

CORRECTING INHERENT IMBALANCE AND CONSEQUENT FAILURE OF VRLA CELLS BY THE USE OF CATALYSTS

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Laboratory tests indicate that high quality AGM cells, designed for 20 year standby service, can fail from negative plate discharge even under steady state float conditions. This paper shows that such discharge is not only possible but inevitable if these cells are "out of balance". For a cell to be in balance the hydrogen equivalent of the positive grid corrosion must not be less than the hydrogen emitted by the negative plate. Imbalance results in excess or unrecombined oxygen being generated in the cell which can discharge the negative plate. A catalyst placed in the cell can correct imbalance thereby preventing negative discharge, reducing water loss and increasing the useful life of the cell, especially in hot operating environments.

1. Introduction

VRLA cells have been very successful in replacing flooded cells in long-life telecom and UPS applications. Much of this success is due to assumptions that VRLA cells will provide 20 years of service without the addition of water. However, despite the fact that these cells are often built to superior quality standards, their actual performance in service has been problematic, with persistent reports of early failures.

Evidence from our own laboratory testing, taken over a 2 year period, tended to confirm the field reports. The tests indicated two possible failure modes:

- First, the cells were emitting hydrogen at rates that were generally too high to sustain a 20 year life without loss of capacity due to dryout.
- Second, and of more concern, the negative plates of some of these cells appeared to be discharging under long term, steady-state float with the possible result of negative plate capacity failure.

The purpose of the present work was to find out what was happening inside the VRLA cell that would explain these apparent problems and, if possible, to find practical solutions.

2. Summary of long-term float test.

This test has been described in detail elsewhere [1]. Three pairs of AGM cells of three different designs from two separate manufacturers were selected for the test. They were all long-life cells designed for 20 years of maintenance free service. Each pair was floated, relatively undisturbed, for a period of two years at an average voltage of 2.27 volts per cell at a steady temperature of 80° F (27° C). All cells were equipped with gas collection apparatus and reference electrodes.

We had assumed initially that the cells would fail from dryout and our original intent was simply to calculate the rate of dryout from the hydrogen emissions. Based on the amount of water available in the typical VRLA cell, the cells had a maximum permissible gas emission rate of 20 ml per day per 100 Ah of capacity. That is, if any cell emitted more than this amount of gas, it would dry out before its 20 year life goal.

The results of the test were pessimistic. The gas emission rates on 5 out of the 6 cells were well above the 20 ml per day target. In one case, it was twice the target value, indicating an expected dryout life of only 10 years.

Gas analysis showed that the emissions were largely hydrogen. This was expected because, in accordance with conventional

understanding of VRLA cell behavior, positive grid corrosion removes oxygen from the oxygen cycle and an equivalent amount of hydrogen will be generated at the negative plate and emitted from the cell. What was unexpected, however, was that pairs of identical cells would have gassing rates varying by a factor of 2:1. It seemed very unlikely that the positive corrosion rates would vary by this amount. We had not realized at that time that our cells were "unbalanced" - a concept we will describe later.

Reference electrode readings indicated that the negative plate potentials were generally slightly below open circuit values; but this seems typical of these kinds of cells so we were not concerned. We did become concerned, however, when some cells showed a serious and steady decline in conductance over the test period [1]. This strongly suggested that negative plate discharge was taking place under steady-state float conditions. Since this reaction can evolve hydrogen, we suspected that the excess hydrogen emission was the result of this reaction. Calculations showed that if negative discharge and dryout are taking place simultaneously, then, for a given amount of hydrogen emitted, negative discharge will be the first to limit capacity.

Our concern appeared justified when, at the end of the two year test period, a capacity test was carried out on two cells in our test series. Both cells failed to meet the minimum 80% capacity target; one cell yielded 75% capacity while its twin yielded only 60%. The results are shown in Figure 1. Both cells failed by negative limitation as measured by their reference electrodes. This was unmistakable proof the negative plates on these cells were discharging on steady-state float. The question now was: what was the cause?

The test itself had done nothing unusual to the cells that would explain such a continuous loss of capacity - no discharges, no long open circuit periods, no high temperature excursions - indeed, no disturbances of any kind. The positive grids of these cells were made from a non-antimonial alloy so capacity reduction cannot be blamed on antimony transfer. (*Note: There was some tin in the positive alloy but normally this is not considered a negative impurity*). A prime suspect, namely leakage of air into the cells during the test, can also be excluded because these cells were emitting gas into collection apparatus during the entire test period and were pressurized to 1.5 psi (100 millibars) at all times. Further, since the conductance readings had shown continuous rather than sudden decline, the mechanism of discharge also had to be a continuous process rather than a sudden event.

Two possible explanations for the negative plate capacity loss remained, involving two different kinds of discharge:

- Self discharge due to impurities in the negative active material.
- Discharge due to oxygen produced inside the cell.

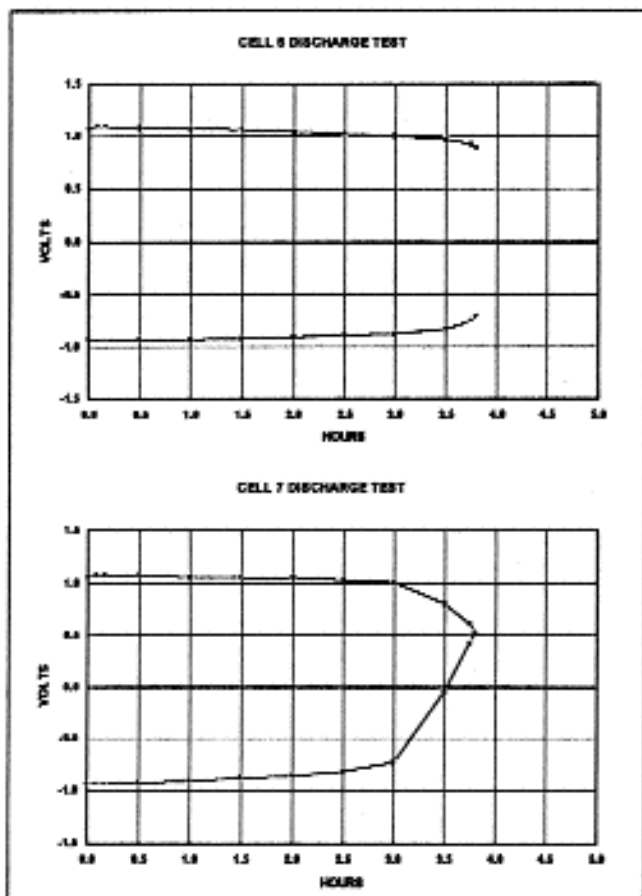


Figure 1: Five hour rate capacity tests showing negative plate limitation after 2 years on float at 2.27 vpc. Cell 6 gave 75% and Cell 7 gave 60% capacity.

3. Basics revisited

The design of VRLA cells is different from that of flooded cells in one crucial respect: **gas management**. In a flooded cell, the gasses produced during charging simply leave the cell and can generally be ignored. (Note: The gas evolution in a flooded cell must be compensated for by periodic water addition, but it is not an aging factor for the cell.)

In a VRLA cell, on the other hand, the success or failure of the cell is largely defined by how much hydrogen and oxygen it produces and at what rate these gases leave the cell. Yet gas measurements have received little attention in the literature. The following is a review of some basic VRLA topics from the perspective of gas management.

3.1 Oxygen cycle. In the oxygen cycle, everything begins at the positive plate where water is broken down into three components:

- oxygen gas which travels in the gas space
- hydrogen ions which travel in the liquid
- electrons which travel in the electrical circuit

All three components converge on the negative plate where they recombine into water; the water then travels back toward the positive plate to complete the cycle. The oxygen gas depolarizes the negative plate to approximately its open circuit value. The hydrogen evolution rate is thereby reduced to a value close to the self discharge rate which results in the cell having a much reduced water consumption.

3.2 Hydrogen oxidation or recombination. For present purposes, we agree with the conventional wisdom that VRLA cells do not normally recombine hydrogen gas (only hydrogen ions). If hydrogen gas is generated, it must leave the cell. (Note: For the record, we have seen examples of cells that appear to be recombining hydrogen but they are the exception, not the rule).

3.3 Negative plate discharge. The negative active material plays a much larger role in the design balance of VRLA cells than it does in flooded cells. Its inherent tendency to produce hydrogen at all normal voltages, thereby consuming water, is in conflict with the limited water loss allowed in a VRLA cell.

Oxygen depolarization does not eliminate hydrogen evolution of negative plates but reduces it to its minimum level possible, namely, its open circuit value. This limiting value has been clearly stated by Berndt [2] and is so important to the understanding of the VRLA cell that we will repeat it here as a basic law:

The self discharge rate describes the minimum hydrogen evolution that can be achieved for the fully charged lead-acid battery.

Dr. Dietrich Berndt.

The open circuit self-discharge of the negative plate is a simple, independent chemical reaction. Yet, in practice, it indirectly determines the service life of many, if not all, long-life VRLA cells. The argument is as follows:

- In all the long-life AGM cells we tested, the hydrogen emission rates on float (controlled by the negative plates) were much higher than the positive grid corrosion rates.
- Therefore, if only two modes of failure were possible, these cells would fail by dryout long before the positive grids corroded. (Note: This assumes, of course, that they do not fail by negative discharge).
- Since the lowest hydrogen emission rate that can be achieved on float is equal to the self discharge rate (Berndt's Law), the maximum operating life of the cells will be limited by water loss based on their open circuit gassing rate.

In other words, for all its complex design, the service life of a present-generation, long-life VRLA cell will usually be determined by the self discharge rate of the negative plate. This rate, in turn, depends mainly on the purity of the negative active material and on the cell's operating temperature. Even improving the positive grid will not improve the life of the cell if, as in our cells, the corrosion rate is already small compared with the hydrogen evolution rate of the negative. Indeed, as we will

show, such an action may actually reduce the life of the cell.

