

Quantifying Secondary Reactions in VRLA Batteries

What purity standards and other factors are necessary to prevent negative plate discharge?

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Abstract:

In a VRLA cell with a fully developed oxygen cycle, the negative plates will suffer discharge during float service if their self-discharge rate is too high to be balanced by the corrosion rate of the positive grids. Positive grids have been developed with very low corrosion rates. However, there is little quantitative data available on negative plate self-discharge rates that are required to balance such low corrosion rates. This paper presents values measured from several different battery brands, American and European. The data shows clearly that some production batteries have high negative self-discharge rates that account for the observed tendency for self-discharge in service. Surprisingly, the data also shows that other brands have achieved extremely low self-discharge rates - low enough to be compatible with the best positive grids that we have tested. These results are very encouraging for VRLA technology and confirm that the principle can be realized. The focus now shifts to the practical issues: finding the source of the impurities that increase hydrogen evolution and weighing the cost and practicality of reducing them.

1. Introduction

This paper represents the most recent stage of a 5-year investigative journey into the subject of negative plate self-discharge in long-life, Stationary VRLA cells. At the INTELEC conference in 1996, we described the problem publicly for the first time:

"...a central problem with VRLA cells...is that their negative plates tend to discharge, even on steady state float, due to the oxygen cycle itself." (1)

The following year, at the Telescon meeting, we presented experimental proof to support that conclusion and explained the obscure process by which VRLA negative plates are kept charged, namely by the corrosion of their positive grids(2). (i.e.: If lead did not corrode, the VRLA cell would be an impossibility – unless equipped with a catalyst).

Our data showed that our U.S.-made test cells had very superior positive grids. This required that their negative plates have an extremely low rate of self-discharge in order to maintain capacity on float, but the data showed clearly that this requirement was not being met.

1.1. The Solutions

We then proposed three fundamental remedies that would "balance" a VRLA cell. All are additive and may be used in combination:

- Reduce the self-discharge rate of the negative plates.
- Increase the corrosion rate of the positive grids.
- Use an internal catalyst to balance the cell.

A fourth, minor, remedy is to reduce the amount of negative active material in the plates. Thus the "negative charge reserve" customary in nickel/cadmium batteries makes no sense in VRLA batteries where more lead simply means more negative self-discharge.

There is also the general remedy, applied by the user, to boost the cells occasionally or to float the cells at higher voltages. But boosting is not feasible in many applications and higher voltages reduce the service life of the battery.

Each of the three fundamental solutions has its own perspective, as follows:

1.2 Reducing Negative Self-Discharge Rate

Under a heading of "Impurities in negative active material" we said (2):

"It is well known that impurities which increase hydrogen evolution also increase the self-discharge rate of the negative electrode and, therefore, can shorten the life of a VRLA cell. What is not 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 evolution and thereby halve the service life of VRLA cells. Therefore impurities must be controlled with unprecedented vigilance".

Impurities in the negative plate are usually blamed on the lead oxide, with good reason, but they may also derive from the lead grid, the sulfuric acid, the expander (carbon, barium sulfate and organic materials) and also indirectly from the positive plate.

To check that our cells did not have abnormally high levels of impurities, we had tested cells from a number of different manufacturers and looked for variations. Only “premium” cells designed for a 20-year life were used. Our original test method involved collecting gas directly from cells. (*Note: With gas-tight cells, the method was reliable but enormous problems were encountered with leaky cells and batteries.*)

The results showed that there were indeed some differences between the various brands, but these differences were overshadowed by a much more important and surprising result: the negative self-discharge rates of *all the brands* were too high to balance the low corrosion rate of superior positive grids.

We, therefore, assumed that the rates we were recording represented the minimum self-discharge rates expected in practice for production batteries. As we shall show, that was an error. Had we tested cells from other manufacturers and other countries, we might have come to a different conclusion. However, given the propensity of cells from many brands, domestic and foreign, to leak and produce false results, we were also in need of a more reliable test.

