

Secondary Batteries: Lead Acid Battery Thermal Runaway

Chapter Heading for **Encyclopedia of Electrochemical Power Sources**

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Abstract

The thermal runaway effect observed in sealed lead acid batteries is reviewed and reassessed as a means for understanding the effect at a more fundamental level. It is to be noted that a popular explanation for the heat generated when a sealed cell is overcharged is that the oxygen recombination taking place at the negative electrode is an exothermic process. Although it is a fact that this recombination reaction is exothermic, the first law of thermodynamics mandates that the net enthalpy of the closed cycle oxygen recombination process is exactly zero (also known as Hess's Law). Since the closed oxygen cycle cannot produce any enthalpic heat, the heat generated must be entirely of Joule origin. In view of this apparent dilemma, an alternative mechanism is developed and discussed that the gas evolution process displaces the electrolyte in the intercell gap. By doing that, this electrolyte displacement causes a substantial increase in the internal resistance of the cell. The consequence of this resistance increase in the presence of current passing through the cell is a significant contributor to the observed heat generation. This paper presents data and discussions that support this interpretation. This mechanistic interpretation has some notable implications. That is, the heat generation process is largely chemistry independent (i.e., it is common to all sealed cell designs), is the consequence of the ability of the separator to manage the electrolyte distribution within the cell and can thermally accelerate thermodynamically spontaneous processes that have slow kinetics under normal ambient conditions. To add additional credibility to the interpretation, the analysis of the thermal runaway that takes place in lithium ion cells is attempted by building on the model developed for lead acid thermal runaway.

Introduction

For the purposes of this article, the lead acid battery thermal runaway shall be treated from a mechanistic standpoint. Further, the thermal runaway shall be viewed as a general phenomenon occurring in sealed cells. The effect shall be described in considerable detail using the lead acid battery as the model. Having developed the general concept, the plan is to extend the general mechanism to show how it applies to the lithium ion

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sealed cell. Doing this serves to add confidence to the understanding of thermal runaway in lead acid batteries.

Before pursuing the discussion further, it is important to establish a preliminary understanding that serves to place the discussion that follows into a perspective. Specifically, to avoid problems of a rhetorical nature, it is necessary to define the things that we are interested in talking about. Often problems arise by failing to note a fundamental aspect of the definition itself. Definitions are characterized as being either descriptive or essential.[1] This is important because the distinction helps to indicate the level of progress that is made in any discipline. The first is the descriptive definition. Definitions of this type define an event or observation in words that are basically a restatement of that which was observed. Actually, a classification has taken place. Definitions of this kind are the first steps toward developing a basis for understanding. A property of the descriptive definition is that one usually gets universal agreement using such a definition. This is a politically wise approach and is favored as a matter of expedience. The second definition is the essential definition. This definition attempts at providing a fundamental statement that uniquely characterizes the thing defined. This kind of definition raises significant problems because there are a number of levels of abstraction that one can appeal to. Further, there are alternative ways to express the same model. For the sake of the present discussion, formulating a mechanism for the thermal runaway process would provide the essential definition.

It is also worth recalling that mechanistic interpretations are mental constructs. Since there can be many different ways to interpret a limited set of observed data, the mechanistic definition can result in considerable debate as many points of view exist. In order to deal with this, it is necessary to resort to the Principle of Parsimony which is also known as Ockam's Razor. Basically, definitions should not be multiplied needlessly. In other words, the simpler of two competing theories is to be preferred. As a point of pragmatism, an essential definition provides the integrating abstractions that become the foundation of scientific understanding.

Moving to the matter at hand, it is often heard that "...Thermal runaway ... describes the condition where the rate of heat generation within the battery exceeds its heat dissipation capacity..."[2] This is an often referenced observation that appears to provide a kind of understanding and one can get an intuitive feel for the basic effect. But there is an essential physical problem with this statement. If indeed the rate of heat generation within the battery exceeds its heat dissipation capacity, the temperature of the battery would rise to infinity. What was really meant by the statement is that the dynamic condition results in a temperature rise. Eventually a steady state is reached where the rates of heat generation and dissipation become equal. That is, at steady state, the power delivered to the battery is exactly equal to the power dissipated by the battery. Implied in this statement are the following. The battery is sealed and that it is in an overcharged condition. The latter point requires that the energy storage reactions have been fully satisfied and no further chemical energy storage can take place. In this case, the power supplied to the system is dissipated as if the battery was effectively a resistor. This point shall be returned to later in the text. A battery, when being overcharged contains not only

an ideal resistance but also a voltage gradient that must be overcome by the charging current.

In effect, thermal runaway is a descriptive name for a failure mode that exists in sealed batteries. It is observed by noting that the batteries continue to accept charge after the active materials are fully charged. This excess power is converted to heat within the battery and can result in a boiling of the electrolyte. The battery surface gets very hot to the touch. This provides a sensible description of the effect.

Thermal Runaway in Sealed Batteries

Thermal runaway in batteries has been observed and recognized for a long time. Many battery systems including nickel-cadmium, lead acid and silver-zinc have been observed to enter into a thermal runaway. The effect is usually associated with constant voltage or bus bar charging. [3]

The empirical perspective on the induction of the thermal runaway effect tends to appear as follows. During the early part of a constant voltage charge, the current decreases in a normal manner. Then as the battery approaches a full charge, the current rather than continuing to decrease, abruptly increases, heat is generated and the temperature of the battery begins to rise. The increased temperature reduces the over-potential for the irreversible gas evolution reaction (i.e., a thermally induced autocatalysis takes place). Since the applied voltage is held constant, the current continues to increase. This increased current causes additional heating that again results in a higher current draw. Thus, the thermal runaway receives its name.

Flooded batteries appear to be almost completely resistant to thermal runaway. The effect can be induced in flooded systems by allowing them to dry out. However, doing that means that the batteries are operating outside of their defined operational specification. In effect, one has intentionally or inadvertently, converted a flooded cell into a starved cell.

Thermal runaway can exhibit itself in different and distinct ways. At the low specific energy battery end as would be the case for VRLA lead acid, the battery gets hot to the touch. Steam is eventually seen exhausting through the cell vents. In many cases the smell of hydrogen sulfide is apparent. The plastic case sometimes shows significant distortions. For the high specific energy batteries, as would be the case with lithium ion, the temperature can reach 750°C. One would see dark smoke, a fire and an occasional detonation. Descriptively speaking, the observations made the thermal runaway of the low specific energy systems and the high specific energy systems appear to be quite different.

Although thermal runaway is possible in all sealed cells, the two major systems of present and substantial interest are the VRLA and the lithium ion batteries. At the time

of this writing, the thermal runaway in lead acid VRLA batteries and lithium ion batteries are treated very differently. It is almost as if they are two different and distinct processes. The presentation in this article will strive toward showing that the process are actually the same in a mechanistic sense but differing in their manifestations. That is, in one case there is fire and smoke and the other is steam generation resulting from a boiling electrolyte.

The development of the presentation will first address the VRLA concept. The investigations in this area develop and provide the link that unifies the thermal runaway as it occurs in sealed cells generally. After establishing the essential points, the relationship with lithium ion thermal runaway shall be addressed.

The reader must keep in mind the admonition presented earlier. Mechanistic interpretations, as useful as they might be, are open to debate, disagreement and, hopefully, revision as new information becomes available.

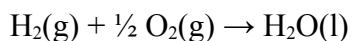
Flooded and Sealed Cells

An observation of interest is the difference between the overcharging of sealed vs. flooded cells. The flooded cell in overcharge becomes sensibly warm to the touch. Whereas the sealed cell becomes very hot under otherwise identical charging conditions.

