

Impact of the Internal Catalyst on VRLA Batteries One Year Later

Bruce Dick, Terry Noveske, Al Williamson
C&D Technologies, Inc.

The growth in the use of VRLA batteries has slowed over the past year due to concerns with the long-term reliability. In February 1998, C&D Technologies had introduced an internal catalyst to improve the operation of its Liberty 2000 VRLA product by maintaining the negative plate polarization. We reported on the introduction and the research effort that led to that introduction at last years BATTCON 98 conference.¹ The favorable impact on battery performance, derived from the use of a gas-recombining catalyst placed within the headspace of a VRLA cell, is one of the exciting discoveries of recent times.² To date, C&D has shipped over 150,000 new cells and have enhanced thousands of older cells, that had been in use for from one to six years, with the internal catalysts. The latter information will address the questions raised at last years conference as to whether the catalyst would be effective in helping older product. This paper will update the participants on how well both new and old products, equipped with the catalyst, are performing. In addition we also have a year more of laboratory testing of product equipped with the catalyst to show the longer term effects on gassing, current draw, and performance.

To summarize last year's paper, there were four benefits of the internal catalyst. They were:

1. To maintain the charge level and therefore the performance of the negative plates while reducing the secondary evolution of Hydrogen due to chemical reactions at the negative plates.
2. The corresponding reduction of the polarization on the positive plates resulting in a lower rate of positive plate corrosion and therefore longer life.
3. The recombination of Hydrogen that is normally vented and therefore a reduction in gassing and water loss.
4. The reduction in float current due to the lower level of recombination occurring at the negative plates and therefore lower internal heat generation and reduced potential for thermal runaway.

The additional work done in the laboratory, by both C&D and Philadelphia Scientific,³ expands the knowledge of what is happening inside a VRLA battery equipped with an internal catalyst and further prove the hypothesis presented last year. The data reported on the impact of catalyst has been generated with commercial Liberty 2000 product. They were all fitted with the catalyst plug, which was mounted to the vent housing just below the pressure relief vent. A patent application (in favor of C&D Technologies) is pending for this design concept, which allows all the gasses trying to escape from the headspace to contact the catalyst plug. In addition, polarization readings were taking on cells fitted with mercury-mercurous sulfate-sulfuric acid reference electrodes. The original data as presented last year is shown as Fig. 1. As can be seen, there is a substantial impact of the catalyst on the negative plates, which receive a healthy dose of polarization that will keep them fully charged. Since the total cell voltage is held constant, there is a simultaneous decrease in the positive plate polarization to a more desirable value. This behavior mimics that of a flooded lead-acid battery. The observed negative polarization shifts can only be the result of the reduction of the recombination activity at the negative plates.

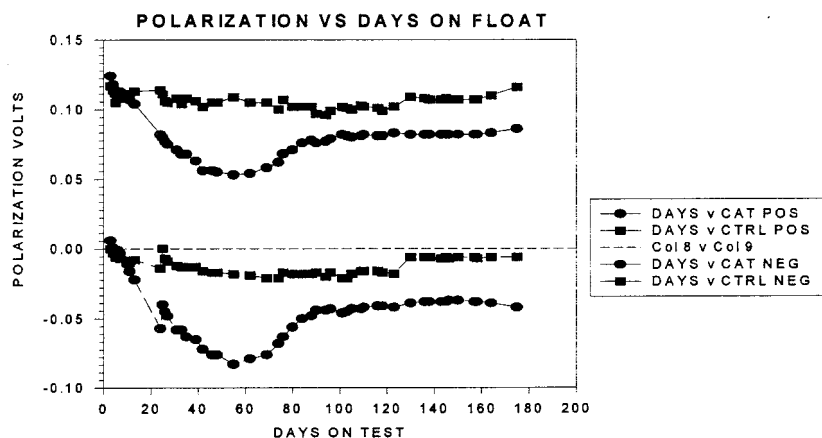


Figure 1

In addition, at BATTCON 98 I showed that there was a corresponding decrease in the float current. This data has now been expanded upon. Fig. 2 shows the original current data with the time extension. Here we can see what happens when the catalyst is removed and then reintroduced to the cell.

