

LEAD PURITY: THE MOTHER OF ALL VRLA PROBLEMS

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Abstract

VRLA batteries seem to have a multitude of problems leading to low capacity and short life including dryout, plate growth, high float current, high hydrogen evolution and negative plate discharge to name a few. This paper shows that all these are related and stem from a single source problem – the fundamental problem of VRLA batteries. That problem, which was not recognized by the industry for many years, was the use of slightly impure lead in the plates. Given that improving lead purity is not feasible the best solution to the problem must fit the given circumstances of the current environment. How this problem can be corrected is explained both for new production cells and for reclaiming older cells in service.

Introduction

This story begins in the mid 1990's with two battery engineers coming to independent but similar conclusions; VRLA batteries are not delivering the life or performance that they were designed to do. They also came to the conclusion that this was not the fault of the users of the batteries nor was it entirely the fault of the manufacturers of the batteries. Once user error and manufacturing defects were taken out there was nobody left to blame, but problems were still occurring on a large scale level. The real culprit was still lurking and was, as yet, undiscovered, but we will get to that part of the story later. While we have said that fifteen years ago the first thoughts on the real problem were just being published, the seeds of the actual problem were first planted back in the early 1980's while the industry was embarking on the launch of an exciting new product.

The Roots of the Problem

In the 1980's a European battery company decided to make the first VRLA starter battery for cars. They built prototypes in Europe and they worked well. They tested them in the southern USA, where under-hood temperatures are high, and they worked well there too. So they built a factory in the United States and went into production using precisely the same specifications and tooling used in Europe. The result? Catastrophe. The batteries failed all over the country. A full investigation was done but the technical people could not figure out what the problem was. So they stopped production and shut down the factory. The financial loss ran into the millions of dollars.

It was not until twenty years later that the real cause of this problem was understood, but not yet by the battery manufacturers themselves. The real cause was devastatingly simple: in the prototype batteries made in Europe the company had used primary lead – straight from the mines - to make the paste for the negative plates. But when they went into production in the US, they had used secondary lead, which was recycled lead. It met the same specification but, unfortunately, the specification was not exacting enough for VRLA batteries and the recycled lead they used was not as pure as the primary lead they had used in Europe - and they didn't know it. However, while this is obvious in hindsight and 30 years of additional information, nobody at that time knew how exacting the purity specifications had to be to make VRLA batteries perform as intended. Even the co-author of this paper, Will Jones, who at the time was Vice President of Technology for the Exide Group, was not aware of this. At the time, Will was responsible for automotive, motive power, standby and specialty batteries and for all R&D done on these batteries. He was well aware of the purity requirements for flooded lead-calcium batteries, which was an area of expertise for him. Most of these long-life flooded cells already used what he thought of as "very pure" active material in the paste. But the problem was that VRLA cells need much purer active material than an equivalent flooded cell; otherwise the VRLA cell will self-discharge. Will believes that he could well have made the same mistake as the European company because the industry was just not aware of the exacting purity requirements for VRLA batteries. So this was not a problem of incompetence, it was a problem of not understanding what was required.

Ten years later, in the mid 1990's, VRLA batteries were widely used in the telecom industry but the industry was awakening to the realization that there were real problems with this design. Dr. Dave Feder and Will Jones led the charge at the Intelec conferences through their papers that described the early failures and the electrochemical imbalances that led to shortened life among other problems.^{i,ii,iii,iv} Dr Feder presented the controversial results of a large study of 24,000 VRLA cells that clearly showed that the majority of these cells would deliver nowhere near the design life of the product.^v Over time various solutions to the problem of VRLA cells were presented, but the root cause of most of the problem was always the same. It was the same problem that caused the failure of the European battery company back in the 1980's, and it was the same problem that caused most of the tribulations with VRLA batteries in the US telecom, UPS and other Standby applications since they first went into wide scale production in the mid 1980's. As a matter of fact this problem still exists today. That problem is impure active material and it is the mother of all VRLA problems.