(Note: The subject of impurities is not just a technical one. There are also complex commercial issues that are discussed later. Also, we should not automatically equate negative polarization solely with purity of materials; organic expanders can also have a strong polarizing effect on negative plates).

1.3 Increasing Positive Grid Corrosion Rates

A positive grid with a high corrosion rate is obviously incompatible with long-life (20-year) cell designs because corrosion means water loss. The corrosion rate is a function not only of the corrosion resistance of the alloy but also of the surface area of the grid. With a thin, fine-limbed grid, the ratio of surface area to grid weight is much larger than that of a thick grid containing few thin wires. Consequently, the corrosion rate of thin grids is generally faster per Ah of capacity than that of thick grids. This issue has importance in shorter-life cells (less than 10 year life) because it makes them easier to balance.

For example, a small spiral-wound VRLA cell showed no sign of negative plate discharge after a long period on float (3). However, the published corrosion rate of its thin, punched-lead, positive grids, corrected for temperature, was about *twice as fast* as that of the thick, cast grids of our test cells. Therefore, such a cell does not require negatives of a particularly high purity in order to be balanced.

1.4 Use of Catalysts

It has been shown elsewhere (**eg: 4,5,6**) that an internally mounted H₂/O₂ recombination catalyst automatically balances a VRLA cell, even if that cell is severely imbalanced to start with. In this sense, it is a unique solution because it can *correct for impure active materials* and also be retrofitted on cells that are already in service. The other solutions are necessarily restricted to new products.

The long-term benefit of catalysts was illustrated when, after almost 5 years on float at 90°F (32°C), our catalyst-equipped test cells were cut apart and examined; all were in excellent condition. In sharp contrast, *all the control cells* were in very poor condition. In addition to capacity loss, they had suffered from severe positive strap corrosion, presumably due to high positive polarizations and dryout.

By definition, the catalyst solution has a similar effect to the pure active materials solution; namely, that both can increase negative polarization. Therefore, if the negative plate can be made pure enough to have some degree of polarization, a catalyst will not be required to prevent negative plate discharge. One of the aims of this paper was to define what that level of purity should be.

However, even if that level of purity were possible in a laboratory, it may not always be practical in the ‘real world’ of the factory. One reason may be a growing price of pure raw materials. Also, as the balance problem has become better understood, design standards have risen and it is no longer seen as acceptable to have a marginal cell with a near-zero negative polarization. A good option, therefore, may be to use the *combined solution* of adequately pure materials plus a catalyst.

To illustrate, consider the case of a hypothetical 20-year life cell that uses pure materials but is still only *marginally* balanced. That is, its negative plate polarization is near zero (the open circuit value). That cell will narrowly escape negative plate self-discharge, but its positive polarization will still be too high. In fact, it will be *no better than an unbalanced cell* - having 100mV or more on the positive plate whereas 60mV would be the ideal to minimize grid growth and corrosion.

A catalyst placed in this marginally balanced cell would increase the negative polarization further and thereby reduce the positive polarization to less damaging levels. It would also reduce the float current substantially. Therefore, the use of both solutions together may permit plate polarizations on heavy-duty VRLA cells to approach those of flooded cells. In short, a few millivolts of polarization is better than nothing but for a VRLA to be successful, 30 to 40 mV is much better.

Recently, we had the opportunity to measure the effect of the combined solutions. In a test of a balanced European battery at 90°F (32°C) a *Microcat*TM internal catalyst cut the float current in half. A similar result was obtained on an Asian battery at 35°C and 2.30V per cell. Therefore, we expect that cell life and thermal problems will be reduced by use of a catalyst even in a balanced cell – especially when the cell is used in high temperature environments. (*Note: The catalyst is also cheap insurance against unplanned variations in impurities and air leaks -- of which we found many. It may also be essential on cycling batteries to permit overcharge without water loss*).