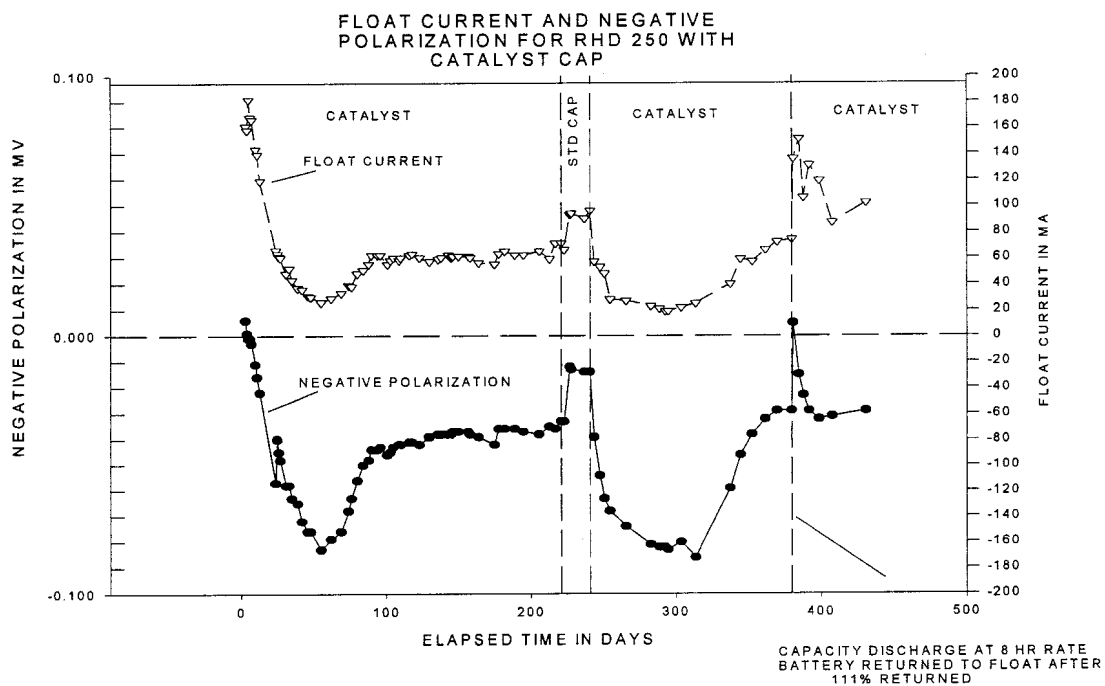


Figure 2

The float current increases and the negative becomes depolarized after the catalyst is removed. The behavior is again reversed as the catalyst is reintroduced to the cell. It is also apparent that it takes days or even weeks to stabilize the active electrodes. After 400 days a capacity discharge was run on the cell and again it can be seen that the cell was able to return to is negative polarized state with the benefit of the catalyst.

In order to reinforce our confidence level, we decided to expand verification testing.⁴ Various size Liberty 2000 cells were used from the RHD -250 to the HD-1300, covering capacities of 260AH to 1440AH. All were fitted with the catalyst plug. The most obvious demonstration of the effect of the catalyst comes from the recombination that takes place in the headspace reducing the gas loss to the environment.

The initial experiments involved the collection of gases that would normally escape from the cells. The vents for these experiments were of an umbrella type that open at slightly over one psig excess pressure. All the fittings were checked for gas tightness and Hydrogen leaks, using a combustible gas detector. Heavy walled Tygon tubing were used to channel the gas to collection devices that consisted of graduated cylinders filled with water and inverted over a large pool of water. The gas collection experiments were done at both high temperature and float voltage. The first set of readings collected at room temperature and 2.27 volts float on two strings of RHD 250 AH cells compares one string with and one string without the catalyst. See Figure 3 below.