Filling the Knowledge Gap

The last section covered 30 years of history quite rapidly, but it is quite clear in the implication that the problem starts with the use of lead that is not quite pure enough for VRLA batteries. While this seems obvious in hindsight, it was not so obvious at the start. What started in the early 1990's as an experiment with VRLA solar batteries led Will Jones to realize that something very strange was going on. The batteries that Will was using were not performing as they were designed to nor as he expected them to. Will discovered that too much hydrogen gas was venting from the cells to allow them to obtain their 20-year design life. Through trial and error he installed a recombination catalyst into some of the cells and found that these cells would emit five times less hydrogen gas than the cells that did not have catalysts. That was the difference between 5 years of life and 25 years of life and it was almost unbelievable to him. Figure 1 shows the initial gassing data from this test and displays the theoretical increase in service life based on gassing rates alone.^{vi}

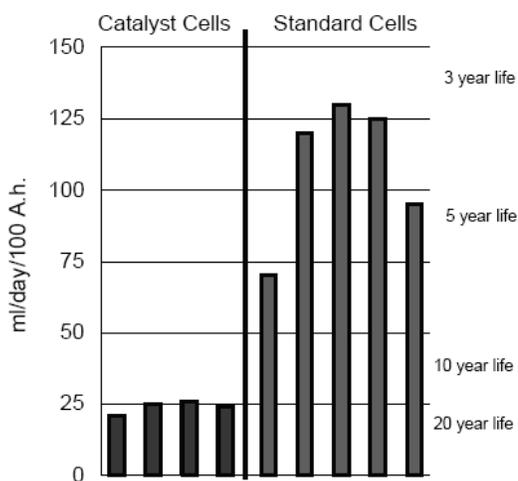


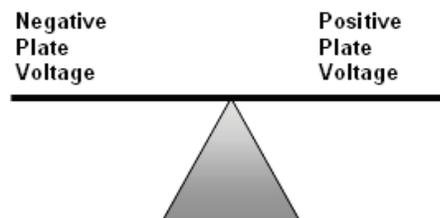
Figure 1

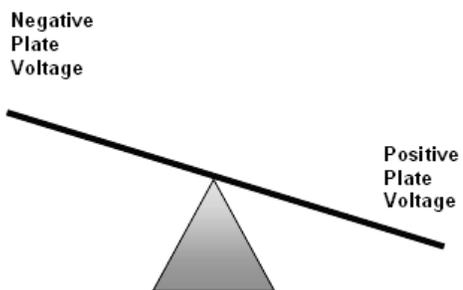
To prove his theory, Will designed the seminal test that we have reported upon at previous conferences. High quality, 20-year design, VRLA cells were tested per the manufacturer's specification but at an operating temperature of 90° F (32° C). Half of the cells employed a catalyst and the remainder of the cells did not. As we have reported on in the past, all of the control (non-catalyst) cells failed in 18 months while the catalyst equipped cells lasted for four years without loss of capacity before the test was stopped.^{vii} The batteries tested were manufactured with what was believed to be "pure materials" and were intended to last for 20 years, but as the data showed this was never going to happen. It was clear that if the hydrogen leaving the cell could be minimized, then there was a chance that the cell would last for a respectable amount of time in service. But to solve the problem we first needed to understand it.

An Explanation of the Problem

For over 100 years standby lead acid batteries have been floated at 100 mV above their open circuit voltage allowing the batteries to charge properly. The VRLA batteries you are used to usually have an open circuit voltage of 2.15 VPC and you float them at 2.25 VPC to allow for the 100 mV of overvoltage. But for this explanation we only care about how we split the 100 mV between the positive and negative plates. We are going to use a simple see-saw diagram to help explain what happens to a VRLA cell when the 100 mV is split in different ways among the positive and negative plates.