The reason for this difference is that the flooded cell has a built-in energy dissipation mechanism. The power supplied to a cell during charge is the cell voltage multiplied by the current passing through the cell. If the cell does not exchange any matter with the environment and no net chemical change takes place within the cell, the cell can be viewed as acting as an ordinary resistor that dissipates the applied power as heat. That is, no energy storage takes place. A sealed cell, for the most part, operates in this way. Alternatively, a cell of a flooded design vents gas into the environment during overcharge.

Although, Berndt gives an excellent analysis of this issue, the matter will be approached in a slightly different way. [4]

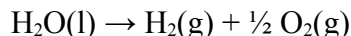
It is instructive to examine this venting effect a little more closely. In the case of water based electrolytes, water is electrolyzed generating hydrogen and oxygen gas that are vented out of the cell. The casual observer might respond by saying that the gas is the carrier that is removing the heat from the cell. If we look at this more closely, the reaction of interest is actually:



The standard heat of formation for this reaction is:

$$\Delta H^\circ_f = -285.8 \text{ kJ/mol}$$

This is a very exothermic process corresponding to the burning of hydrogen in oxygen. However, the reaction of interest in the flooded cell is the reverse reaction:



The enthalpy of reaction for this process is +285.8 kJ/mol. This is a very endothermic reaction that absorbs energy as the means for raising the energy state of the hydrogen and oxygen atoms in water. By producing hydrogen and oxygen gas, a power dissipation mechanism exists that can store the delivered power, escape the system in the form of vented gases, and recombine releasing the stored energy somewhere else in the universe. This is the major energy dissipating mechanism. Some energy is removed by virtue of the heat capacities of the gases themselves through a temperature gradient that is for estimation purposes, 100°C to 25°C. This energy dissipation mode is very small compared to the electrolysis reaction that produces the gases. Using the heat capacity of the gases as about 29 J/mol, the heat dissipated by the electrolytic reaction is greater than two orders of magnitude compared to that dissipated by the gases through the small temperature gradient.

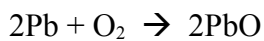
The slight warming of a flooded cell is largely due to the competition between the Joule heating associated with the EI power component delivered by the charger and the highly endothermic electrolysis of water. The other heat dissipation components, convective and radiative heat transfer from the surface of the cell and the heat capacities of the vented gases produced are minor and in most cases, insignificant contributors.

In the case of a sealed cell, the heat dissipation mechanism associated with the highly endothermic electrolysis of water is not available in the same manner as the vented cell. The sealed cell is designed to be recombinant. Doing that adds the highly exothermic oxygen recombination reaction to the mix and a suppression of hydrogen evolution by the reduction of lead sulfate to lead. The exothermic reaction could be viewed as the oxidation of metallic lead by oxygen. Since this is a thermodynamic discussion, the exact mechanism of the reaction is not a concern because the energetics of the overall closed oxygen cycle process is necessarily the same no matter what the oxygen recombination mechanism actually is (Hess's Law).

Another way of viewing the process taking place in the sealed cell is to consider a highly endothermic reaction and a highly exothermic reaction taking place simultaneously. In that case, the predominant mechanism involving the venting of gases that was available for heat removal from the flooded cell design is no longer available in the sealed cell.

The Closed Oxygen Cycle

The closed oxygen cycle used to explain and justify the heat generation in sealed cells has been around since 1947. The implementation of the closed oxygen cycle is associated with the work of Georg Neumann.[5] The following reaction could be considered the fundamental overall process associated with the recombination of oxygen in sealed VRLA cells.



$$\Delta H \text{ (standard heat of formation)} = - 390.4 \text{ kJ/mol Pb}$$

Note that Pb is being used as the referenced reactant. The reaction shown can be found in critical tables of heats of reactions and it is exothermic. It is important to note that this reaction constitutes an overall effect and is not to be interpreted as a mechanistic statement of the oxygen recombination reaction. This will be elaborated on further below. Using the exothermic oxygen recombination reaction as the source of heat generation in the closed oxygen cycle has made the interpretation of the thermal runaway mechanism unnecessarily complex. This becomes evident as one reads how Berndt tried to deal with this issue in his text.[4]

A departure from the viewpoint that the closed oxygen cycle is exothermic shall be made by invoking Hess's Law in the discussion that follows. The first step is to represent the closed oxygen cycle as a closed chemical cycle. This cycle is shown in Figure 1 in the form of a Born-Haber Cycle. The cycle shows the path taken by the reactants so as to return to their original state. One can easily rationalize that two paths exist. One goes around the cycle and the other represents no change (i.e., the reaction stays in the same place).

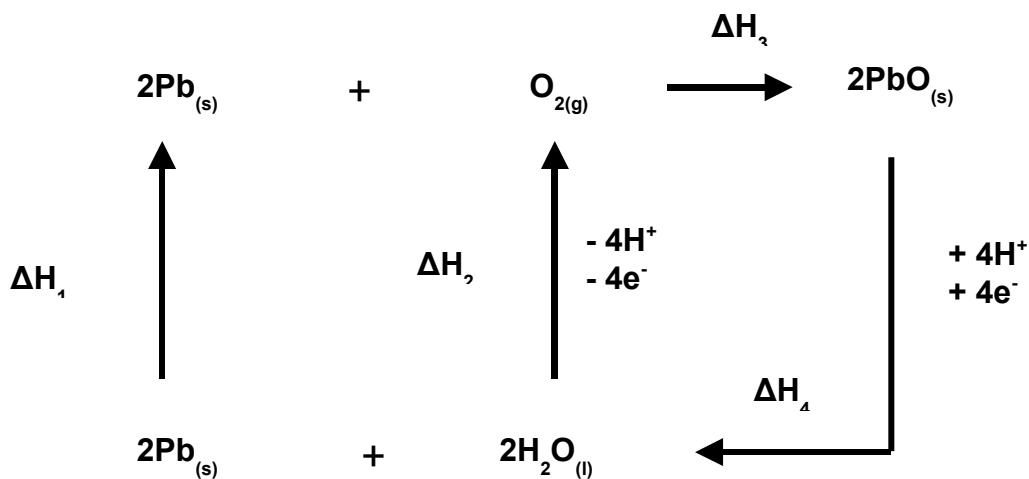


Figure 1. A Born-Haber Cycle illustrating the closed oxygen cycle.

It is critical to note also that the discussion that follows applies to all conceivable cyclical process representations without exception. One might disagree with the formulation of the cycle shown in Figure 1 but however one might choose to express the steps in the cycle, the same arguments apply. The representation is not intended to suggest a determined mechanism. The graphic illustrates a simple representation of a possible sequence of steps that form a closed cycle. One can reformulate the cycle to represent any favored sequence of steps that might show the formation of lead sulfate, lead bisulfate, lead hydroxy bisulfate or even the direct reduction of oxygen through a

peroxide intermediate. The point is that no matter how one writes the cycle, the conclusion is always the same. The sum of the heats of reaction for a closed chemical cycle leads to one unique result.

To proceed, the evident problem is that the cycle is composed of a collection of steps and each has its own associated enthalpy. The net heat associated with the closed cycle is actually the sum of the heats associated with each of the steps shown. It appears that focusing only on the oxidation of the metal ignores the other chemical or electrochemical processes that are taking place concurrently.

To add to the problem is that the first law of thermodynamics, i.e., the energy conservation law, mandates that the sum of the enthalpies is zero for all closed chemical cycles. This is a corollary of Hess's Law of Heat Summation.[6] Hess's law states that *"the heat evolved or absorbed in a chemical process is the same whether the process takes place in one or in several steps."* To claim that the net heat produced in a close cycle is other than zero would suggest that the direction by which one moves around the cycle would result in either the creation or destruction of energy. The discussion that follows shall adhere to the assumption that the energy conservation law is always true.

Having said that, we are left on the horns of a dilemma because it is known that cells placed on overcharge generate heat but we have just declared that the traditional mechanism for justifying the heat generation process constitutes a violation of the energy conservation law. In effect, one is forced into the position of either agreeing with the dilemma or claiming that the closed oxygen cycle is an exception to Hess's Law.