GASSING RATES FOR RHD-250 CELLS AT FLOAT:
TWO SIX-CELL STRINGS AT FLOAT, NO CATALYST
Note: No gas measured with Catalyst

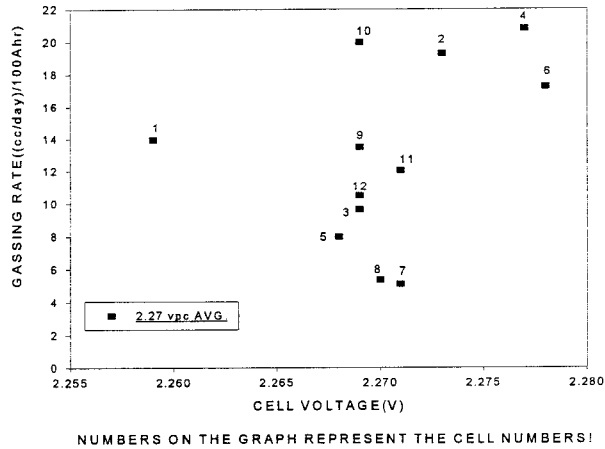


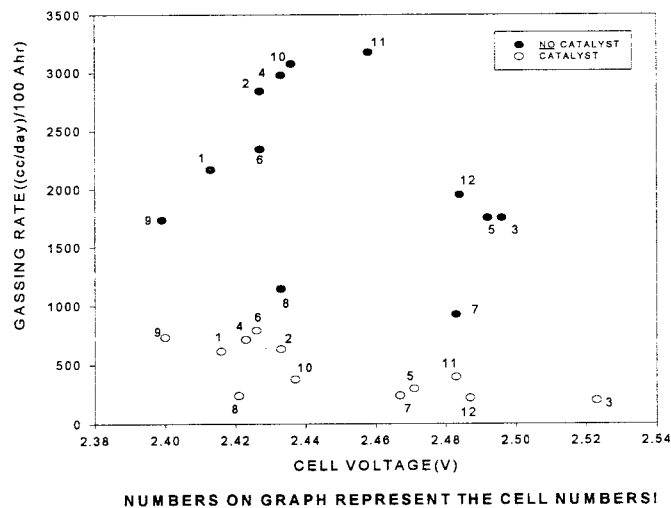
Figure 3

The cells were on float for 14 days and the average gassing rate was plotted versus the individual cell voltage. The numbers on the graph represent individual cells. The gassing rate for cells without the catalyst varied widely, between 10 and 60 cc's per day. For the cells with the catalyst there was no measurable gas collected during this fourteen-day period for any of the cells.

While this data is encouraging, we felt that it was necessary to measure the effect of the catalyst at somewhat higher voltages and temperature. Figure 4 below shows the effect of 2.45 volts per cell float, indicative of a string with two shorted cells.

Figure 4

GASSING RATE COMPARISON FOR RHD-250 CELLS
TWO SIX-CELL STRINGS AT 2.45 vpc WITH AND WITHOUT CATALYST



This chart shows that the string without the catalyst averaged from 1000 to over 3000 cc's of gas per day. The cells with the catalyst averaged from 200 to 800 cc's per day (3.5 to 5 fold reduction in gas lost).

We also looked at the effect of higher temperatures (95°F) that are seen at many locations both because of lack of environmental control or outside plant applications. Figure 5 below shows the cumulative gas collected over a period of 78 days. Again, there is a substantial benefit (a six to eight fold reduction in gas lost) for cells with the catalyst plug within the headspace. The calculated dry-out rate from this gassing rate is well within the tolerance level for achieving the design life of ten years at this ambient temperature. In addition, the float current with the catalyst was lower than for cells without the catalyst, which in turn will enable the cells to run cooler.