The first see-saw shows the 100 mV split evenly among the positive and negative plates, which is close to what we want. In this case the reactions are in balance in the cell and problems should be minimal. There is some debate as to the exact split with some wanting more or less on the positive plate as compared to the negative plate, but this is close to the ideal that we want and we will leave the academic arguments for another paper.



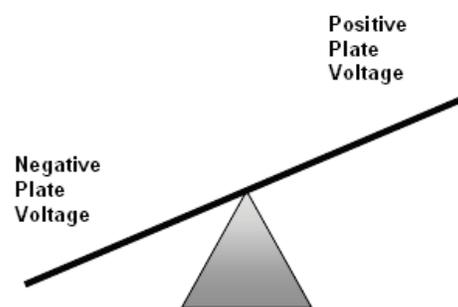


In the second see-saw, the negative plate is taking all of the voltage while the positive plate receives none. This is not good because the positive will discharge and this is dangerous. Why? Normal charging preserves an impervious lead dioxide film on the positive grid, but discharge of the positive allows accelerated corrosion to occur as follows. First, the grid gets crystals of lead sulfate all over it that can be seen with a flashlight. Next, this layer cracks and lets acid through to the grid surface beneath it, which is made of lead. Quite literally, therefore, the positive active material in the plate short circuits with the underlying lead grid and this causes the ultimate destruction of the grid. This is the situation that Bell Labs found themselves in when they first made their flooded Round Cell and used very pure primary lead. While we want high lead purity for VRLA cells, we do

not want this for flooded cells. This problem is exactly the opposite from what we mention in the opening of the paper. To solve the problem with the Round Cell, Bell Labs had to poison each cell deliberately with a very toxic platinum compound to get the 100 mV to split properly.

The third see-saw shows the case where the positive plate steals all the 100 mV available and leaves the negative with nothing. This is the case we are discussing in this paper and is typical of all VRLA batteries with impure negative active material. This situation will cause a host of cell problems to develop, all of which have already been mentioned in the literature:

- the negative plate will discharge because there is no charging voltage being applied to overcome the self discharge that is constantly occurring. This will cause capacity loss in the cell.
- cell dryout will occur due to the increased hydrogen emission from the impure negative active material. This will also reduce capacity and life.
- positive grid corrosion will accelerate due to the high voltage on the positive grid.
- the float current will increase causing higher hydrogen emission rates and higher cell temperatures which shortens the life of the positive grid and increases the risk of thermal runaway.
- the positive grid can grow and short out under the negative straps in a monoblock battery. This is the prime cause of thermal runaway.
- negative strap corrosion will occur now because cathodic protection has been removed along with the overvoltage on the negative plate. Negative strap corrosion is almost never seen on flooded batteries.



All of these problems ultimately result in early cell failure; however, these problems are merely symptoms of the same fault: impure negative active material. At one time, all of these symptoms were all treated as separate and individual problems, but we now know that they are all “daughter” problems. Only by solving the “mother of all problems” can we solve them all.

A Physical Explanation

How all this works is relatively simple. Imagine being inside a VRLA cell with only two plates: one positive plate and one negative plate. There is a pressure relieving vent plug above us in the top of the cell. When the cell is on open circuit (not being charged) the negative plate produces hydrogen simply by self discharge; this is a chemical reaction between the lead and the sulfuric acid. If the active material is very pure, the hydrogen produced is miniscule. If the active material is impure, that impurity causes the plate to self discharge at a higher rate and to produce a lot more hydrogen. (That is why antimony flooded cells use a lot more water than lead calcium cells – antimony is a poison for the negative plate, which causes gassing). This hydrogen escapes to the atmosphere through the vent plug and, once it has gone out, is lost forever.

When the cell is on float, oxygen is constantly being produced by the positive plate and most of it is absorbed on the negative plate pulling down its voltage. The hydrogen produced by the negative plate, however, cannot be absorbed and must leave the cell through the vent. What a waste! Here we have hydrogen and oxygen – potential water – already inside the cell. If we could just recombine them together we would get much needed water inside the cell where we want it. A catalyst is the only way to do this because it is specifically designed to recombine hydrogen and oxygen into water. The catalyst, by stealing some of the oxygen, prevents that oxygen from reaching the negative plate and depressing its voltage. In other words, it tilts the see-saw back to a healthy balance. Thus simple chemistry is put to a practical use. Our 2002 Battcon paper has more detail on this topic.^{viii}

How Pure is Pure?