2. Rates of Positive Grid Corrosion

There are no accepted corrosion standards that distinguish a good positive grid from a mediocre one. Feder et al (8), came closest by collecting published values and standardizing the unit of grid corrosion into the same units as negative plate self discharge, namely **ml/day/100Ah**. (*ie: The corrosion current is compensated for by this amount of hydrogen evolution; see Berndt (7) for equivalent corrosion currents*). This simplified the comparison of the two main secondary reactions and also showed that there was a large variation in the published data ranging from 13 to 102 ml/day/100Ah.

The following are some corrosion rate values that we have some confidence in:

Thick pasted plate – pure lead

This was a test done in our own laboratory. The pure lead grids of the test cells had a corrosion rate equivalent to 20ml/day/100Ah at 32°C (1.8mA/100Ah). This is the best corrosion performance that we have measured to date on any positive grid from any source.

Thick pasted plate – lead alloy

One major U.S.A. manufacturer has stated that its positive grids (lead alloy) corrode at a rate of 0.001 inches per year or more. The equivalent hydrogen evolution rate is a over 20ml/100Ah per day (9). Temperature was not specified.

Small wound cell – pure lead

One direct corrosion measurement, made on a small, spirally wound cell, was recently reported (3). The technique used was to float the cell for several years and then disassemble it and weigh the PbO₂ formed during the float period. The corrosion rate, corrected to 32°C, is compensated for by a hydrogen evolution of 40 ml/day/100Ah (3.6 mA/100Ah) on the pure lead grid. *In the same reference, a thin lead-tin grid recorded over 60ml/day/100Ah (5.4 mA/100Ah)*.

Non-antimony spine - tubular plate

Berndt mentions that the penetration rate of corrosion on a European tubular plate spine (1.6% Sb) during float service is about 30 microns per year (10). This corrosion rate will

balance a hydrogen evolution rate of 38ml/100Ah/day at 32°C (3.4 mA/100Ah).

3. Required Standard for Negative Plates

Since the best VRLA positive plate we presently know about in terms of corrosion rate is the thick, pure-lead, cast grid, the only negative plate that is a suitable match for this superior positive grid is one with a hydrogen evolution rate of less than 20ml/day/100Ah at 32°C. Any negative plate with a higher hydrogen evolution rate will suffer gradual self-discharge.

We, therefore, propose that this nominal gassing rate of 20ml/100Ah/day at 90°F (32°C) - or its calculated equivalent at other temperatures, or its equivalent in ml/100g/day - be used as a standard for defining “good” negative plates for long-life VRLA batteries. This is summarized in Table 1 where a relationship of 10 grams of negative active material per ampere-hour is assumed.

Hydrogen evolution rate	90°F (32°C)	25°C	40°C
ml/100Ah/day	20	12	35
ml/100g/day	2.0	1.2	3.5

Table 1: Proposed Purity Standard for Negative Active Material in Long-Life VRLA Cells. The Actual Test Temperature was 40°C. The Rates are Calculated for 90°F and 25°C for Reference Purposes.

4. Measured Rates of Negative Plate Self-Discharge

Published quantitative data on negative plate self-discharge rates (ie: gassing rates) are rare and the following measurements were all taken from our own tests. This time, our gas collection test method did not involve leaky cells. Shown in Figure 1, the test was a modification of a 1988 procedure by Culpin et al (11) but made less prone to hydrogen diffusion leaks. For this part of the procedure, we used whole or partial negative plates, including the grids. The test consisted of these steps:

- Remove an *inside* negative plate from a charged, healthy cell and submerge it in pure, reagent grade acid.
- Charge it thoroughly (eg: for several days at 2.60V) against two positive plates from the same cell.
- Remove it from the acid, and quickly roll it into a cylindrical shape. Place the rolled plate into a graduated cylinder, invert the cylinder into a beaker of pure acid and, using a suction pump, draw acid up to fill the cylinder and submerge the plate.
- Place the apparatus in an oven at 40°C to provide an accelerated result and measure the gas directly.