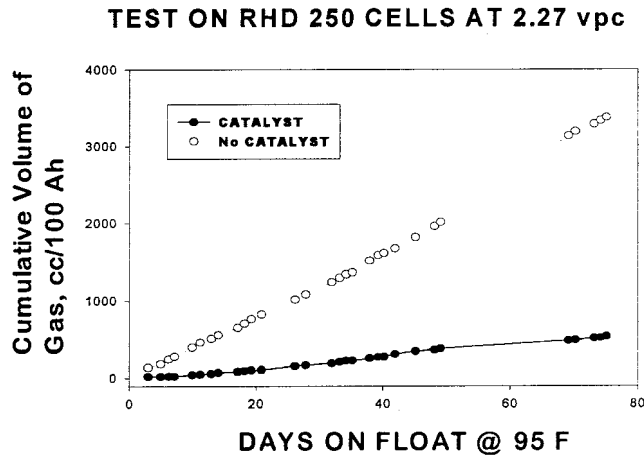


Figure 5

It is because of the improved performance at higher temperatures that we have decided to test ten-year designs with the catalyst. Table 1 below shows the benefit in both gas evolution and current for our LS 6-125 AH product. Field trials of such improved ten-year products will be beginning shortly.

Gassing rates of LS6-125 modules

Effect of Catalyst

A. Without / Catalyst

MODULE A	test time (hour)	avg miliamps	cc/cell/hr
2.27 VPC	71	49	0.93
2.35 VPC	4.5	154.7	16.8
MODULE B			
2.27 VPC	48.5	23.5	1.4
2.35 VPC	5.8	40.7	7.8

B. With / Catalyst

Note: Modules C, D with Catalyst

MODULE C	test time (hour)	avg miliamps	cc/cell/hr
2.26 VPC	27	24	0
2.35 VPC	27	169.5	0.62
2.45 VPC	22	245.3	2.2
MODULE D			
2.26 VPC	27	22	0
2.35 VPC	27	92	0
2.45 VPC	22	128.1	0

Table 1

One of the experiments we said we were going to try last year was to add the catalyst to cells that had already been in service. The next chart shows the effect of experiments done on several relatively new (six month old HD-1300s). Cell conductance, ambient temperature and float current were recorded. The cells had been installed in an environmentally controlled battery room. However, because of the layout of the rectifiers and the battery strings, the actual battery temperatures were measured to be about ten degrees higher, i.e. between 85°F and 90°F. Unfortunately this was not an isolated incident. Over the past year C&D personnel have visited dozens of installations and have found temperature problems, both high and low at many of the sites, even though they have controlled environments. I will discuss this point later. The cells had their vents replaced with the catalyst vents. After a period of stabilization, the float current and cell conductance were measured again. Figure 6 below shows the effect on cell current and you can see it is quite significant. Figure 7 below shows similar improvement in the conductance values. These are new batteries and hence we would not expect to see improvement in performance but expect to prevent deterioration in performance over the long term. Sometimes a quick improvement in performance is observed when a catalyst vent is inserted due to the development of a vacuum within the cells and the consequential increase in compression. Such improvement may be short-lived, but the catalyst is able to maintain cell performance and prevent premature degradation. A recent report⁵ claims substantial performance shortfall without the catalyst for a different manufacturers product after a little more than a year on float at an elevated temperature. That same report stated that companion cells fitted with the catalyst did not exhibit the shortfall. We have not seen such a dramatic effect for our products primarily because we have not seen such a significant short fall in performance after such a short time.