Although this may appear to be a digression, it is important to appreciate that demonstrating that a long held believe is inconsistent with first principles does not bring automatic acquiescence. There is a natural tendency to save the old belief. The only remaining objection is to raise the question of irreversibility within the thermodynamic cycle. It is agreed that for all chemical closed cycles, the net enthalpy is necessarily zero but this applies only to reversible processes. If one looks back at the cycle, two electrochemical steps are shown. Clearly, an overpotential for activation can be involved. By looking at the cycle this way, an inefficiency is added to the cycle and therefore heat is generated during that cycle. The response to this argument requires that one observes that the heats of formation of each of the material components in the cycle have not changed nor can they change. These are thermodynamic constants that are independent of how the process is carried out. The irreversible energy component cannot be stored within the cycle and is dissipative as heat. The irreversible component is a Joule heating component. It can be seen that in order to save the exothermic claim about the cycle, one has to include within the thermodynamic cycle an additional Joule heating component. By defining the closed cycle in this way, the closed cycle would be exothermic. But a problem remains. The Joule component associated with the activation polarization is actually a component of the net polarization resistance. One has intentionally divided the Joule heating and the chemical parts of the cycle so as to justify heat being produced within the closed oxygen cycle. One cannot deny that it is possible to define the cycle this way as an approach to envisioning the exothermic closed oxygen

cycle. However, it is important to note the resistance contribution associated with activation polarization is a component part of the polarization resistance of the battery. That is, the component parts of the polarization resistance are composed of ionic resistance and concentration and activation effects. Finally, it will be shown below that the heat contribution of the polarization resistance is a very minor component of the overall heat generation in the cell. In effect, the claim that the major contributor for heat generation during overcharge is the exothermic closed oxygen cycle is nonviable.

At this point a critical observation appears. In applying thermodynamic arguments, the partition of the energies is often arbitrarily stated provided that the summation of the steps is consistent with the relevant conservation laws. The division of a closed cycle chemical process component and a Joule heating component allows a significant insight to be made about the thermal runaway process. Given that the closed chemical cycle can generate no net heat, the heating effect becomes chemistry independent. That is, the heating that takes place during overcharge is a physical process and there may well exist a common mechanism that governs thermal runaway in all sealed cells that involve these same physical processes.

Although the essential point has been made above, as a practical matter the discussion should be carried further. The next step is to propose an alternative mechanism for justifying the heat generation effect. The hypothesis is constrained in that it can contain no heat generated by closed cycle chemical processes. That is, the heat generation must be the consequence of Joule heating and that heating must be of resistive origin. Note that one can associate the resistance build-up with some sort of resistive film formation associated with known effects such as PbO or PbSO_4 formation. For the discussion that follows, the growth of resistance shall be postulated as the consequence of electrolyte being displaced out of the inter-electrode gap by gas generation. The gas would be the oxygen (and perhaps some hydrogen) that is generated by the overcharge reaction taking place as part of the closed oxygen cycle. This hypothesis specifically requires that no closed cycle chemical process can generate heat. It is noteworthy that this hypothesis builds upon many of the fundamental concepts identified previously by Pavlov.[7]

Actually, the proposed hypothesis is not very original. Other workers have observed this behavior in transparent plastic cells. Test VRLA cells show an electrolyte rise in the cells when the cells begin to gas. This is an obvious displacement of the electrolyte by the gas produced. Starved cells such as the starved electrolyte Nickel Cadmium wound roll have been observed to fizz and drip electrolyte when placed into overcharge. By replacing the highly conductive electrolyte with nonconducting gas would lead one to conclude that the resistance within the inter-cell gap is increasing. This whole mechanism was almost fully described by Weighall as he discussed the influence of capillary pressures on preferential cell filling by the electrolyte.[8]

An Examination of the Alternative Hypotheses

Since the argument raised thus far is of a theoretical nature, it would be nice to generate some experimental support for the claims made. In summary, there are two hypotheses under consideration:

Traditional Hypothesis: the heat generation on overcharge is largely the consequence of the closed oxygen cycle caused by oxygen recombination at the negative electrode.[9, 10, 11]

New Hypothesis: the heat generation on overcharge is controlled by the build-up in inter-cell resistance caused by electrolyte displacement by the gas evolution process and the current passing through that resistance (Joule heating). Although the heating associated with the battery resistance is small, the remainder is the power dissipated as heat by the passage of a current through the remaining voltage gradient of the battery. Also, the dissipation can be associated with an equivalent resistance so as to make this a Joule heating component. This latter component shall be discussed further below.

Another point that might be missed is that when one pushes a charge through a voltage gradient, it is necessary to do work on the system. If the energy that is applied is not stored, as would be the case during an overcharge, the supplied energy appears as heat. The total power delivered to a battery is the applied current multiplied by the battery voltage. This power can be broken out into two parts:

$$EI = E_0I + I^2R(\text{pol})$$

where E is the imposed battery charging voltage, E_0 is the open circuit battery voltage, and $R(\text{pol})$ is the polarization resistance of the battery. This is a classical description of a power input to a source. [12] To give an indication of the relative sizes of these quantities, the polarization resistance of a 12 V-120 Ah Military Grade SLI battery is about 3 mOhms. If a current of, say, 10 A passes during overcharge, the $I^2R(\text{pol})$ term amounts to 0.3 W. The E_0I component is about 120 W. The major contributor to battery heating on overcharge is the heat dissipation associated with passing an ionic current through the voltage gradient of the battery.

Three studies follow that are consistent with the new hypothesis but not the traditional hypothesis. The first study involves observations made of the thermal runaway effect. While performing that study, a peculiarity appeared that was totally inconsistent with the traditional hypothesis. At that point, the new hypothesis was developed. It is well established that the characteristics of any good scientific theory is that the theory can be verified and that the theory could be predictive. Then, the second study describes measurements made to determine the resistance changes in a cell when it goes into overcharge using Electrochemical Impedance Spectroscopic (EIS) techniques. The third study predicts that a condition can exist where the cell goes into electrical oscillation. This could be an example of electrochemical chaos. Since electrochemical cells are the classic example of a generator of a pure direct current, a case that reveals a self generated oscillatory current component is quite novel.

Case 1 – Thermal Runaway

The impetus for generating the new hypothesis came as a consequence of a peculiarity observed while performing a study on the thermal runaway of VRLA batteries. The details of this study have been presented elsewhere.[13] In short, the battery was preconditioned to induce the thermal runaway and then the battery was charged in the usual manner. Figure 2 shows the relevant data.