3.4 Impurities in the negative active material. It is well known that impurities that increase hydrogen evolution also increase the self discharge rate of the negative electrode and, therefore, can shorten the life of a VRLA cell. What may not be intuitively clear is how drastic the effect of impurities can be. Minor impurities can be tolerated in flooded cells because they merely increase the frequency of water addition. But even trace impurities can easily double hydrogen emissions - and thereby **halve the service life** - of VRLA cells. Therefore, impurities must be controlled with unprecedented vigilance.

3.5 Two types of negative discharge. All discharges of the negative active material involve a conversion from Pb to PbSO₄. However, there are two distinct processes by which this can be accomplished and it is important to distinguish between them because they have different end products which, in turn, can help identify modes of failure:

- Direct discharge according to the formula:
$$\text{Pb} + \text{H}_2\text{SO}_4 = \text{PbSO}_4 + \text{H}_2$$

This is the kind of discharge the negative will receive if the cell is on open circuit. It is usually called "self-discharge". Note that there **no oxygen gas** involved in this discharge reaction. Also that the hydrogen emissions from this source can never exceed the amount defined by Berndt's Law.

- Indirect discharge according to the two formulae:
$$\text{Pb} + 1/2 \text{O}_2 = \text{PbO}$$
$$\text{PbO} + \text{H}_2\text{SO}_4 = \text{PbSO}_4 + \text{H}_2\text{O}$$

with the overall result:



This is the kind of discharge the negative will receive if it is first oxidized by excess oxygen in the cell's atmosphere.

Note that there is **no hydrogen** produced by this reaction so it cannot account for the excess hydrogen produced by our test cells. Note also that there is **no loss of water** from the cell in this reaction. This is an interesting observation because it may be consistent with some field failure reports of cells with sulfated negatives but which still retained plenty of water (i.e.: have not dried out).

3.6 Critical interaction of rates

The two critical reaction rates that must be balanced in a VRLA cell are:

- the self discharge rate of the negative plate
- the corrosion rate of the positive grid

At first sight, these two reactions do not seem to have much in common; but, on the contrary, they are very closely related. The difficulty lies in explaining the relationship in simple terms. We will attempt to do so first with a simplified explanation and then with a more scientifically rigorous explanation.

The simple explanation is this:

Positive grid corrosion during float absorbs oxygen from water in the electrolyte and releases hydrogen ions and electrons; these migrate to the negative plate to become hydrogen. If the rate of this "incoming" hydrogen to the negative plate is the same as the

"outgoing" hydrogen evolved on open circuit, then the negative plate will remain fully charged. If it is less, the negative will self discharge.

The more complete explanation is this: [3]

The two reactions are linked by the fact that the same current flows through both electrodes. When the efficiency of the internal oxygen cycle is close to 100%, oxygen generation at the positive electrode is compensated by oxygen reduction at the negative electrode. Both require the same equivalent of current. As a consequence, grid corrosion at the positive electrode and hydrogen evolution at the negative electrode must also balance each other. Otherwise, the same current cannot flow through both electrodes which would be inconsistent with a closed circuit. In such a situation, discharge reactions at the electrodes automatically appear that re-establish current balance.

This leads us to the crucial concept of hydrogen balance in a VRLA cell which is explained in detail in Section 6.

4. Experimental approach

As described in a previous paper [4] earlier limited experiments with catalysts in our long term float tests had led to significant and intriguing results including reduced hydrogen emissions, reduced float currents and increased negative plate polarizations. This led us to carry out a definitive comparison test between two strings of cells, one with and one without catalysts. The results of the test not only showed that catalysts could dramatically improve the service life of AGM cells but they also produced a great deal of insight into the complex reactions taking place inside the VRLA cell.

4.1 Test of catalyst versus non-catalyst cells

Details of this test have been published elsewhere [1] but can be summarized as follows: Ten cells of the same design were installed in a single (common) water bath and maintained at a temperature typical of the operating temperature of these cells: 90°F (32°C). The cells were floated at different voltages and the gas emitted from each of the cells were collected in individual glass containers. Five cells were then equipped with catalyst devices of our own design and five were left as standard control cells. Reference electrodes were installed into one cell in each set to measure typical negative plate potentials.

The results were impressive;

- In less than one day, the negative plates on the catalyst cells were significantly polarized - showing that they were not discharging. The negative plates on the control cells were all at open circuit or a little below as is typical of these products.
- The float current of the catalyst cells dropped to less than half that of the control cells and stabilized there for the entire test period of several months.
- The gas measurements, also made over a period of months, showed the emissions of the catalyst cells to be consistently about 5 times lower than those of the control cells. This implies an increase in potential service life from about 5 years to about 25 years. (*Note: Second order effects such as unmeasured diffusion*)

losses through the container walls will reduce this ratio somewhat).

- The gas emissions from the catalyst cells were relatively uniform while those from the control cells were erratic; possibly the result of minor impurities.
- The negative plates of the catalyst cells were polarized slightly even at float voltages as low as 2.21 vpc while those of the control cells were below open circuit at all voltages up to and including 2.30 vpc - normally considered a boost voltage.