**FLOAT CURRENT COMPARISON:
SIX MONTH OLD CELLS, 24 Cells/String, at 85-90 F**

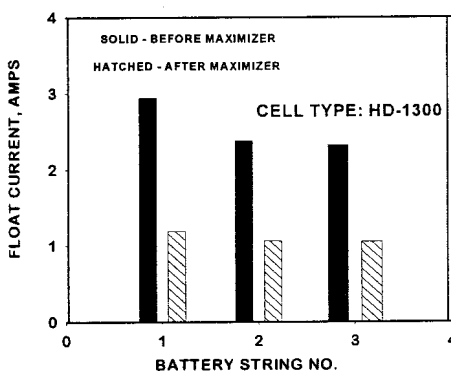


Figure 6

**EFFECT OF MAXIMIZER ON CELL CONDUCTANCE
Six Month Old Installation, About 85 to 90 F**

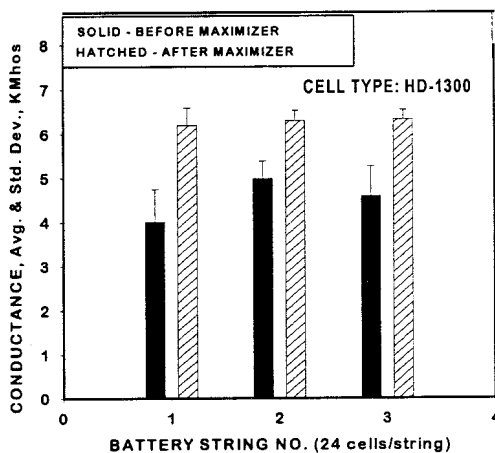


Figure 7

In our attempts to introduce the catalyst into product already installed, C&D personnel examined over 93 battery strings comprising over 2000 cells at 53 different sites. This survey was undertaken to get a better understanding of how C&D's products were doing considering the concerns being raised about VRLA batteries in general exhibiting capacity fall off and high impedance readings.⁶ It is during this survey that C&D personnel were able to conclude that all was not well with the site installations. Although not practical at all sites, 168 cells had been tested for capacity. Cell voltage, float current, impedance, temperature, and physical appearance were recorded for all cells. Of particular importance were the observations made about the environment in which the cells were operating.

Cell Location – this was found to be the most significant factor associated with cell problems. The most common problem was various degrees of elevated temperature due to either inadequate air conditioning or poor distribution of cooled air or both. Cells adjacent to rectifiers in an otherwise adequately cooled room were also observed. In a surprising number of locations, cells were operating in environments, which were too cold, and the cells were consequently undercharged. It has been reported that in cold temperature environment without the benefit of temperature compensating chargers or catalyst it is even harder to maintain polarization of the negative plates. What was also surprising was that the incidence of improper temperature control was far higher in buildings than it was in huts.

Cell Impedance – Although every cell had its impedance taken the results are best seen by the two charts shown below for the HD-900 and the HD-1300, since these two sizes were the ones found in the greatest numbers.