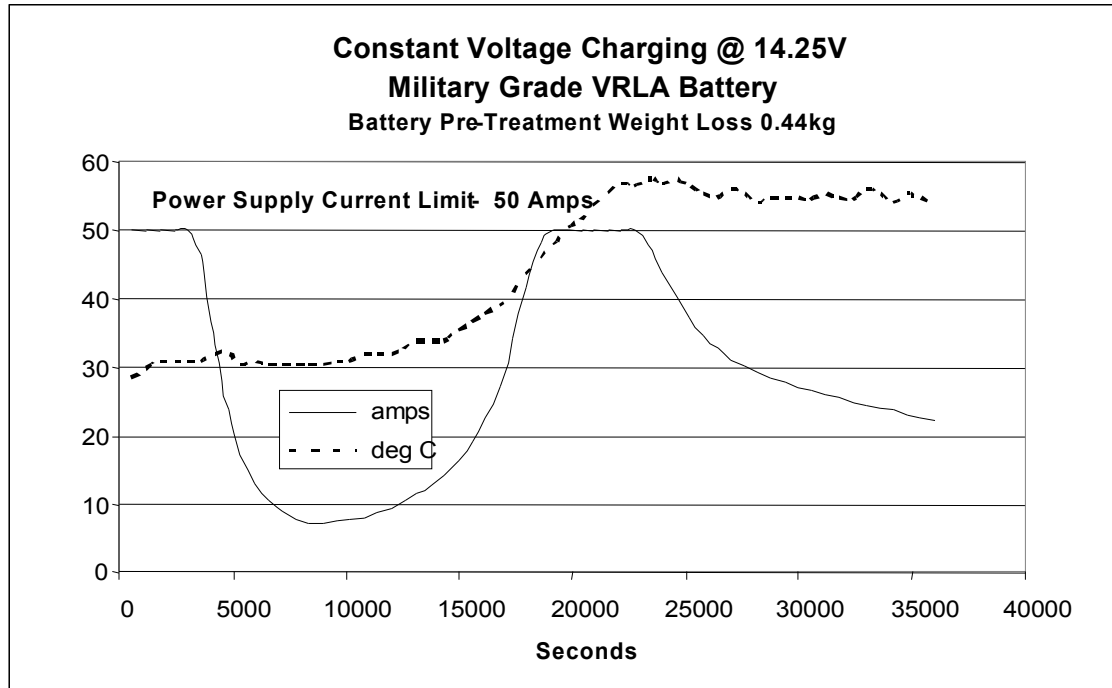


Figure 2. Thermal runaway in a VRLA battery being charged at constant voltage. A typical AGM of this size (120 Ah) has an approximate water content per cell of 684 cc at 97% saturation.

It is worthy of note that this battery contains about 684 cc per cell of electrolyte. The volume of electrolyte for the battery is 4.1 liters. After the pretreatment for inducing the thermal runaway, a weight loss of 440 grams was observed. All cells were observed to be venting gas so that the loss is not attributable to a single cell. This is a very small water loss which suggests that the electrolyte is largely moved around within the battery and the battery is not in a dried out condition. Also, when this battery was allowed to stand for a period of one week it returned to “typical” behavior. That is the battery was not severely damaged to the point where it could not be returned to service.

Early in the constant voltage charging, the battery showed the exponential fall off of current until the thermal runaway took place. Just as the charging process was being completed, the current rose with a corresponding increase in the temperature. It must be noted that the temperature is that measured at the negative terminal. The internal

temperature of the battery is actually greater than that value. The critical observation comes at the point where the current begins to fall off. What is observed here is that the temperature appears to remain approximately constant whereas the current passing through the battery falls off.

As a point of clarification, the observation that the temperature is constant requires that the system is in steady state. That is, the rate of heat generation is equal to the rate of heat removal. But, the current is falling off and the current is proportional to the rate of oxygen generation. The traditional hypothesis at steady state requires the following sequence: (1) the rate of oxygen generation is equal to the rate of oxygen recombination and (2) the rate of oxygen recombination is equal to the rate of heat generation. If one claims that the heat generation is determined by the oxygen recombination reaction, there is an obvious logical contradiction.

We have established that this thermal runaway data is totally inconsistent with the traditional hypothesis defined above. This creates a problem of interpretation that is extremely difficult while adhering to the closed oxygen cycle heat generation mechanism.

The new hypothesis, where the heating is the consequence of electrolyte displacement within the inter-electrode gap, provides a simple interpretation for this temperature-current response.

Since only Joule heating is involved, the existence of a constant temperature requires that the rate of Joule heating is also constant. To further explain this, the constant temperature indicates that a steady state exists between the rates of heat production and removal. Since the rate of heat removal is determined by environmental and geometric considerations that have not changed, the rate of Joule heating is constant. Then,

$$I^2 R = k_1 \text{ (steady state condition)}$$

The constant is given by k_1 . I and R are the current and resistance. By definition, the resistance R is defined as:

$$R = \rho l/A = k_2 / A \text{ (at constant } T)$$

where ρ is the resistivity, l is the length of the current path and A is the cross-sectional area. Since the resistivity and the path length are fixed quantities, they have been lumped together and shown as k_2 . Substituting this back into the previous equation,

$$I^2 k_2 / A = k_1$$

Collecting the constants and assigning them the quantity k_3 , then

$$I^2 = k_3 A$$

and rearranging:

$$I = k_4 \sqrt{A}$$

This very simple analysis shows that if the current changes so as to be proportional to the square root of the cross-sectional area of the conductive electrolyte in the inter-electrode gap, the Joule heating must remain constant. The point here is that a current through a resistance can fall and at the same time the heat generation can remain constant. This experimental observation is consistent with the new hypothesis but inconsistent with the traditional hypothesis.

The next step is to attempt a verification of the physical model. Since the new hypothesis requires that the resistance must be increasing as gassing is taking place, then it would be reasonable to expect that this internal resistance increase could be measured. This prompted the next study using EIS instrumentation.

Case 2 - EIS measurements during overcharge

The object of this study was to measure the impedance and phase angle as a function of frequency as a VRLA battery goes into overcharge. The experimental approach was to fully charge the battery and then bleed off some of the charge. The battery was then put back on charge and repetitive EIS sweeps were taken as the battery went into overcharge. The charger was limited to 3 amperes and the voltage limit was set at 15.5 volts. The data was resolved to fit the equivalent circuit shown in Figure 3.

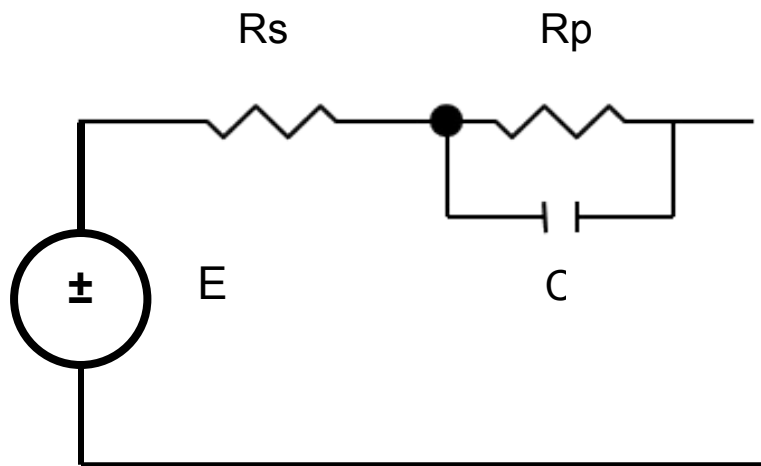


Figure 3. Equivalent circuit diagram that was fit to the data obtained by the EIS technique

For the sake of clarity, the charger used was a standard float charger designed for charging automotive batteries. The calculated equivalent series resistance of the charger is 5.2 Ohms. The naturally occurring parasitic current passing through the battery also

passes through the equivalent series resistance. The applied voltage minus the IR drop across the equivalent series resistance is the voltage applied to the battery. The consequence of all this is that the charging voltage falls within the acceptable range for lead acid battery charging. The test conditions are not abusive and no cell venting occurs.

The specific values obtained during each of the scans are given in Table 1. The scans were successively taken. The scan identified as run 1 was taken with no applied charge current as a reference point. The subsequent runs had the charger attached.

Table 1. Resolved values of R_s , C and R_p fit the equivalent circuit shown in Figure 3.

run	R_s	C	R_p
1	0.00287	10.48	0.00363
2	0.00286	7.38	0.0061
3	0.00281	5.709	0.01577
4	0.00285	5.225	0.03119
5	0.00292	4.725	0.12134
6	0.00287	4.504	0.12702
7	0.00286	4.353	0.10791
8	0.00283	4.313	0.2202
9	0.0029	4.313	0.6323
10	0.00288	4.33	0.77724
11	0.00286	4.323	0.79293
12	0.00289	4.282	0.74458
13	0.00285	4.273	0.8281
14	0.00286	4.261	0.82805
15	0.00293	4.242	0.82254

The values obtained are illuminating. The values of R_s basically remained constant. R_s represents the resistance associated with the kinetics of electron transfer. R_p represents the resistance associated with the ionic charge transfer through the solution. Finally, C represents the interfacial capacitance associated with the electrochemical cell.[14] The values of R_s hardly changes as the battery goes into overcharge. Alternatively, R_p shows a huge change in excess of two orders of magnitude. This large change in resistance is what was anticipated from the new hypothesis and found.

There is another interesting feature about this data and it becomes evident when the data is plotted as shown in Figure 4.

Figure 4 shows the capacitance decreases first. As the capacitance decrease stabilizes, the resistance makes its move to higher values. What is interesting about this data is that it is perfectly consistent with the new hypothesis. That is, the gas generation model that displaces the electrolyte can explain this behavior.

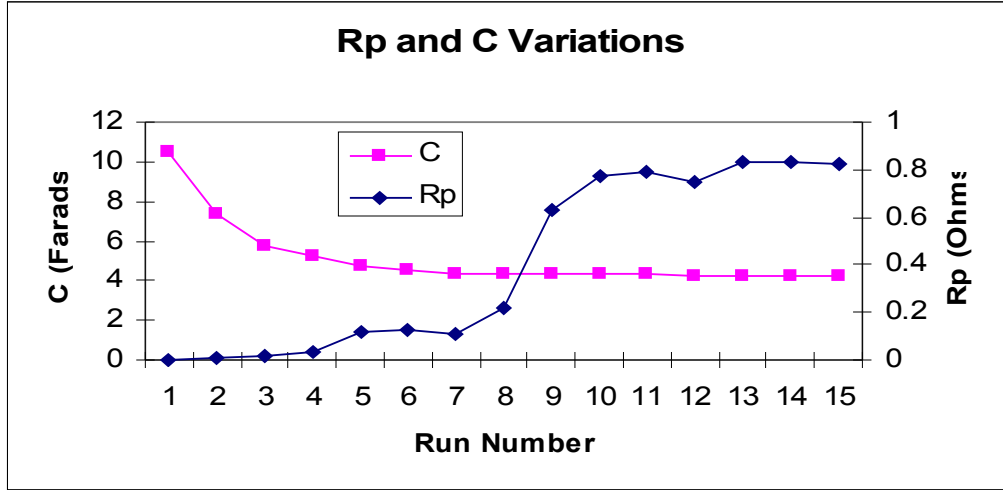


Figure 4. Comparison of the capacitance the resistance changes in the order of their measurement.

To show that this behavior is consistent with the new hypothesis, it is helpful to review some fundamental physical concepts. Capacitance is defined as:

$$C = \epsilon_0 A^*/d$$

where C is the capacitance, ϵ_0 is the dielectric constant, d is the separation of the plates of the capacitor and A^* is the plate area. In the case of resistance:

$$R = \rho l/A$$

where R is the resistance, ρ is the resistivity, l is the length of the resistive path and A is the cross-sectional area of the resistor.

Two key observations need to be made here. The first is that A^* and A are not the same. A^* represents the interfacial surface area where charge can be stored by some sort of charge separation. A , on the other hand is the cross-sectional area of the resistor. It represents the projected area of the surface as if it were planar. The inner surfaces of a porous electrode that do not face the counter electrode do not participate in determining that area term. So,

$$A^* \neq A$$

In fact,

$$A^* \gg A$$

The second observation is the dielectric constant for a conductive ionic aqueous solution is about 30 and that of a gas such as oxygen is approximately 1.00. The resistivity of an aqueous ionic solution is very low compared to a gas, which is virtually infinite.

With these considerations in mind, we can visualize a hypothetical pore in a flat surface as that shown in Figure 5. Certain liberties were intentionally taken in illustrating the pore in this way for the sake of conceptual convenience. However, the analysis would apply to all pore geometries. At this point, the rationalization that is consistent with the EIS data becomes evident. Taking the new hypothesis as being operative, gas generation begins over the entire electrode surface. The gas bubbles on the front surface have no barrier and can move away from the surface. The gas bubbles generated within the porous matrix are basically trapped.

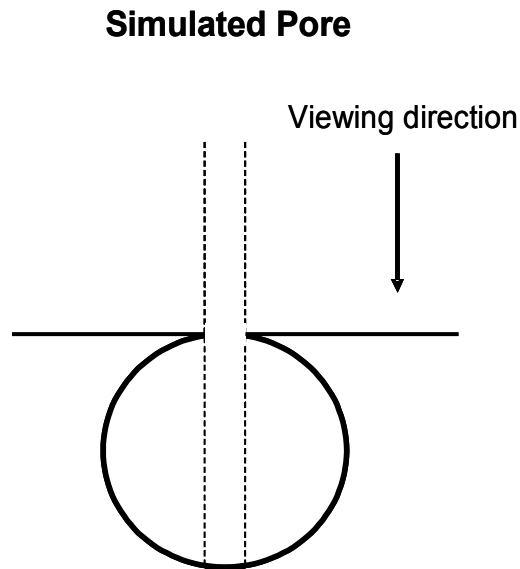


Figure 5. Idealized comparison of actual vs. projected surface of a pore. The argument follows directly. As a gas bubble fills the pore, the area that affects capacitance is covered by a medium having a lower dielectric constant. However, the area that controls resistance is very small (as designated by the dashed lines at the bottom of the pore). The resistance change caused by the gas bubble within the pore has a small effect relative to the capacitive effect.

After the gas displaces the electrolyte in the pores, the gassing then begins to displace the electrolyte within the inter-cell gap. With this visualization in mind, the data in Figure 4 becomes interpretable. That is, as gas generation begins, the pores fill with gas causing a small change in resistance and a large change in capacitance. Once the pores are filled with gas, the subsequent displacement of the electrolyte in the inter-electrode gap causes the big change in the cell resistance.

Another interesting point can be inferred from the preceding discussion. It is to be noted that the interfacial capacitance decreased by about one-half. Since the interfaces have, in this case, a total applied voltage of about 14 volts, the capacitor, as shown in the circuit diagram, is charged and must discharge about half of its stored energy as a direct

consequence of the change in interfacial capacitance. This energy is converted to heat by discharging across the resistor R_p shown in Figure 3. This is a relatively small quantity when considering the size of the battery but this released energy is converted to heat at the immediate electrode interface. Then, this heat generation step may be the initiating step for the thermally induced autocatalytic gas evolution that eventually results in a thermal runaway.

Although the discussion here does not necessarily “prove” the model, it does provide a means for interpreting the EIS data observed during the initiation of overcharge. In this section an attempt was made to generate some evidence for the model supporting the new hypothesis.

This observation applies generally. It should be determinable in all sealed cells in overcharge. It appears to be the case.

Next, the new hypothesis will be used to predict an effect that is somewhat startling. Specifically, the next study concerns itself with an oscillating electrochemical system. This could be an example of electrochemical chaos. The prediction of this effect follows directly from the new hypothesis.

Case 3 – The electrically oscillating battery

A very interesting situation arises as one begins to speculate on the implications of this new model. There are physical consequences that are to be expected as the result of electrolyte displacement from within the inter-electrode gap. Specifically, the physical movement of the highly conductive electrolyte leaves gas filled voids that results in an increased resistance and, as a consequence, an increased IR drop within the cell.

One could envision a sequence of events that might occur in the following manner. That is, electrolyte movement acts in the following sequence:

- (1) The electrolyte movement increases the IR drop in the inter-electrode gap;
- (2) by holding constant the battery voltage, the IR drop decreases the oxygen electrode potential;
- (3) the reduced electrode potential decreases the rate of the oxygen gas evolution reaction;
- (4) this reduction in the rate of gas evolution allows the electrolyte to flow back into the inter-electrode gap;
- (5) the consequence of this is a decrease in the cell resistance and the cell IR drop decreases;
- (6) this causes the rate of gas evolution to increase displacing more electrolyte;
- (7) the resistance of the cell increases
- (8) and the IR drop in the cell increases again.

From the preceding description, a dynamical model can be generated by, again, studying the response of the mathematical functions associated with the physical and chemical processes.[15] During overcharge the applied voltage can be written as:

$$V(\text{cell}) = E(\text{Pb}) + E(\text{O}_2) + IR$$

Solving for the oxygen electrode potential gives:

$$E(\text{O}_2) = V(\text{cell}) - E(\text{Pb}) - IR$$

Since:

- (a) $V(\text{cell})$ is a constant applied voltage
- (b) $E(\text{Pb})$ is depolarized by O_2 recombination

then

$$E(\text{O}_2) = k_1 - IR$$

The mathematical analysis of the dynamical system has been carried out and can be found in another place.[13] However, the intuitive awareness of the effect is clear. The IR drop plus the oxygen electrode potential is constant. As one increases the other must decrease. It is also noteworthy that these processes are nonlinear. That is, the current is exponentially related to the electrode potential and the current is also exponentially related to the applied temperature (i.e., the exponential form of the Tafel and the standard form of the Arrhenius Equations).

A point of contention may arise over the assumption that the negative electrode is depolarized. The alternative that can be proposed is that the electrode voltage can vary between generating hydrogen and depolarization by the oxygen recombination. This possibility exists. However, this voltage change amounts to about 0.10 volts/cell or 0.60 volt as a worse case for a 12 V battery if the cells switch concurrently. Since the battery resistance can vary over two orders of magnitude and the current is ever increasing, this consequent voltage variation is insignificant and can be considered as being constant. To be specific, the IR drop can be of the order of 0.8 Ohms multiplied by 18 A for 14.4 Volts which accounts for the entire applied voltage to the battery. The gas evolution reactions are virtually completely suppressed in terms of the applied voltage. The effect of possible changes in the potential of the negative electrode is insignificant or constitutes a very minor refinement.

For the purposes of this presentation, it is only necessary to say that under a certain set of conditions we can expect a sealed cell to develop oscillatory behavior. This, in fact, happens as shown in Figures 6 and 7. Figure 6 reveals the oscillations as a function of the charge passing through the battery. Since the battery under test was rated at 120 Ah, it can be seen that a substantial overcharge has taken place.

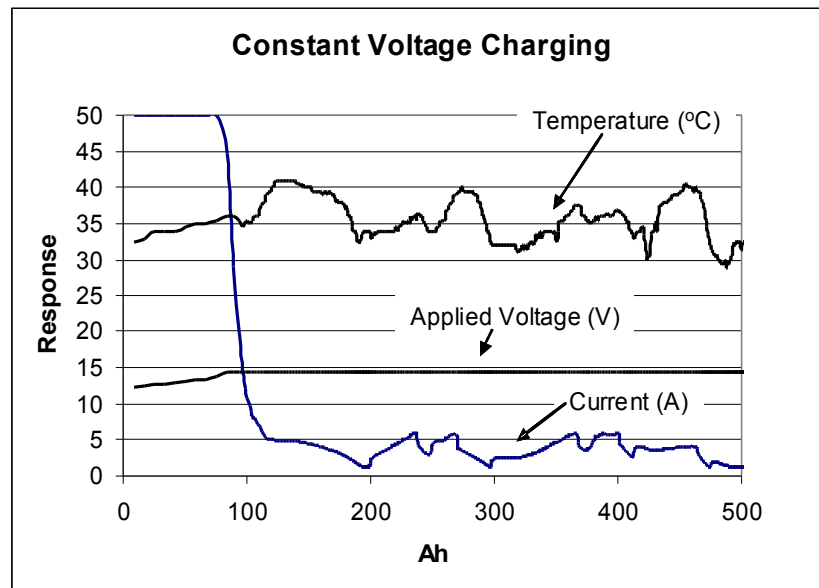


Figure 6. Temperature (measured at the negative terminal), current and applied voltage to the VRLA battery are shown as a function of charge passing through the battery.

Figure 7 shows the same data plotted against time which is the usual representation of the charging curve for a battery. This is another way of viewing the oscillatory behavior of the battery. It is note worthy that this oscillatory response occurs as a transition zone between stable performance and a complete thermal runaway. A more detailed discussion of the mathematical analysis can be found in another place. [13]

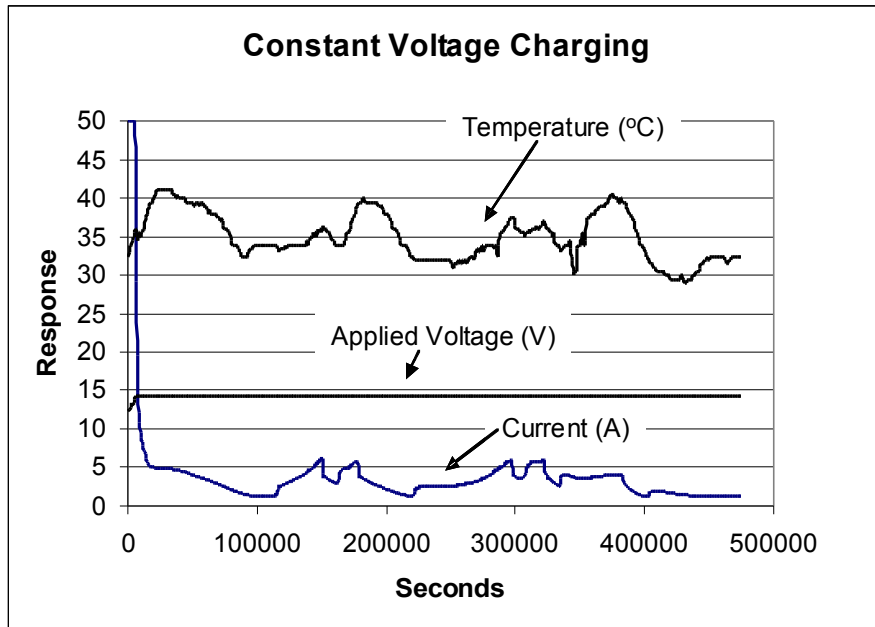


Figure 7. Temperature (measured at the negative terminal), current and applied voltage to the VRLA battery are shown as a function of time as the battery is charged.

Discussion of the power dissipation across the voltage gradient of the battery

An important part of the heat dissipation is the consequence of the passage of current across the voltage gradient established by the battery itself. Figure 8 is an equivalent circuit representation of a battery operated as an electrical load (not as a power source). The battery is in overcharge so no energy storage is taking place.

The graphic in Figure 8 shows a classic Thévenin representation of a power source using linear components. The applied currents are being generated by another power source that is not shown.[16] Although the battery is inherently a power source, it is being affected as an electrical load. The key observation here is that there are two power dissipation components.[12] The first is the equivalent series resistance which corresponds to the polarization resistance of the battery. The second is the voltage gradient of the ideal voltage source that corresponds to the voltage of the battery at open circuit. Since the thought experiment involves no energy storage, the total dissipation is the sum of the power dissipated across the resistor plus the power dissipated across the voltage source.

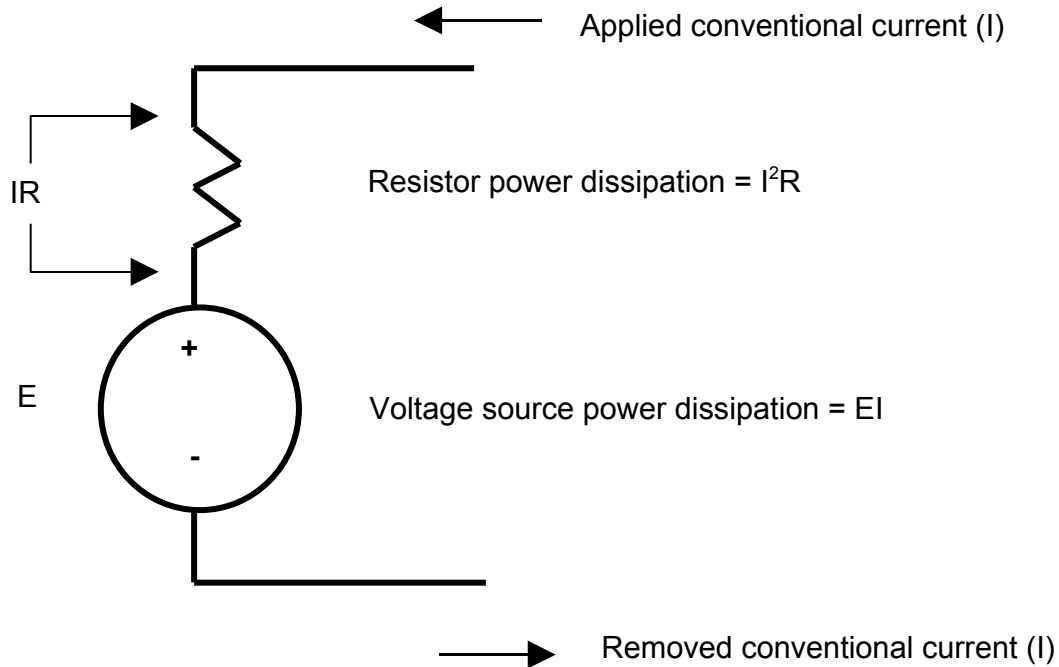
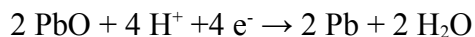
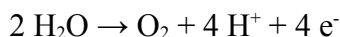


Figure 8. Equivalent circuit of a battery as an electrical load under steady state dc charging.

To review the relative magnitudes of these quantities, we can take the polarization resistance of a 12 volt battery to be 3 mOhms. Assume that a 10 A current is passing. The power dissipation across this component is I^2R which is 0.3 W. The power dissipation across the voltage source is EI or 120 W. Note that from the proposed new hypothesis, as the overcharge continues, the polarization resistance should increase as electrolyte is pumped out of the inter-electrode gap and replaced by nonconductive gas. It would be nice to have a physical interpretation for this huge power dissipation but that interpretation may not involve claiming that the closed oxygen cycle is producing the heat (by virtue of Hess's Law). One plausible scenario is that the power dissipation across the ideal voltage source is the consequence of the rate of change of the kinetic energy carried by the ions in the solution that are carrying the charge within the cell. The actual changes in their kinetic energy take place when the ions stop their forward motion by colliding with the electrode to which they are attracted. This collision would be the energy transfer mode serving to provide the path for power transfer. It is important to also point out that this power dissipation mechanism applies only when the battery is an electrical load. When the battery acts as a power source, the only element within the battery that is expected to serve as a power dissipating component is the polarization resistance. For example, a short circuited battery dissipates all of its power through the polarization resistance. Note that this example is an ideal situation as the current carrying conductors are assumed to have no resistance. The preceding discussion appears to be a plausible interpretation.

Revisiting Figure 1, the Born-Haber Cycle

Returning to one of the points made earlier, Figure 1 illustrates the rationale justifying the assertion that the closed oxygen cycle cannot generate any heat. Additionally, it also shows the two electrochemical steps identified by the enthalpies ΔH_2 and ΔH_4 . The specific reactions involved are:



These reactions were written in this form to indicate that different electrode potentials are involved and that the electrons in the external circuit are replaced by hydrogen ions as the charge carriers within the cell. It is clear that the external circuit is doing work on the system to drive the hydrogen ions across a voltage gradient which is determined by the two electrode potentials. Note that the oxygen molecules carry no charge so they are not involved directly in the power transfer. This discussion serves to indicate that the closed oxygen cycle serves as a power transfer conduit. The earlier discussion showed that the closed oxygen cycle is not involved in the heat generation process.

In a recent paper by Culpin, a thought provoking discussion was presented on the mechanistic influence of the separator on the thermal runaway process in VRLA batteries.[17] Again, it is the action of the separator that is being identified as the controlling component in the thermal runaway effect. It appears that the analysis presented in that paper could be reframed consistent with the discussion presented above and leads to the same conclusions.

Another observation that is noteworthy is that perhaps we misspoke when we used the identification, “closed cycle oxygen reduction” and that we are dealing with an open cycle. This is a subtle and complex point. Over the life of a VRLA battery, a number of processes take place that eventually lead to an inevitable failure and removal from service. For example, hydrogen accumulates and an occasional venting takes place. There is also a degradation of carbonaceous materials and, of course, the ultimate failure mode caused by positive grid corrosion. The vents (valves) in a VRLA battery have a purpose inconsistent with that of a sealed system. This observation serves to place the preceding discussion into a perspective. As the time interval during which we observe the battery becomes very small, the effects attributable to battery aging diminish. So the discussion regarding the closed cycle process is a discrete event that must be coupled with the other effects if one is going to give a full description of battery behavior. Consequently, the discussion presented here refers to an ideal situation which can be rolled into a very complex model to fully describe and predict battery behavior. The discussion in this presentation serves to describe the closed cycle oxygen reduction when the battery is actually sealed. Another point of interest, in this connection, is that whenever a battery vents gas during charge, matter is released to the environment and the gas exists in a higher energetic state than that of the originating solvent. That is, water

has been converted to hydrogen and oxygen which requires an energy input. The eventual recombination reaction produced water plus heat but that heat is generated somewhere outside of the battery. The gases carry with them the heat of reaction that produced them and the energy associated with their heat capacities within the operating temperature gradient. This provides a mechanism for energy removal from the system without raising the system's temperature significantly.

The Lithium-Ion Thermal Runaway Effect

Building on the model developed from the analysis of thermal runaway in VRLA batteries, other systems can be assessed in a similar manner. As was mentioned earlier, the investigations covered in technical conferences and in the literature on the subject of thermal runaway in lithium-ion batteries focus on the issue from an entirely different perspective. It is the fire and smoke production that appears as the primary investigative focus. Investigations have shown that the possible exothermic reactions that affect the thermal runaway in lithium ion batteries include:[18]

- (1) thermal decomposition of the electrolyte;
- (2) reduction of the electrolyte by the negative electrode;
- (3) oxidation of the electrolyte by the positive electrode;
- (4) thermal decomposition of the electrode's active materials;
- (5) melting of the separator and consequent electrical short.

However, it has already been established that the cell temperatures required to initiate these processes are:[19]

- Solid Electrolyte Interface (SEI) layer decomposition 90-120°C
- Reaction of intercalated Li with electrolyte >120°C
- Electrolyte decomposition >200°C
- Positive active material decomposition >180°C
- Positive active material reaction with electrolyte >150°C

In view of all this, the necessary question that becomes the elephant in the room is: Specifically, what causes the temperature to rise to the level necessary for initiating these reactions? That is, what is the triggering mechanism for the thermal runaway that occurs in the lithium ion batteries? At this point it should be clear that the reactions being studied are a manifestation of the presence of the fundamental thermal runaway process and do not constitute the initiation process for the thermal runaway.

The implications of the previous discussion relating to the heat generation model points out that to control thermal runaway, either keeping the inter-electrode resistance as low as possible by rapidly reintroducing the displaced electrolyte (as is the case in the flooded cells) or to quickly increase the inter-electrode gap resistance (as is the case in the “shutdown” separator proposal).

The Synthesis and Application of the Preceding Discussions to Lithium Ion Thermal Runaway

The preceding discussion has attempted to describe a common mechanism controlling the thermal runaway effect in sealed cells. It was also pointed out that this mechanism, as is the case with all other mechanisms, is the creation of the human mind. The best that one can achieve by attempting this inductive methodology is to remain consistent with the weight of the evidence with the reservation that a better interpretation could be forthcoming as a consequence of new findings. Also, an electrochemical cell is a complex system. It is unlikely that a single discrete process is involved. Rather, there probably exists a series of concurrent and parallel processes. A problem with complex systems is that the cause and effect presumption gets fuzzy. The best we can hope to attain is that the major effect has been identified and by doing that, provide a means for controlling or eliminating the TR effect.

