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The role of recombination catalysts in VRLA cells

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Abstract

Use of gas-recombining noble metal catalysts in valve regulated lead acid (VRLA) cells has added a new dimension to the design of these products. In standby 'float' operation, there appears be some difficulty in uniformly charging a VRLA battery string. This may be due to oxygen recombination promoting a depolarized negative that continues to self-discharge. While use of catalysts for VRLA cells has been explored for quite some time, realization that there is a lack of stoichiometry in oxygen and hydrogen evolution did not promote focused investigation in this direction. However, recent data shows that inserting a catalyst in the headspace changes the dynamics of the oxygen recombination reaction — recombination is suppressed at the negative plate and diverted to the surface of the catalyst. This changed dynamics overcomes the problem of negative self-discharge and ensures effective recharge of VRLA battery strings on float. This paper reviews the experimental work from C&D, which culminated in the commercialization of catalyst-equipped VRLA cells in long-life products. A laboratory device for investigating the quality of catalysts is also discussed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Catalyst; VRLA; Oxygen recombination; Self-discharge

1. Introduction

The lead-acid battery, introduced around the mid-19th century, has gone through many changes as it evolved from the flat lead sheets of Plante to the pasted plates of Faure and Volckmar [1]. It has found widespread industrial use, even as the two world wars brought more interest to this technology. Use of lead–calcium alloy grids became common after World War II when emphasis shifted to "low maintenance" designs with reduced water loss. Valve regulated lead acid (VRLA) batteries, initially called 'dry batteries', were introduced as early as the 1950s. They embodied the 'gelled' electrolyte (i.e. the acid was immobilized with silica gel). However, it was not until the early 1970s that the absorbent glass mat (AGM) technology developed, utilizing glass felts made from micro-fine fibers that allowed the acid to be absorbed completely into the separator. VRLA technology, utilizing AGM separators as the means of electrolyte immobilization, have since become the preferred technology for standby "float" applications. They are in widespread use, notwithstanding the various well-documented shortfalls of the technology. The present paper discusses one approach to improve their reliability and longevity, by utilizing gas-recombining catalysts internal to the cell, i.e. inside the sealed headspace of the battery.

Looking back over the past almost 150 years, it is apparent that a main driving force in lead acid technology has been the effort to reduce maintenance. Integral to this is the effort to conserve water, consumed during the recharge (or charge back) that follows a discharge. Early on, inclusion of a battery cover with a small vent opening for the open Plante cells was a worth noting achievement — this truly curbed the water loss. More recently, use of lead–calcium grids succeeded in reducing water loss much beyond that achievable from lead–antimony alloys. The mechanism for this is electrochemical. Water is conserved because of the increased hydrogen over-voltage at the negative, which suppresses the evolution of hydrogen gas during charge. VRLA designs (where adding make-up water is not an option) seek to reduce water loss even more, by curtailing oxygen loss and suppressing hydrogen gas evolution even further — through oxygen recombination at the negative plate. This action, however, promotes depolarization of the negative and thus creates a potential barrier to efficient recharge [2]. As discussed by Berndt and Jones [3] this is a particular problem for VRLA batteries on 'float' duty. Thus, when the negative is depolarized due to oxygen recombination and remains close to the mixed potential, hydrogen continues to evolve due to local cell reaction that cannot be adequately suppressed. At the same time, since the positive plate continues to evolve oxygen on 'float', it (the oxygen) will preferentially recombine at the negative. Hence, the partially discharged negative plate will continue to resist recharge. A related consequence is the increased

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over-potential at the positive, leading to enhanced grid corrosion. These reactions are summarized in Table 1. It shows the two aspects — 'chemical' and 'electrochemical' of the various reactions occurring at the plates. For the chemical components, there is no requirement of charge balance between the electrodes. For the electrochemical components, however, electron balance is required and hence the various opposing current segments have to balance out. This is shown as notes to the Table 1. As seen there, self-discharge at the negative plate, which is a chemical component, results in hydrogen evolution that cannot be recombined. Analysis of headspace gasses (for cells on float) shows a predominance of hydrogen, as expected, but there is also a significant amount of oxygen present at any time. Hence, any oxygen that cannot recombine due to kinetic limitations will also escape when the venting pressure is exceeded. The net result is that VRLA batteries will continue to experience water loss through escaping hydrogen and oxygen gasses. Self-discharge, which is the reaction of sponge lead at the negative with the battery acid (and which could not be suppressed due to the depolarized negative), also leads to electrolyte loss and hydrogen. