battery temperature and float voltage, resulting in a greater chance of thermal runaway.

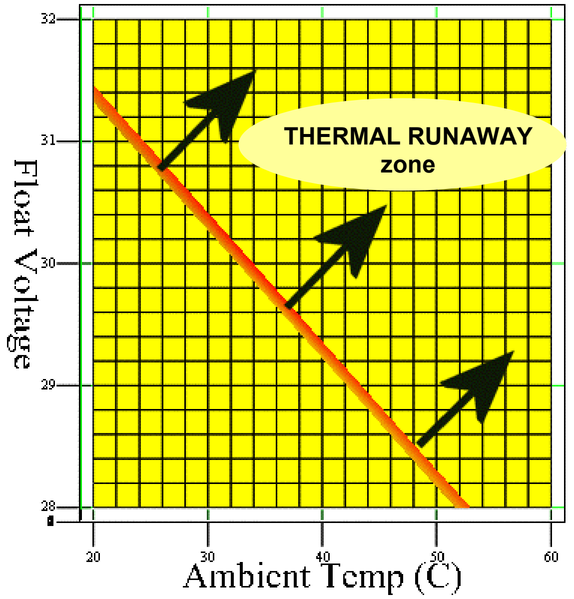


Figure 6. Thermal runaway zone for a representative battery

Figure 7 shows this relationship modeled for the same four batteries shown in Figure 3, to compare how different batteries are affected by float voltage and ambient temperature with respect to each other.

Figure 7 shows that for various batteries, there are significant differences in the float voltages that will cause different makes, models and ages of batteries to go into thermal runaway at any given ambient temperature. The lower this line, the more susceptible the battery is to thermal runaway.

The following factors contribute to the position of these lines for each battery:

> ***Battery chemistry and construction:*** Certain alloys of the active material can promote or reduce float current, which moves the thermal runaway zone up or down. Each manufacturer mixes in its own proprietary list of additives to the cell construction and these have measurable effects on float currents.

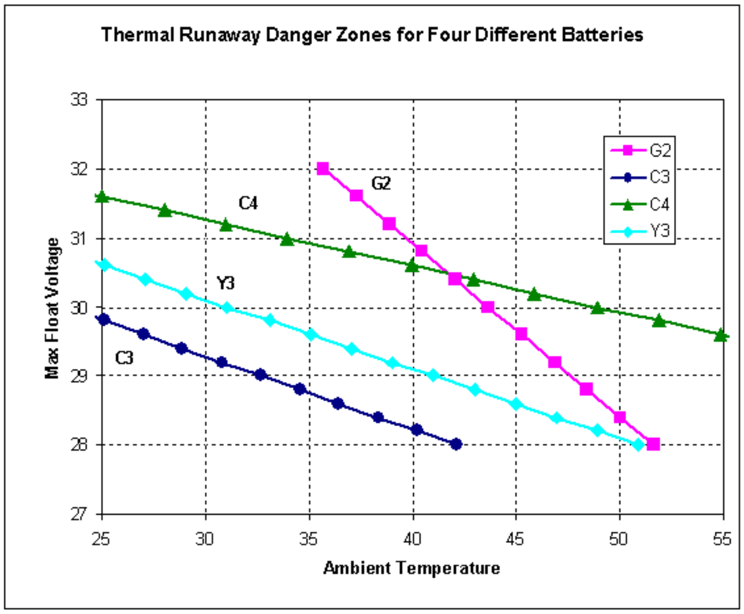


Figure 7. *Temperature/voltage boundary of thermal runaway zone for four batteries from different manufacturers*

> ***Battery construction:*** Cell wall material, thickness, and contact with the internal active material can change the battery's thermal conductivity (G_{TH}). The higher the thermal conductivity, the more heat can be dissipated and the higher the thermal runaway boundary line.
>
> ***Battery age:*** Older batteries tend to have higher float currents and lower G_{TH}, which moves the thermal runaway boundary lower.
>
> ***Battery installation:*** Any material that insulates the battery from outside air decreases its effective thermal conductivity (G_{TH}), which moves the thermal runaway boundary lower. Packing batteries together with no air space between them reduces their effective surface area, which reduces G_{TH}.