A gas evolution reaction is common to all sealed cells. In the case of aqueous solvent based electrolytes, the gas evolution reactions are reasonably well understood. In the case of the lithium ion system, the gas generation process is much more complex.

In a study performed on lithium ion cells where the electrolyte was 1M in LiPF₆ dissolved in a mixture of ethylene carbonate and ethyl methyl carbonate. The following gases were identified after overcharge: carbon dioxide (CO₂), carbon monoxide (CO), methane (CH₄), ethane (C₂H₆), ethylene (C₂H₄) and hydrogen (H₂). [20]

What is interesting about this combination of gases is that olefinic compounds are present and oxygen is absent. Very likely the oxygen, if it is produced at all, reacts quickly in that environment. The existence of the alkenes suggests that an overall reductive environment exists in the gas phase within the cell. The consequence of lithium reducing the electrolyte solvent is an obvious inference. Also, these cells should be somewhat recombinant but not to the extent observed in starved cells using aqueous electrolytes.

Data on Lithium Iron Phosphate (LFP) cells

At this point the author would like to present some previously unpublished work that was guided by the model described above. In these experiments, cells of the 26650 design were intentionally abused for the purposes of observing their thermal runaway behavior. Consistent with the rationale discussed above, the objective is to observe the initiation of the thermal runaway without inducing the decomposition of the internal materials. In these experiments the overcharge was terminated when the external temperature of the cell reached 45°C. This was done to prevent the previously discussed exothermic electrolyte/electrode decompositions from taking place.

Figure 9 shows the overcharge and identifies the regions of the plot. These regions fall naturally out of the mechanism proposed above. There are some interesting features that

need to be discussed further. The recombinant region was studied without venting the cell. If the charging is terminated at 4.95V, the cell swells but not enough to bring about a gas pressure induced vent. The gas that is generated recombines internally so that the cell can be cycled without losing any significant capacity. The gas pressure is not cumulative from cycle to cycle which indicates that it is recombining. When one exceeds the vent activation point, the pressure release causes the voltage to drop. This suggests a reversibility of the gas evolution reaction because the voltage is dependent on the partial pressure of one or more of the contained gases. Note also that the temperature does not rise significantly while in the recombinant region. Once the cell has vented, the cell is electrolyzing off the solvent. The temperature rises but reaches a limiting value. This is consistent with the venting off of reactive gases. This is the means by which flooded cells dissipate applied power as was discussed earlier. As the electrolysis proceeds the internal resistance rises and this cell would then enter into the next stage of the thermal runaway initiation if the charging was not terminated.

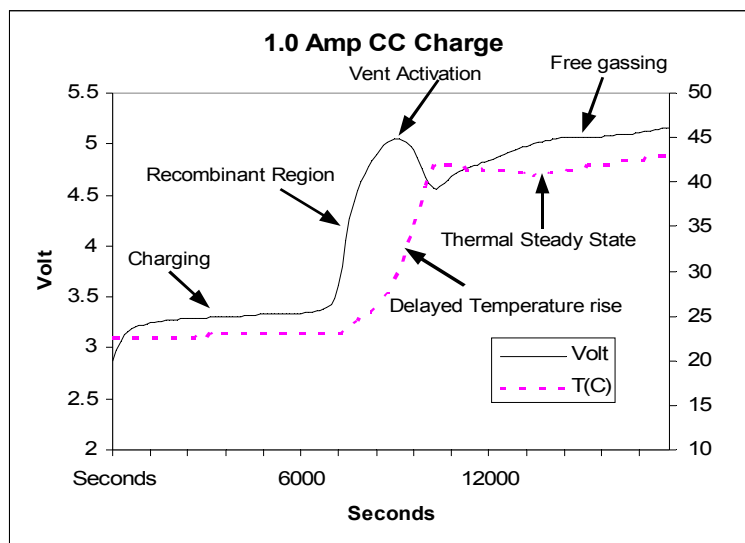


Figure 9. Description of a 26650 LFP cell response under a 1.0A constant current overcharge.

In accordance with the model described above, if the applied current is low enough and the heat generation is kept low enough, it should be possible to dry out the cell before the thermal runaway occurs. Figure 10 shows the charging taking place at one-fourth the applied current of the previous figure. Basically the electrolysis takes place over a longer interval. The increasing voltage at the very end of charge is the consequence of the increasing resistance. The temperature was climbing until the final charge cutoff limit. In this case the internal resistance is suppressing the electrode reactions and eventually the cell would dry out before the induction of the thermal runaway takes place.

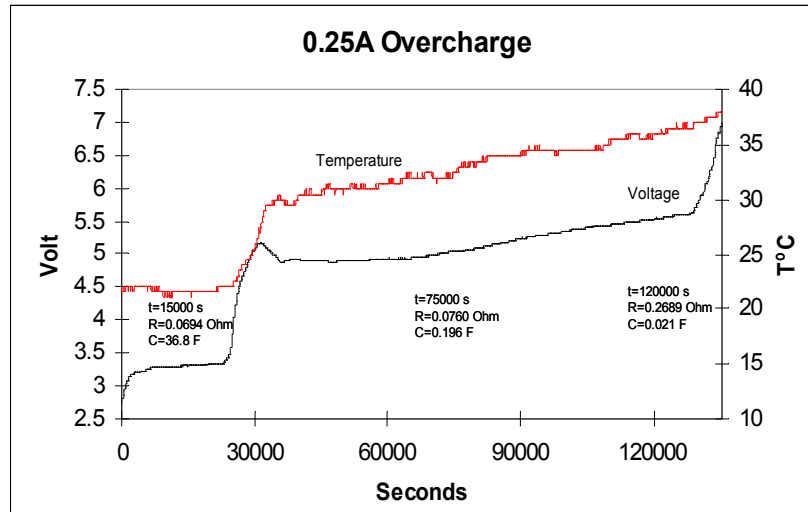


Figure 10. Response of a 26650 LFP cell under a 0.25A constant current overcharge. Periodic ESI measurements of the the total resistance and capacitance are shown.

The data includes periodically taken EIS measurements during the overcharging. The cell resistance and capacitance showed the same behavior as the VRLA battery in overcharge. The internal resistance increases as the solvent continues to be electrolyzed beginning at 0.07 Ohms and arriving at 0.28 Ohm as shown in the figure. Also, the capacitance decreases as the electrolysis proceeds from 37 F to 0.02 F. This was attributed to the displacement of the electrolyte in the pores of the electrodes. The dielectric constant of the gas is much lower than that of the electrolyte. A detailed discussion of this point was presented above.

It would appear from the preceding that the coupling between the non-linear thermal autocatalysis (Arrhenius response) and the non-linear gas evolution electrode reaction suppression (Tafel response) can be affected so as to control the thermal runaway effect.

Concluding Remarks:

The above presentation argues for a unified interpretation for the heat generation behavior of sealed cells on overcharge. An important implication from the above analysis is that a substantial portion of the heating effects appear to be associated with an electrolyte management issue within the separator.

Also, the hypothesized mechanism is chemistry independent and appears to apply to cells having a constrained electrolyte that can be displaced by gas generation (i.e., all sealed cells).

The presentation has developed a general perspective into the effect known as thermal runaway. A unified interpretation is attempted and presented. The proposed interpretation provides a basis for an integrated model of all sealed cell behavior with respect to thermal runaway. The model allows an observer to interpret and propose

alternative approaches for controlling the effect. The discussion attempts to provide a fresh look at the TR effect and provides an opening for further elaboration of the TR effect and methodologies for dealing with it.

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