For thick plates, we cut the plates, including grids, into strips before placing the strips in the graduated cylinders.

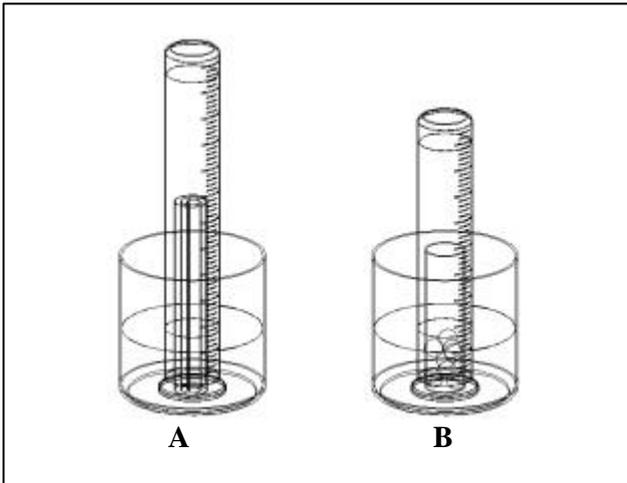


Figure 1: Leak-Free Gassing Test Using Graduated Cylinders and Beakers. (A) Test with Rolled Up Negative Plate. (B) Test with Active Material in a Vial.

This particular plate/grid test was based on the rated amp-hour capacity of the plates. Generally, however, a fixed mass of negative active material is used as a sample and its ampere-hour capacity deduced. Both methods should yield the same result but some deviation is caused by the fact that active material utilization varies about 20% between brands (11 g/Ah versus 9 g/Ah).

Compared with the endless problems with hydrogen leaks from testing actual cells and batteries, this test was commendably free from leakage problems. It is, therefore, by far the most reliable method of measuring gas evolution from battery plates that we know. The measured gassing rate corresponds to the initial self-discharge rate of the fully charged negative plate. In a real battery on float, this is the minimum hydrogen evolution rate at zero polarization of the negative electrode. If this value is smaller than the corrosion rate of the positive grid, then some degree of polarization of the negative electrode during float is assured.

At 40°C, the test normally takes 15 to 20 days although useful qualitative results can be had in a week or so. The results, being cumulative, are potentially accurate. But there are a few critical requirements, such as making sure that the plates are properly charged, minimizing plate oxidation in air before immersion in acid, and keeping the plates from getting contaminated during removal from the donor cell.

5. Test Results

The tests were carried out on plates taken from several different cells and monobloc batteries made by various manufacturers from the USA and Europe. The results, shown in Figure 2, are contrasted to the purity standard of

20ml/day/100Ah at 90°F (32°C) proposed earlier, with quite a dramatic effect, as follows:

- There was an *enormous* difference between the brands in terms of hydrogen evolution. The worst plate had a gassing rate well over 20 times higher than the best plate.
- The gassing rates of the two best brands were very low indeed; lower than anything we had seen previously.
- The best plates had self-discharge rates that were low enough to be compatible with the very low corrosion rate of our superior positive grids.
- The hydrogen evolving from the high-rate plates was visible as bubbles rising to the surface of the acid. By contrast, there was no hydrogen visible from the low rate plates. (*Note: This gives the possibility of a simple and instantaneous test, especially if a high temperature is used*).

The current equivalent and self-discharge rates derived from the above data are listed in Table 2.

Average H ₂ evolved ml/day/ 100Ah	Current equivalent mA/100Ah	Self-discharge % per month
151	13.5	9.7
80	7.1	5.1
39	3.5	3.5
12	1.1	1.1
4	0.39	0.28

Table 2: Hydrogen Evolution, Current Equivalent and Self-Discharge Rate During the First 10 Days, Derived from Figure 2

The values in Figure 2 underline the great differences between the various samples. The derived self-discharge data are only valid for full charged negative plates so that with progressing discharge the rates will decline. During float charging, however, the gassing rate will be approximately proportional to the figures in Table 2 since the plates should be fully charged.