The gas emission results for the individual cells are shown in Figure 2. The gas emissions of the catalyst and control cells at three separate float voltages are shown in Figure 3 which is based on an earlier published graph but with more data points [1].

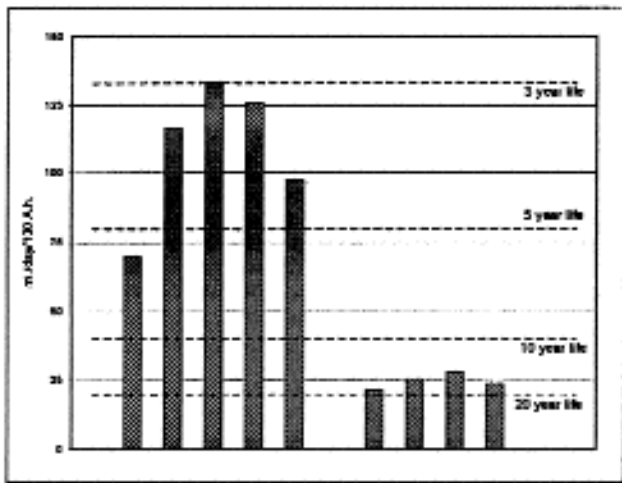


Figure 2: Comparison of gassing rates of standard cells versus catalyst cells at 90° F (32° C) showing increase in theoretical service life.

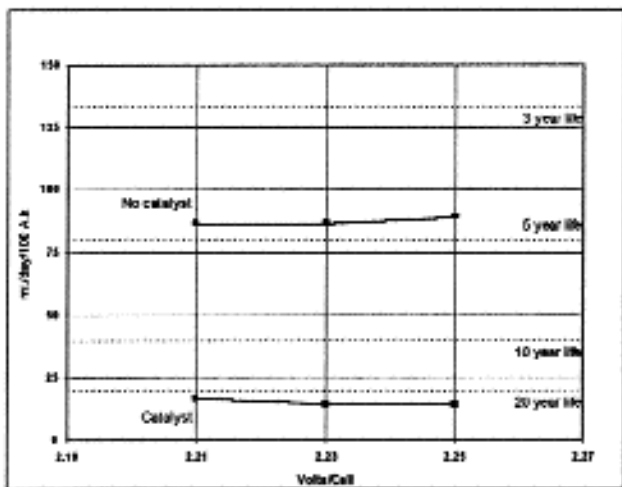


Figure 3: Gassing rates versus float voltages for catalyst and non-catalyst cells. The open circuit gassing rates were the same for both cell types.

5. Discussion

As can be seen from Figures 2 and 3, the magnitude of improvement in gassing rates is difficult to exaggerate. Note that these are real production cells floating at recommended

voltages and operating at realistically warm temperatures. Without question, the catalysts improve the potential service life of these cells to a remarkable degree.

Debates will, no doubt, follow on the precise mechanism of the reactions involved but the important result is that the catalyst has established a very high numerical standard by which cell designs can be judged. For example, if one were to claim a superior cell design, one would have to demonstrate equal or lower hydrogen emissions at the same elevated temperature as our results. (Note: It is theoretically possible to do so without using a catalyst, as we will show, but we do not know if it is practical).

Note that while the catalysts reduced the gassing rates dramatically, they did not reduce them to zero. Rather a new, stable, lower level of gas emissions was achieved. The reason for this is fundamental: lead acid cells cannot avoid positive grid corrosion which, by consuming oxygen, must always cause an equivalent production of hydrogen. The lower level of hydrogen emissions from a catalyst cell is, therefore, directly related to the rate of positive grid corrosion. More of this later.

Figure 3 is a remarkable graph for the amount of useful data it contains. Recognizing that the upper curve represents the gas emissions of the control cells and the lower curve likewise for the catalyst cells, these are some salient points that can be derived from the graph:

- The lower curve represents the much lower rate of emissions that is approximately proportional to positive grid corrosion.
- The flatness of the upper curve in the region of 2.21 to 2.25 vpc represents the stability of emissions over this range. (i.e.: There is no advantage in lowering float voltages below 2.25 in the case of these cells).
- The flatness of the lower curve in the same region represents a relatively uniform corrosion rate for these float voltages.

During the test, we switched off the power supplies to both strings of cells to see what the open circuit gassing rates would be. The result was fascinating: Both catalyst and control cells gassed at almost the same rate, and that this rate coincided with the **upper curve** in Figure 3. In other words, the catalyst cells were now gassing at the same, higher rates as the control cells. The further implications of this result is as follows:

- The catalyst has little oxygen to work with on open circuit compared with float conditions. (To put it another way, there is surplus oxygen available during float for the catalyst to use).
- Berndt's Law was elegantly demonstrated because the control cells' gas emissions on open circuit were almost identical to their emissions on float.
- The possibility that the low emission rates of the catalyst cells were actually due to leaks was eliminated because their low emissions rose dramatically as soon as the charging current was turned off.
- Since the upper curve represents the rate of hydrogen evolution of the negative plate (on both float and on open circuit) and the lower curve represents the positive grid corrosion rate on float, the figure shows graphically the crucial relationship between these two

reactions discussed earlier. In an ideal VRLA cell, they should be equal whereas in these cells they differ by a factor of 5:1. (Note: Taking second order effects into account, particularly the likelihood of gas losses through the cell walls of about 5 ml/day/100 Ah, both emissions increase by this amount and the ratio decreases to about 4: 1).