Temperature Compensation

Figure 7 also shows that for all batteries, a reduction in float voltage is necessary at higher ambient temperatures in order to avoid thermal runaway. This explains why temperature compensation is recommended for float operation in all lead-acid battery installations. By automatically reducing the float voltage in higher ambient temperatures, the battery system can maintain a healthy distance from the thermal runaway zone for that battery for all ambient temperatures.

THERMAL RUNAWAY TESTING

In any battery installation there are a number of factors that can contribute to thermal runaway. They include:

- High ambient temperature
- High float voltage
- High maximum charge current
- Battery design and quality
- Battery health
- Insufficient battery cooling

By testing each of the above conditions, the limits of a particular battery can be determined. The purpose of these experiments is to determine what factors most affect thermal runaway. From this information, the limits of the battery can be determined, and charger designs as well as battery chassis designs can be implemented so that these limits cannot be reached.

Test Specifications

Two series of tests were outlined to complete these experiments:

1. Vary the voltage and temperature while holding a constant maximum charge current.
2. Vary the maximum charge current for a set of voltages and temperatures that are known to induce thermal runaway.

The first series of tests hold the maximum charge current constant, while the float voltage and temperature were varied. By holding the current as the common parameter among the tests, it could be determined at which voltage thermal runaway will occur for a specific temperature.

Once the voltage and temperature combinations that produce thermal runaway are determined, the maximum charge current will be varied for the second series of tests. Varying the current limit affects how much power is inserted into the battery. The object of this test is to determine if reducing the current limit can keep a battery out of thermal runaway even though the conditions may be ripe for it.

These tests were repeated for different batteries of different make, model, and condition to determine what variables affect thermal runaway. Performing each series of tests for different manufacturers and different battery states of health provides much more information than testing only one battery and assuming all batteries of the same nominal rating behave identically.

Procedures

To perform the three series of tests described above, four temperature-controlled environmental chambers were set up. Each chamber contained a 24-volt pack of lead-acid batteries, a heat lamp to heat the boxes, a fan to mix the air in the chamber, and a thermistor to regulate the temperature inside the test chambers. The batteries were connected to a charger from which they were exposed to various controlled voltages and currents. To monitor the ambient temperature, battery temperature, voltage, and current, a web data-acquisition device called a WebDAQ was used. By accessing the device's IP address, a user can monitor any channel on the WebDAQ. To monitor the four parameters, a Windows application was used to access the IP address of each WebDAQ. The program then read the values from the defined channels, and logged those values into a text file.

In each of the series of tests, the major factor in determining the presence of thermal runaway was battery current. As a starting point, it was thought that once a set of batteries had been brought down to its float current, if the current was to go above 1 amp after that time, it could be concluded that thermal runaway had been initiated. However, a few tests showed that the current might not go below 1 amp. Other problems with this detection method include the cases in which the current never decreases, but rather stays at the maximum charge current limit. Therefore, the thermal runaway detection algorithm had to be modified to detect a positive slope of the current within a specific range, after the battery's float voltage reached the desired level.

Results

Test Series #1: Constant maximum charge current with varying voltage/temperature

Initially, each test box was set to a different temperature between 35°C and 60°C. The first three test boxes all contained batteries from one manufacturer while the fourth test box, at 50°C, contained a pack from another. Each box started at 27 volts as a float voltage. The results showed that thermal runaway would not happen at 27 volts in any of the batteries regardless of the temperature. Once it was determined that no set of batteries was going to begin thermal runaway, the next set of tests began by increasing the voltage on the batteries to 28 volts, but keeping the set temperatures the same for each test box. This process was repeated for 28.5, 29, 29.5, and 30