6. Discussion

The large variation in these results and, especially, the low gassing rates of the “good” plates, are the more impressive because they were measured on real plates, taken from real batteries, and not from laboratory-made lead samples.

However, it would not be fair or correct to say that one brand will always be high and another brand always low, for three reasons: First, there can be large variations between cells of the same brand, indicating *instability in the purity* of the

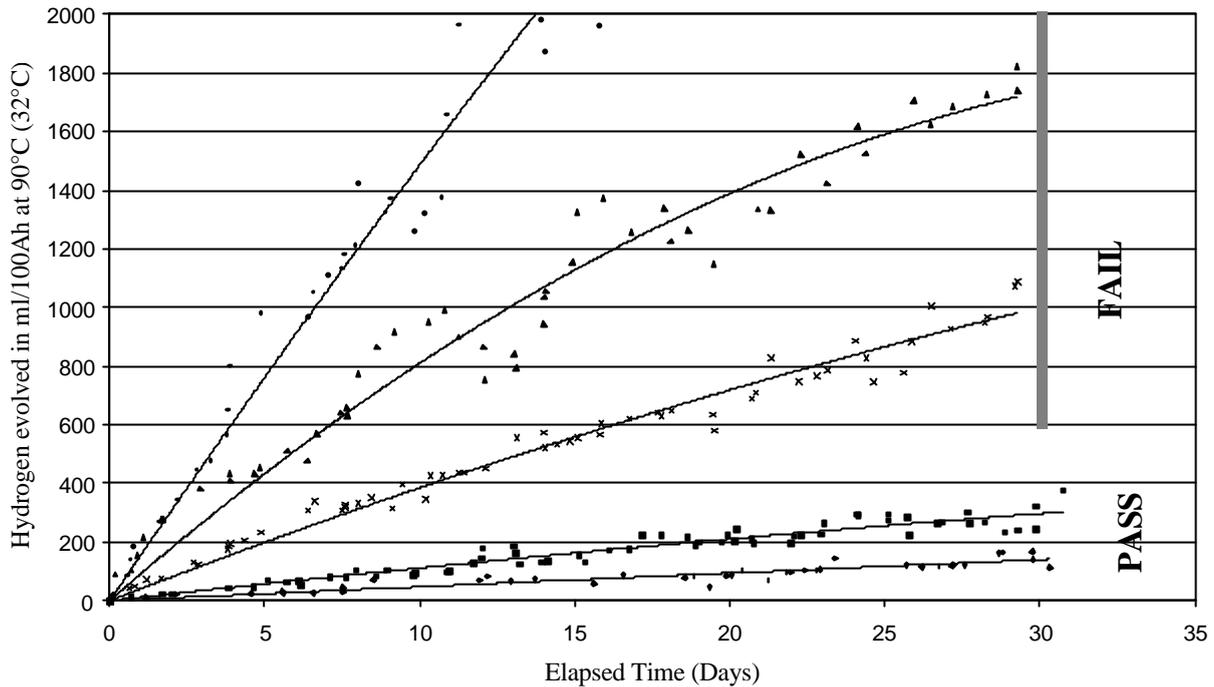


Figure 2: Hydrogen Collected from the Negative Plates from Five Different Battery Brands. Each Curve Represents the Average of Three Plates.

active materials within a brand; in fact, there is no guarantee that these data would be repeatable, brand-by-brand, in another experiment. Second, the purer the material, the more effect a tiny amount of impurity has on it, so the *volatility of the data* may be its primary characteristic. Third, the high gassing-rate plates cannot be the norm for their manufacturers or else there would have been much higher levels of field failures. It can probably be concluded from these data that *variation of impurities* lies at the root of the problem.