- Since the hydrogen evolution rate of the negative plate is much higher on these cells than the positive corrosion rate, these cells will fail from dryout much sooner than from positive grid corrosion. (Assuming, of course, that they will not fail even earlier from negative discharge or other factors).

Grid corrosion test. Figure 3 also shows that the lower curve can be used as a relatively direct means of measuring the hydrogen released as a result of positive grid corrosion. In the absence of a catalyst, this corrosion hydrogen is mixed with and overwhelmed by other hydrogen emissions and becomes difficult to isolate. In the presence of a catalyst, however, if the emitted gases are analyzed and spurious effects eliminated, the quantity of hydrogen emitted from a VRLA cell should be a useful, direct, in-situ grid corrosion test. For high accuracy, the second order effect of gas loss through the cell container, etc., should also be minimized. Low temperature testing such as 20°C should be avoided because the gassing rates are so low that losses through the containers become very significant, leading to over optimistic (low) gassing rates. Higher temperatures such as 30°C are much more practical if gas emission figures are to be taken seriously.

An interesting observation from Figures 2 and 3 is that the control cells - the standard production cells - are predicted to fail by dryout in less than 5 years at the test temperature of 90°F (32°C) - assuming no earlier failure from negative discharge. The catalyst cells, however, will (theoretically) not fail by dryout for well over 20 years - the design life of the cell. Further, since the negatives of the catalyst cells are polarized and not discharging, the catalyst cells will not succumb to negative discharge failure either. In short, while a temperature of 32°C is a very hostile environment for the control cells, it is a perfectly acceptable operating climate for the same cells equipped with catalysts.

6. Hydrogen balance in cell design.

We now come to the theoretical explanations for the quantitative gas emission results and negative polarization effects measured in our experiments. In particular, we are led inescapably to one of the most important and least understood concepts in VRLA cell design - **hydrogen balance**.

Hydrogen balance is not well understood because it is a technical quirk that is only applicable to "sealed" lead-acid cells and has no relevance in flooded cell technology; accordingly, even experienced battery designers have not had to deal with it in the past.

It should also be mentioned that, while there is no dispute about the need for hydrogen balance in VRLA cells, there is room for debate in describing the exact mechanisms of the processes involved. Our following attempt may not be correct in every

detail but should serve to move the debate forward.

6.1 The gas and ion flow diagram.

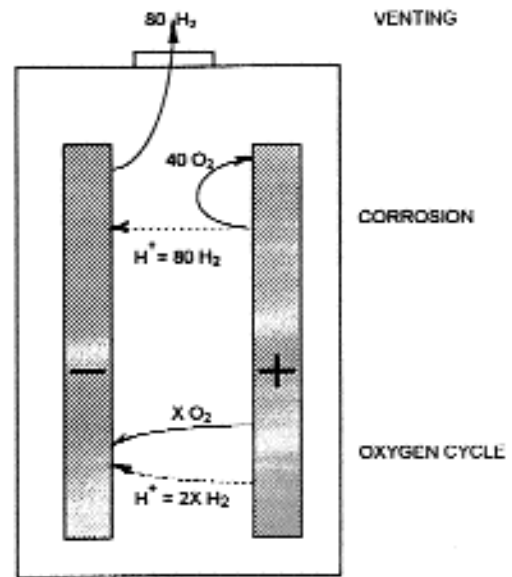


Figure 4: Diagram of gas and ion flow in a balanced cell.

Figure 4 shows a diagram of the flow of gases and ions inside a hypothetical VRLA cell with a nominal capacity of 100 Ah. The diagram needs some explanation. We developed it to attempt to describe the very complex concept of VRLA cell balance in a way that would produce more insight rather than more equations. As will be seen, that is no simple task. The drawback to our model is that it takes liberties with well established electrochemical conventions and so will probably not appeal to the purist. Its advantage, however, is that it breaks down complex reactions into a simple process flow diagram and may, therefore, appeal to the practical battery engineer.

The gas flow in the diagram, which includes the oxygen consumption in positive grid corrosion, is represented by solid lines while the hydrogen ion flow is represented by dotted lines. The electrons which move through the external electrical circuit are not shown but can be implied from the ion flow; that is, the hydrogen ions will always have matching electrons. Also not shown is the water returning from the negative to the positive plate as part of oxygen cycle. Any gases produced other than oxygen and hydrogen are also ignored for the sake of simplicity...

A potentially confusing breach of convention is that we are denoting the flow rate of hydrogen ions as "equivalent gas" because it can then be conveniently assigned the same units of flow as the gases in the diagram (ie: ml per day).

6.2 The balanced cell

Figure 4 shows the gas and ion flow model for a hypothetical VRLA cell with a nominal capacity of 100 Ah. The amount of gaseous hydrogen given off by the negative plate is 80 ml per day - a number approximately equal to measured values taken from the control cells in our catalyst vs non-catalyst test described earlier. This amount of hydrogen was typical of our test cells at 90°F (32°C) and all the following data also applies to this temperature.

For the purpose of illustration, an unusually high corrosion rate of the positive grid in this cell has been selected so that 40 ml/day of oxygen is consumed in the corrosion reaction. Since that oxygen is removed from the water in the cell, the corresponding amount of hydrogen ions and electrons, equivalent to 80 ml/day of gas, will leave the positive plate and migrate to the negative plate.

Therefore, the 80 ml of "equivalent hydrogen" produced by corrosion is precisely equal to the amount required to replace that evolved from the negative plate by self discharge. This is the simple definition of a "balanced cell". In this balanced cell, the negative will be neither polarized nor discharging; the "equivalent hydrogen" will become hydrogen gas and leave the cell a rate of 80 ml per day.

The reactions marked "oxygen cycle" on the diagram do not produce any excess gases of any kind and do not affect the hydrogen balance of the cell; therefore they can be ignored in this analysis, whatever their absolute quantity. In a practical cell, of course, they do cause heat.

Inside this balanced cell, no excess oxygen is generated to cause discharge of the negative plate. The cell, therefore, will theoretically not fail by negative discharge but from some other normal or expected condition such as dryout or positive corrosion. In that sense, the balanced cell is the perfect VRLA cell.

6.3 The unbalanced cell

Figure 5 shows the model for a cell having a positive grid of superior design (i.e.: a very low corrosion rate). The negative hydrogen evolution figures are based on those taken from the control cells in our catalyst test (Figure 3); as far as we know, they should be typical of present-generation long-life cell designs.

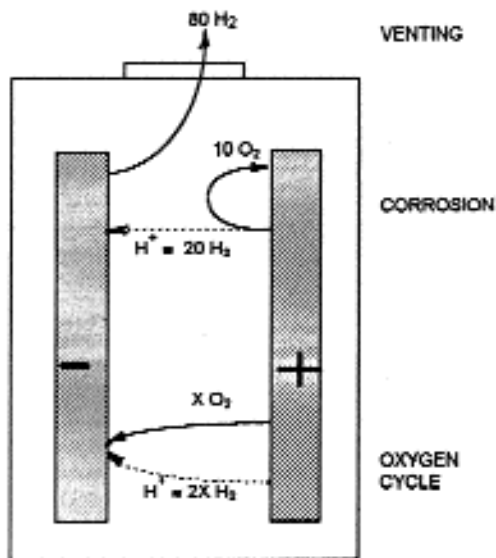


Figure 5: Gas and ion flow in a unbalanced cell at low float voltage. The negative is self discharging.

This cell has the same nominal 100 Ah capacity as the cell in Figure 4 but the corrosion rate of the positive grid is **four times lower**; that is, only 10 ml per day of oxygen is consumed in that reaction. (Note that while the balanced cell in Figure 4 had a hypothetically high corrosion rate; this unbalanced cell has a very low corrosion rate based on real values as measured on our catalyst equipped cells).

It follows that 20 ml per day of "equivalent hydrogen" is being released by the corrosion reaction which is only one quarter of the amount necessary to provide the 80 ml per day required by the negative plate. Thus the cell is severely unbalanced, in this case by a ratio of 4:1.

Since the negative plate is receiving less incoming hydrogen (ions plus electrons) than it needs to maintain equilibrium, it will suffer discharge of the first kind (i.e. to $PbSO_4$ and H_2). Note that the cell will still emit the same 80 ml of hydrogen but now 60 ml of that is coming from self discharge and only 20 ml from the charging current.

In other words, this cell on open circuit would emit 80 ml of hydrogen, all of which would be from self discharge. Here, the negative is discharging at three quarters of the open circuit rate. Simply put, the cell is being undercharged so the float voltage must be increased. But when that is done, another serious problem emerges which is shown in Figure 6.

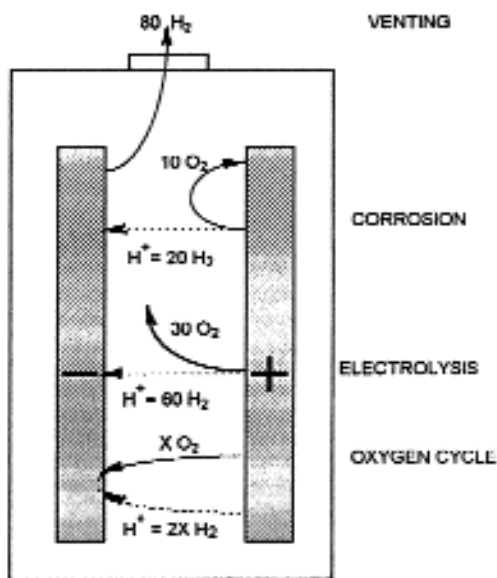


Figure 6: Gas and ion flow in a unbalanced cell at an adequate float voltage showing the excess oxygen produced.