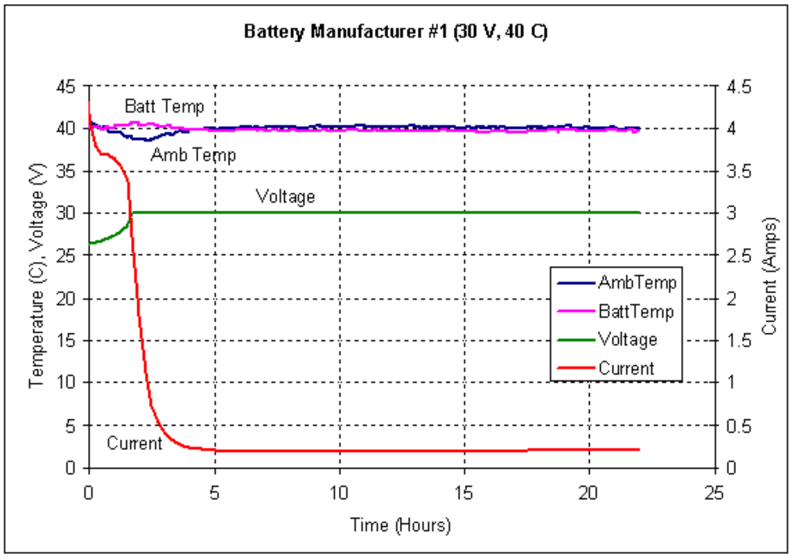


Figure 9. *Ambient & battery temperature, voltage, and current over 23 hours.*

volts. Figure 9 shows the test on a set of batteries that had run for 30 hours at 30 volts in a 40°C environment.

The bottom curve in Figure 9 shows what the current should look like under normal charging conditions, when the voltage and temperature are set to safe values. It starts charging at a high current, and then tapers off toward zero, getting to as low as 250 mA. The temperature curves also remain relatively constant. Under conditions where the float voltage and temperature are set too high for the battery to withstand for very long, the current curve would look more like that of Figure 10.

The bottom curve in Figure 10 is a perfect example of what occurs in thermal runaway. After some time, the current gets down to the float current, and then starts to go back up due to the internal heat generation becoming greater than the power being dissipated. This test also shows that the float current could be just above 1 amp rather than dropping all the way to 250 mA as in the previous example. This shows why using absolutes to determine thermal runaway is not reliable. It is also important to note that the ambient and battery temperatures start to increase along with the current, which is more proof that the batteries are beginning to experience thermal runaway.

Figure 10 shows a battery from manufacturer #2 charging with the same parameters as that from manufacturer #1 in Figure 9. It is easy to see that there is a clear difference in the way different manufacturer's batteries are affected by higher voltages and temperatures.

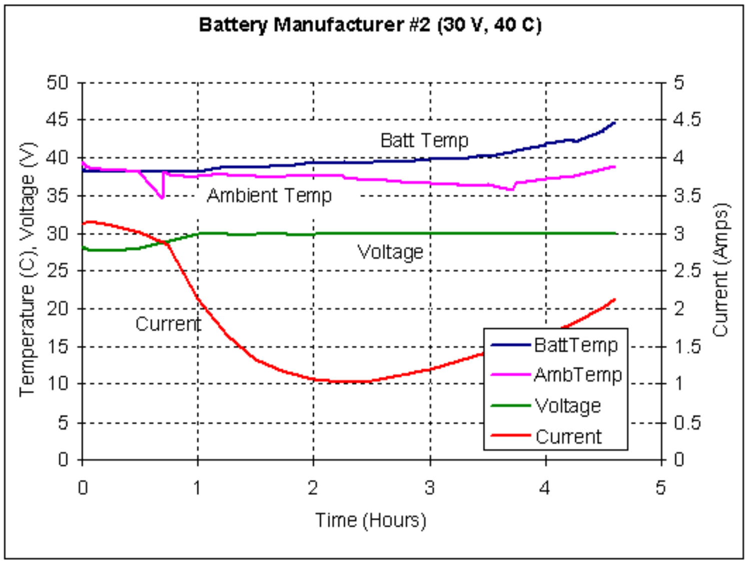


Figure 10. *Graph showing the effects of thermal runaway on current and temperature.*

In the first series of tests, the battery pack from manufacturer #2 experienced thermal runaway in several tests. Manufacturer #1's batteries showed something quite different: after many tests under conditions identical to those for manufacturer #2, in only one test did thermal runaway occur. Additional testing with that battery pack is impossible because it was destroyed in the process of an uncontrollable thermal runaway event. This clearly showed that not all VRLA batteries are created equally. In conditions that cause one manufacturer's battery to go into thermal runaway, another manufacturer's will remain stable.

The voltage and temperature relationship produced by this series of tests shows that the relationship between the voltage threshold and ambient temperature is linear. This relationship is depicted in Figure 11. As one would expect from the analytical models, the higher the temperature, the lower the voltage required to induce thermal runaway. As the temperature decreases, the voltage required to begin thermal runaway, increases. In the case of the batteries from manufacturer #2, for every 5°C increase the voltage threshold for thermal runaway will decrease 0.5 volts. One data point for the battery from manufacturer #1 is plotted along with a projected estimate of how it will behave at other temperatures.

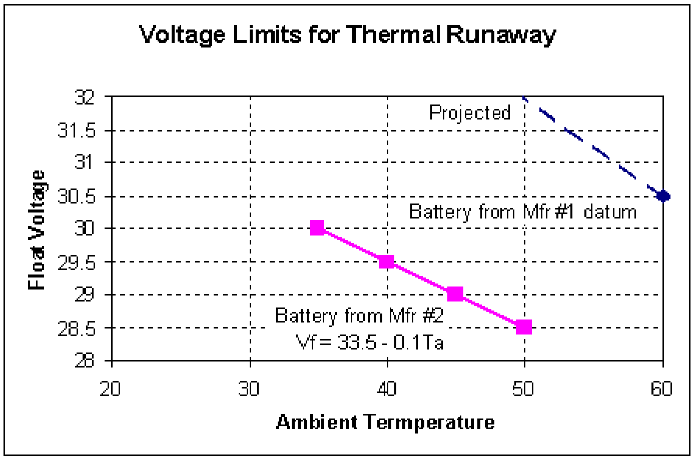
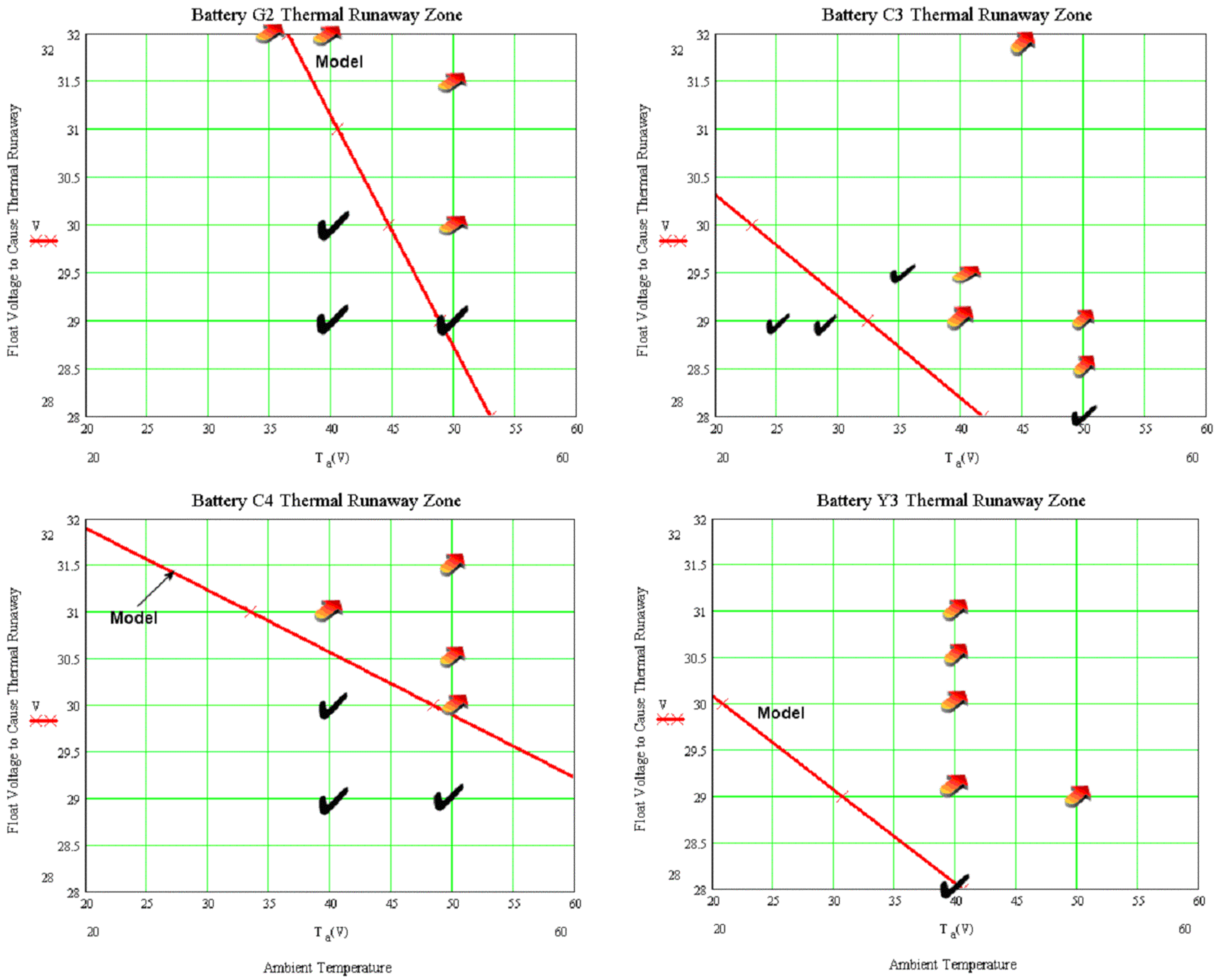