The purity of lead is a contentious area of discussion and revolves around how many “9’s” are involved in the measure of the purity. Most battery companies own spectrographs costing half a million dollars to check for impurities in the lead they purchase. The European company that we mentioned earlier had one too, but it didn’t help because they were not aware of what the true standards were. Amazingly, the best device for measuring this complex chemical process involves a few dollars of laboratory glassware and some time. But before we get to that let’s start with some background.

The lead that we are concerned about is that which is used in the negative plate active material. The lead used in the positive grid is generally an alloy, of lead and other materials, designed to minimize corrosion rates and is already very controlled and well understood. Because the positive grids of VRLA cells have such low rates of corrosion there must be a balancing reaction from the negative plate where self discharge is minimized in order for the cell to function as designed. This is only possible if impurities in the negative active material are very very low.^{ix} The self discharge of the negative active material occurs because of a very basic chemical reaction between the lead and the sulfuric acid of the electrolyte that yields hydrogen gas.^x The more impure the lead the more it will gas when exposed to sulfuric acid; the more that this occurs the larger the amount of hydrogen that escapes the cell. This creates the imbalance in the cell that eventually spirals the cell down to premature failure.

The misunderstanding that has developed here comes from the long history of flooded lead acid batteries where minor impurities are necessary to balance the voltage see-saw. In VRLA cells the lead purity standard needs to be higher than that for flooded batteries because the internal reactions are balanced differently, and the downside for lack of purity is also a lot worse than for flooded cells. Lead purity is measured as how close to 100% pure the material is. Generally the discussion centers on how many “9’s” are used to quantify the purity of the lead in question. Four “9’s” or 99.99% pure lead is very good and is generally what is available from the secondary lead market and is what is used in most stationary batteries, including VRLA. Secondary lead is the name for lead that has come from recycled batteries, which is then smelted and purified to remove impurities so that the resulting lead is 99.99% pure. However there are trace impurities that are left in the lead and these leftovers are what cause the problems that we are talking about; it is actually a question of the specific leftovers. Lead of a higher purity level is available, such as five “9’s” or 99.999% pure, and it generally is produced from primary lead sources. Primary lead is virgin lead that comes directly from the mines and is then smelted and purified. Some mines produce leads of higher purity than others and it is also possible to remove impurities from recycled lead to the five “9’s” level. Generally, primary lead is more expensive than secondary lead, and certainly the higher the level of purity the more expensive the lead is.^{xi} As worldwide supplies of primary lead are exhausted and, more importantly, as environmental pressures increase the use of recycled lead, primary lead is becoming harder to find.

In a test of the lead purity used by VRLA battery manufacturers we discovered that a large variation existed among manufacturers. We found that the best examples had such a low self discharge rate that they could be kept charged even by the minimal corrosion rate of superior positive grids. However, many of the batteries we tested did not make the grade and more pure materials were needed. The way that we tested these batteries is a way that we recommend be used as a low cost and highly effective method of determining if the lead is acceptable to be used in a VRLA cell. The test was developed by Dr Brian Culpin of Chloride in England. The very clever test was first published in the Journal of Power Sources in 1988^{xii} and is outlined below.

The test involved the charging of a single negative plate made from the active material that you want to test. The single negative plate is charged in between two positives until it is absolutely bright gray in color. Then, under acid, put the negative plate into a glass, graduated beaker, anyway you can, and invert the beaker in a bowl of acid so the plate is submerged in acid with no gas bubbles in the beaker. Run the test at 90°F and just wait for days or weeks and record the amount of hydrogen gas given off. Figure 2 is a sketch of the apparatus that we used when we conducted this test ourselves.