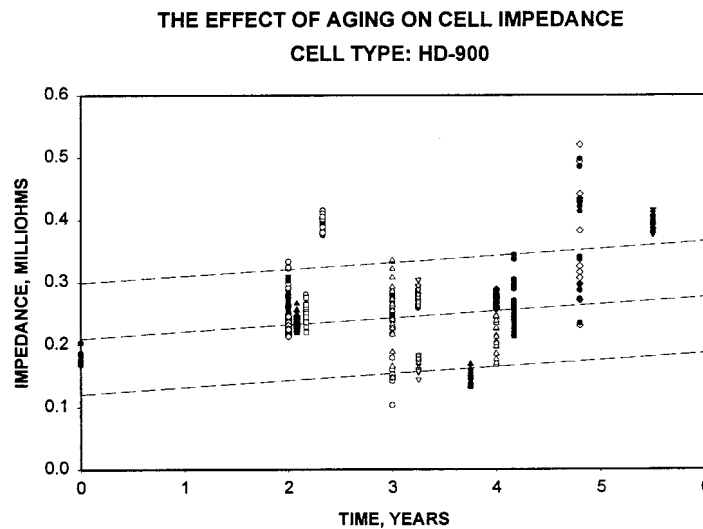


Figure 8

THE EFFECT OF AGING ON CELL IMPEDANCE
CELL TYPE: HD-1300

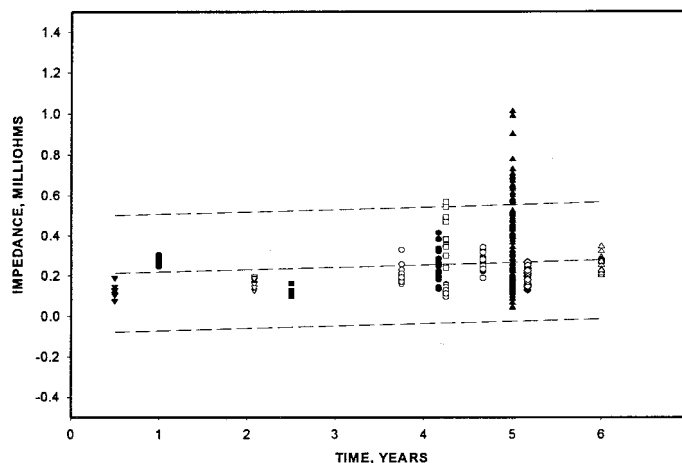


Figure 9

While the impedance data itself is not totally conclusive, some observations should be noted. For the HD 1300 cells it is immediately clear something is very unusual about the strings at the five year service level. Close examination reveals the float current was at 6.2 amps. This site was not part of a random sample but was visited because the battery was known to be in trouble. The battery temperature was 93°F and it was winter.

Another observation that can be made is that while the mean impedance is around 200 milli-ohms, figures of twice that number or half that number were also evident. Looking at the spread of new or fairly new HD 900 and HD 1300 cells shown on the charts it would be inappropriate to expect a direct correlation with capacity. However, enough data has been collected to expect that cells falling within the two 95% statistical lines will probably have acceptable capacities. The only capacities we were able to ascertain from test run on these groups of cells were the two year old HD- 900s of these 167 of the 168 cells had capacities exceeding 100% the other cell was at 99%. C&D Technologies has never subscribed to the concept that impedance is a reliable, direct, measure of the capacity of a VRLA cell in service. Even brand new cells have a larger spread of readings than might be considered to be the case as indicated by the initial readings for the HD-900s. There is however, a substantial amount of data around which shows that when the capacity of VRLA batteries decline then this decline is accompanied by an increase in the impedance of the cells. It therefore follows that if the impedance of the cells remaining essentially constant then the capacity is likely to be doing the same. Assuming this statement is true, then this is a very encouraging situation for the Liberty 2000 cells in general. Conversely, where the impedance of the cells fall outside the boundary lines, the chances are that something is very wrong.

Conclusions: While it is too soon to pronounce that we have now a full understanding of everything that affects and can influence the long term performance of VRLA product. We feel the evidence is overwhelming that the use of an internal catalyst can improve the cell operating parameters and allow the cells to function better in conditions that clearly are having a harmful effect on VRLA products. We believe that the use of the internal catalyst to be an improvement for VRLA products in general. We also believe that design, manufacturing control and better control of the operating environment can prevent the majority of VRLA cells from failing within five years as reported in recent papers.⁶ It is too soon to report on how well the enhancement of VRLA product with catalyst is affecting projected cell life. However, based on initial information taken at sites that have had the catalyst added, some improvement in the battery has been evident at all sites upgraded.

¹ Bruce Dick: BATTCON 98, 2nd National Battery Conf., Boca Raton, FL, Paper 8 (1998)

² W. Jones and D.O. Feder, Intelec 96, Proc. 18th Int. Telecom Energy Conf. Paper 11-5, Boston, MA

³ W. Jones et al: Intelec 98, Proc. 20th Intl. Telecom Energy Conf. Paper 19-4 (1998)

⁴ S. Misra, T.Noveske et al: Long Beach 99, 14th annual battery conference, Long Beach, CA.

⁵ W. Jones et al, Intelec 98, Proc. 20th Int. Telecom Energy Conf., Paper 19-4 (1998) San Francisco, CA

⁶ D.O.Feder et al, Intelec 98, Proc. 20th Int. Telecom Energy Conf., Paper (1998) San Francisco, CA