Figure 11. *Voltage limits at a specific temperature on two sets of batteries at which thermal runaway happens*

Other Batteries

In a continuation of the above testing, other batteries (G2, C3, C4 and Y3) were tested in a similar manner with similar results. A summary of the data shows graphically how the batteries performed relative to their models. Figures 12a-d show the individual maximum V_{FLOAT} vs. $T_{AMBIENT}$ linear relationships along with actual test results. The solid line represents the model for each of the batteries from Figure 7. The check symbol (✔) represents a test where no thermal runaway occurred, and a slanted upward arrow (↗) represents a test where thermal runaway was detected.

A complete set of data is not available to fully resolve the V_{FLOAT} vs. $T_{AMBIENT}$ relationship but the majority of data points are consistent with the analytical models.



Figures 12a - 12d. *Data and models showing where thermal runaway occurred for four different batteries*

Age Dependency

Note that battery Y3 was one of the worst performers. It was about three years old with an unknown history. A set of new batteries of the same model is now being tested and they are performing somewhat better than this one. This seems to show that older batteries are more susceptible to thermal runaway than newer ones. Although a full set of testing is not complete to show this dependency, literature has indicated this trend to have some validity. Multiple references[5,6] concur that aged batteries have increased float currents. Increased float currents increase the power input for a given combination of float voltage and ambient temperature, resulting in a higher propensity for thermal runaway.

Test Series #2: Vary maximum charge current on voltages that induce thermal runaway

This series of tests was not performed as of this writing. The objective would be to determine if thermal runaway could be prevented by limiting the power into the battery to a point below what the battery can dissipate through its case. It is hypothesized that if the charger were current limited while the battery is subjected to adverse temperature and voltage, the charger output voltage would fall to a point that would create a thermal equilibrium in the battery. Even though these conditions are not optimum for a long battery service life, the battery would NOT continuously rise in temperature and rapidly destroy itself in thermal runaway.

SOME GENERAL OBSERVATIONS

Besides the discoveries made concerning the linear relationship between the maximum float voltage and the ambient temperature, there were other noteworthy observations.

Dynamic Response

Batteries sometimes exhibit a dynamic response to changes in test conditions. Consider the chart in Figure 13 that shows the reaction of the battery to a quick change in its test conditions.

Even though, ultimately, the battery's float current settled to a low value for a new set of conditions, right after the change its current rose to *twice* its stable level. For higher float voltages or temperatures, such a change of conditions and resulting current surge could launch the battery into thermal runaway even though the nominal conditions wouldn't otherwise be conducive to thermal runaway. More testing needs to be conducted to show to what extent this could happen.

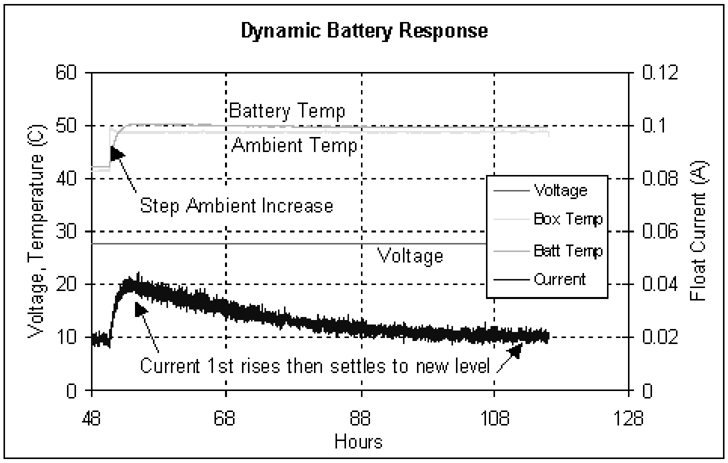


Figure 13. *Battery responding dynamically to changes in its environment.*

Failures and Unexplained Phenomena

During the course of the testing we ran across several interesting cases where the batteries behaved quite unpredictably.

Shorted Cell. In one case, the battery pack under test never reached the desired float voltage, yet its float current and internal temperature continued to rise, as one would expect in a thermal runaway condition. This led us to believe that one of the battery's cells was shorted, dragging the terminal voltage down, while the other cells were being overcharged and going into thermal runaway. This indicates two things: (1) one can't rely on the fact that a battery will get to its desired float voltage before it starts going into thermal runaway, and (2) thermal runaway of a subset of cells within a string can be detected by watching for a growing current after the string's terminal voltage has settled to a fixed level.

Sudden Death, Fits and Jerks. One of the batteries was starting to go into thermal runaway, when we shut off the heat in its chamber. This had an immediate effect of decreasing the float current and internal battery temperature. The current took several hours to tail off to about 100 mA, when suddenly it rose quickly, bringing the battery's internal temperature to 55°C. At this point, we had to shut off the charger to stop the thermal runaway. We surmise that a failure in the battery occurred, despite the fact that the battery was brought back into the safe operating zone, which caused it to go into thermal runaway the second time. This indicates that it is not enough to keep the batteries in a safe operating environment to protect them from thermal runaway. Failures can happen, particularly at the end of life, which need to be detected autonomously so that the charger can act appropriately to stop the thermal runaway process.

SUMMARY

By carefully measuring float currents with respect to a number of voltages and battery temperatures, it is possible to create a model for how a battery will respond to any combination of float voltage and ambient temperature. Using this model, with data on the battery's float characteristics and thermal conductivity, it is possible to create a straight line plot depicting the maximum possible float voltage / ambient temperature pairings, above which the battery will go into thermal runaway. This model corresponds to various spot-checks done to a variety of batteries. These plots show that

1. Batteries from different manufacturers respond to their temperature and float voltage in different ways. Even batteries with the same model number from the same manufacturer have been shown to perform dramatically differently from each other.
2. Compensating the charger system's output voltage for higher temperatures increases the safety margin between normal operating conditions and thermal runaway.
3. Older batteries have lower thermal runaway zone limits, showing a higher propensity for thermal runaway.
4. Batteries that are insulated from ambient air are more likely to go into thermal runaway than those with more surface area exposed.

Testing to validate these models showed that the models are relatively consistent with actual battery behavior and revealed some other useful information as well. In addition to adverse temperature and voltage conditions, other factors were found to cause batteries to go into thermal runaway. Batteries can exhibit a dynamic response to changing environmental conditions that could be the source of some thermal runaway events where conditions are already close but not completely conducive. Batteries can also fail internally due to old age, abuse, and nasty test algorithms, which may cause them to go into thermal runaway even though their operating conditions are within their safe operating zone.

In all test cases, we were able to detect thermal runaway, by observing both a rising or high-level float current along with a rising battery temperature after the float voltage stabilized to a steady value. Terminating the thermal runaway process, once started, was usually possible by reducing the ambient temperature (shutting off the heat lamps), but in some cases it was necessary to shut off the charging device as well. ∞

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