When the float voltage is raised to the ideal level (i.e. such that a further 60 ml of "equivalent hydrogen" is delivered to the negative plate and the negative is on the point of polarizing) then electrolysis takes place and a proportional 30 ml of oxygen per day is simultaneously given off by the positive plate into the cell's atmosphere. This oxygen has no useful purpose inside the cell and must either leave the cell or cause discharge of the negative plate. (Note: In a severely unbalanced cell, the float voltage that produces the results in Figure 6 will be very high).

Berndt has pointed out [3] that as the negative plate discharges, its hydrogen emissions slow down until, eventually, they come into balance with the positive corrosion; that is, the cell becomes balanced at a lower capacity. This only applies if the cells are nearly balanced to begin with. In our cells, on the other hand, this balance point would only be reached after the cell had already failed with a serious loss of negative capacity. Therefore, it is important to find out what happens to the oxygen. (Note: This analysis is corroborated by the results of our long-term test which showed no significant decline in hydrogen evolution over the two year period [1]).

Gas analysis on our cells floating at 2.25 vpc indicated a hydrogen content of 93% with an oxygen content of less than 6%. This allows for only 5 or 6 ml of oxygen in the vented gas and there is certainly no place for emissions as large as 30 ml of oxygen in these measurements. This data suggests, therefore, that our cells were in between the conditions shown in Figures 5 and 6.

It appears, then, that floating an unbalanced cell, even at normal float voltages, will generate unrecombined oxygen inside the cell. Since any oxygen produced stays inside the cell, all unbalanced cells will suffer from negative discharge on steady state float. (Note: This component of the discharge will be of the second kind to $PbSO_4$ and water, not self-discharge as in the case of the undercharged cell).

7. Description of the solution

Once the cause of the problem is understood, it becomes evident that the solution must involve protecting the negative plate in some way. There are at least three possible options:

- Balancing the cell
- Forcing the excess oxygen to leave the cell
- Recombining the excess oxygen with hydrogen

Balancing the cell. As stated already, balancing the rates of hydrogen generation and grid corrosion is one of the most important prerequisite for VRLA batteries. In cells that are almost balanced already, increased float voltage would increase grid corrosion sufficiently to balance the cell. On our long-life cells, however, with their very large imbalance, this is not an option. The only way of balancing these cells (other than deliberately increasing the corrosion rate of the positive grids by a large amount) is to reduce the hydrogen evolution rates of the negative plates. Perhaps the negative active material of our cells contained trace impurities; if so, greater purity of the raw materials would be an obvious approach. Also, perhaps variations in expanders -particularly organics - or other dopants would make a significant reduction in hydrogen evolution. It is certainly an option worth investigating. (Note: In quantitative terms, this means lowering the negative gassing rate below about 20 ml/day per 100 Ah at a temperature of 30° C).

Forcing the oxygen to leave the cell. This admittedly untested solution involves protecting the negative plate from the free oxygen by the use of gas barriers (oxygen shields) of some kind. Design options that come to mind might be the use of silica gel, microporous separators, negative dopants, and, perhaps lower vent pressures. Although this option appears to negate the basic design aim of the VRLA cell (i.e.: to permit free oxygen transport

to the negative plate in the gas phase) it is also true that the rate of oxygen transport in an industrial AGM cell is hundreds of times higher than it needs to be for standby service. For example, a flooded cell can be depolarized by dissolved oxygen alone at low enough float voltages and is, in that sense, an extreme form of a VRLA cell with very strong gas barriers. Therefore oxygen shields may have some value in increasing the resistance of oxygen transport such that the negative polarizes earlier and any surplus oxygen is ejected from the cell. (Note: Implied here is that gel cells may be less prone to negative discharge from excess oxygen but here we have very limited experience).

Recombining the oxygen with hydrogen gas. Another option is to put a recombination catalyst into the atmosphere of a VRLA cell to recombine any excess or unrecombined oxygen with the hydrogen gas that is always available. Not only is the excess oxygen removed, restoring perfect balance to the cell and preventing negative discharge, but the water re-formed by the catalyst can increase the dryout life of the cell. Indeed, the more the cell's imbalance, the better the effect of the catalyst. In the case of our cells, the theoretical improvement in service life went from under 5 years to over 20 years. (Note: This assumes that the catalyst itself will last 20 years, or is replaced from time to time).

The gas and ion flow diagram of the cell equipped with a catalyst is shown in Figure 7. All the conditions are the same as the unbalanced cell of Figure 6. This time, however, the 30 ml of oxygen that threatened the negative plate is harmlessly recombined with 60 ml of hydrogen gas that would otherwise have to leave the cell. The total hydrogen emissions drop to 20 ml per day - which is precisely the same as the equivalent hydrogen due to the corrosion reaction.

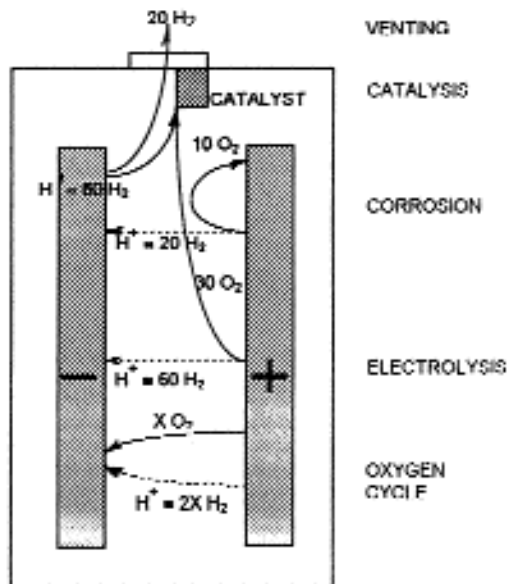


Figure 7: Gas and ion flow in an unbalanced cell equipped with a catalyst.

In practice, the conditions shown in Figure 7 would be transient because the negative plate would soon polarize and change the values shown.

7. Arguments for a catalyst.

The use of catalysts in flooded cells is well known. Normally they are used to recombine bulk oxyhydrogen gases created during overcharge. The heat of recombination can be rather high. For example, on a typical 600 Ah traction cell, the finishing rate can be 30 amps. In this case the catalyst would have to dissipate nearly 45 watts of heat per cell.

On a stationary VRLA cell, the purpose of the catalyst is different and more subtle. The VRLA cell is already a (partially) recombinant cell whose entire purpose is to minimize water loss. The oxygen cycle achieved by the cell itself has an efficiency of 95% or more. This means that the catalyst need only recombine a few percent of the Faradaic oxygen produced. Accordingly, the catalyst can be much smaller and the heat generated much lower. For example, a 600 Ah standby VRLA cell may be charged at 2.25 vpc and 0.3 amps or a total power of less than 1 Watt; and the oxygen cycle would reduce this further so the actual power dissipated by the catalyst is very low. The catalyst used in standby VRLA service is a "balancing catalyst" not a bulk recombination catalyst.

The reliability of catalysts should be higher in VRLA cells than in flooded cells because the acid density is higher in the former. This means that the cell atmosphere is dryer and will act to dry the catalyst if it is wetted by its own product water - a feature we have demonstrated in the laboratory.

While it may, theoretically, be possible to build a balanced long life VRLA cell with hydrogen emissions in the region of 20 ml/day/100 Ah at 90°F (32°C), it may not be practical to do so consistently in a production environment due to the problems of trace contaminants. Indeed, even a quality control test for this variable would be difficult to implement. A catalyst makes the cell more tolerant of impurities as may be implied by the uniform emissions of the catalyst cells in Figure 2.

If a cell has already suffered negative plate discharge, either due to self discharge or due to oxygen inside the container, a catalyst may be able to recover the cell without boosting or any other action on the part of the user. For example, the cells shown in Figure 1, after failing their capacity test was equipped with a catalyst and put back on float to recharge. At the time of this writing (several weeks later) the cells had polarized negatives (7 to 10 mV) and, at least for a period, a zero gas emission rate. The polarized negative means that the negative plate is now recharging on float instead of discharging.

If a cell has a small leak in it, a catalyst will not only be able to prevent discharge by the atmospheric oxygen but will actually use that oxygen to extend the dryout life of the cell. In an earlier test, one cell with such a leak gave zero emissions for a period of over 4 months, with lower than average emissions thereafter. A catalyst, therefore, can make a cell tolerate and even benefit from small leaks.

8. Conclusions

The making of a balanced cell is by no means impossible. All it takes is a cell with positive grids that corrode faster than the negative plate generates hydrogen. The issue is not how to make a balanced cell but how to make a **long-life** balanced cell. The problem with long life cells is that they will, by definition, have superior grids with very low corrosion rates. The requirements for the negative plate will therefore be for very low hydrogen emissions indeed. Further, those low rates must be kept stable for 20 years.

It is an irony that, if an attempt is made to improve a balanced cell by incorporating a better positive grid (ie: one with a lower corrosion rate), that cell will no longer be balanced, will suffer negative plate discharge and quite likely have a shorter life than before.

Nevertheless, designing a stable balanced cell should be the first aim of the battery designer. This implies making negative plates with hydrogen emission rates about four or five times lower than those on our test cells. Whether this is possible or not in production cells is a question that is outside the scope of this paper; but the variation seen between cells of the same batch (Figure 2) tends to argue that it is a difficult aim.

If a stable, balanced long-life cell cannot be reliably manufactured, then the use of a catalyst becomes almost mandatory. The catalysts automatically balance the cells, constantly adjusting to their ever changing aging characteristics. In doing so, they prevent negative discharge, reduce water loss and extend the useful life of the cell - particularly at high ambient temperatures.

9. References

1. W.E.M. Jones and D.O. Feder, Proc INTELEC 96
2. D. Berndt, Maintenance Free Batteries, John Wiley & Sons, New York
3. D. Berndt. Private correspondence
4. W.E.M. Jones and D.O. Feder, Proc. INTELEC 95