A note of caution is that organics in the expander may influence the results of the test. Lignin compounds are known to raise negative plate polarizations on float, at least on flooded cells, thereby mimicking the effect of pure materials. High amounts of lignin induce precipitation of extremely small crystals in the negative active material. This, in turn, can cause hydrogen to fill the pores and reduce the effective, “wetted” surface area of the material. So it is possible that this phenomenon may affect the gassing rate, particularly in the “flooded” environment of the test. Further studies are planned.

On the other hand, assuming that the low gassing rate data of the best plates are repeatable in a non-flooded VRLA environment, they appear to show that *it is quite possible to make a pure negative plate* that will match a superior positive grid. This, then, must be the target for all manufacturers of long-life cells.

6.1 Finding the Source of the Impurities

The most probable causes of the high gassing rates are impurities in the lead oxide, followed by impurities in the expander. Conversely, the low gassing rates are probably due to purer lead oxides with, perhaps, help from high lignin expanders. Since it is well known that many manufacturers use secondary lead made from recycled batteries, there is a general bias to this conclusion but not yet any certain proof. Unfortunately, a full chemical analysis of the active materials from our test was not available at the time of writing and will be published later.

To check the possibility of the *expander* being a source of contaminants, we reverse-formed some positive plates, which contain no expander, to see if the hydrogen evolution would be higher or lower. This time, pellets of active material were tested instead of sections of plates. The gassing rate of this modified positive active material was indeed significantly lower than its negative counterpart, which suggests that the expander may be a contributor of impurities to the system. A controlled experiment will now be carried out.

(Note: A curious observation was that the hydrogen collected from the all the negative plates, both “good” and “bad”, showed a high component of hydrogen sulfide. The reversed positive plate, however, emitted no H_2S so we can say with reasonable certainty that the H_2S derives from the ligno-sulfonate component of the expander).

6.2 The Commercial Problems of Pure Lead Supplies

Whatever the outcome of these technical experiments, the *commercial* risk from impure lead supplies is substantial and growing. Even primary lead might not necessarily be pure enough to meet our proposed VRLA standard, depending on the impurities in the ore. Further, primary lead is in short supply, and smelting ultra-pure lead from secondary sources may be unrealistic. Therefore, if all battery manufacturers demand lead of an extremely pure standard, the supply will be limited and the cost high.

Some battery companies say that they cannot return to primary lead under any conditions because recycling is an imperative for environmental reasons. But recycled lead is under pressure to reduce standards further. The dilemma for future supplies is illustrated by the present concern in Europe that the silver content in the DIN standard for pure lead may be raised from 10ppm to 30ppm; on the one hand, silver is an important alloying ingredient for automotive batteries while, on the other hand, it has a severe discharging effect on VRLA negative plates.

At the present time, these practical issues have not been fully addressed by the battery industry. The data presented here and the proposed standard for purity may help bring some focus. Perhaps there will be a ban on certain alloying additives; perhaps there will be more sophisticated refining processes developed. Or, perhaps, super-purity will become a thing of the past, falling victim to environmental pressures, in which case the catalyst will be the only available solution.

7. Conclusions

1. The hydrogen evolution rates of several different brands of negative plates has been measured. The results show a very large variation between the lowest and highest gassing rates.
2. The best plates have such a low self-discharge rate that they can be kept charged even by the minimal corrosion rate of superior positive grids.
3. The likely cause of the high gassing rates is impurities in the raw materials; that is, in the lead, the expander or the acid. The lead is the prime suspect but there is no direct proof yet. Preliminary results indicate that the expander may be a contributor to the problem.
4. The purity of recycled lead is an increasing concern to battery designers all over the world. A strong effort should be made by the battery industry to prevent decline in pure lead purity standards.
5. A combination of catalysts and pure materials has the perhaps the best chance of producing plate polarizations

close to flooded cell standards and the best life characteristics, especially for high temperatures.

6. A "purity standard" based on acceptable hydrogen evolution of VRLA negative active material has been proposed. The adapted test is cheap, accurate and practical for use in a production or laboratory environment.

8. References

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