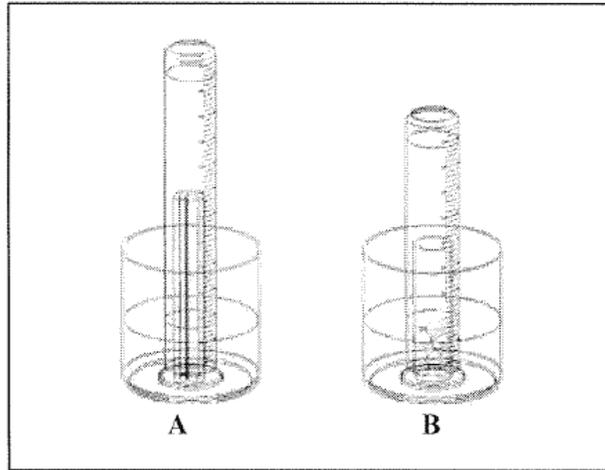


Figure 2

This cheap device actually beats any spectrograph because it measures ALL the hydrogen given off by ALL the impurities in a material. At the very least, it should be used as a means of calibrating spectrographs so that the issue of impurity can be managed.

The data that we obtained from our testing was quite conclusive. Figure 3 shows the experimental results we got from this simple device when we tested the negative active materials from five different batteries from world wide suppliers.^{xiii}

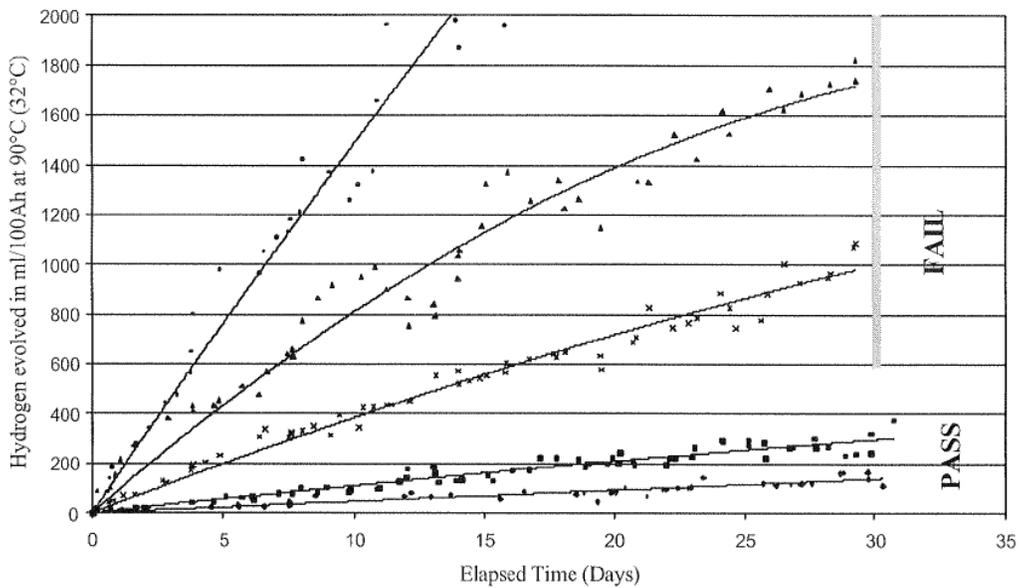


Figure 3

In figure 3 the horizontal dimension is time while the vertical dimension is the amount of hydrogen produced/captured in the beaker. We standardized the measurement using equivalent capacity of the active material to get a meaningful comparison. You can see that the “worst” battery produced 10 times more hydrogen than the “best” battery. The bottom of the vertical bar is the cutoff point for a long-life cell. If the cell is to last a long time in service, its line on the graph should pass under the bar. As you can see, only two of the batteries passed this test. The worst battery gave off so much hydrogen that you could see a stream of tiny bubbles with the naked eye. The fact that we found such disparities in our simple test ties in very clearly with what we have seen over time in real world performance of VRLA cells and that we still see today. Most battery manufacturers use 99.99% pure secondary lead in their VRLA batteries. The batteries that we tested were most likely made with this lead. But what accounted for the difference in the results? It was the impurities that remained in the lead and that need to be better specified, controlled and tested for. This is the key to solving the mother of all VRLA problems. It should be emphasized that the papers, the research and the data that we are citing is 10 to 25 years old. This paper started off with an example of VRLA failure that was based on lack of knowledge about a new product. We said that it was not incompetence that had caused this problem but simply lack of knowledge and understanding. However, in the year 2010 this excuse can no longer be used. The information that we are presenting here is not new anymore and has been published widely. The next logical question is what can be done about it?

Options and Solutions

The VRLA battery is a wonderful design that has the potential to deliver many benefits: high power density, low maintenance, low gassing levels, the promise of a long life, and reasonable value per price all while being fully recyclable. However, it is a delicate system that is sensitive to fluctuations within its design parameters. Over time most, if not all, of the basic manufacturing related problems and defects have been worked out of the system and only one problem remains, but it is the mother of all problems and has been the hardest for the industry as a whole to accept. The last remaining challenge to the design is lead purity; specifically for the lead used in the negative active material. The question is can the trace levels of impurities be controlled/eliminated reliably enough for VRLA use? The purity of the lead used in the negative active material still largely follows standards that were set for flooded cells many years ago. The chemical reactions that occur inside the VRLA cell must be kept in balance and it all starts with the self discharge reaction involving the negative active material and the sulfuric acid of the electrolyte. As with a row of dominoes, if the first one falls the rest will topple over in quick succession.

In the past we have proposed using lead of higher purity to address the problem. In this paper we also propose that a more exacting test be used to measure the incoming lead to be sure that it passes a functional standard of acceptance. A third option is to install a recombination catalyst into the headspace of a VRLA cell. How a catalyst works in a VRLA cell and the benefits it provides has been proven and presented before.^{xiv,xv} The advantages of using a catalyst can also be imparted to VRLA cells that have been in service for a number of years that never had catalysts to begin with. The benefits of installing a catalyst as a retrofit, along with the addition of water to replace that which has been lost, has also been proven and presented at previous conferences.^{xvi} A brief description of what a catalyst does in a VRLA cell is now provided so that this paper can be self standing, but for a more complete explanation any of the references in the endnotes should be consulted.

In our research on 20-year, 2-volt VRLA cells, we have shown that we can shift the voltage of the positive plate to minimize corrosion by using a catalyst mounted inside the gas space of the VRLA cell. We know that this happens by measuring the float current of the VRLA cell. Generally we see a float current in a catalyst equipped cell that is half of what it is in an equivalent cell that is not equipped with a catalyst. Since float current and positive plate voltage (polarization) are directly linked and directly proportional we know that by reducing the float current we are reducing the positive plate voltage and therefore reducing the rate of corrosion on the positive grid. We also know that by reducing the positive plate voltage we are increasing the voltage on the negative plate, which is essential to the cell. Remember the first see-saw that we looked at earlier in the paper. Without a catalyst the cell will look like the third see-saw and with a catalyst the cell will look like the first see-saw; in balance.

Conclusion

The fundamental problem that we have seen in VRLA batteries since the 1980's has been one of impure lead used in the negative active material. There are only three solutions available to address both lead purity and the delicate balance of reactions in a VRLA cell. The solutions must also take into account the business and environmental considerations that face the world today. The solutions are as follows:

1. Use very pure lead – which is getting harder and harder to obtain and is therefore more expensive.
2. Use super refined recycled lead. This also has problems chief of which are impurities getting into the lead recycling stream, i.e. silver from automotive batteries.
3. Use a catalyst that will recombine hydrogen and available oxygen to make water inside the cells and keep the negative plate from self discharging.

In the end, the best solution is the one that fits the given circumstance.

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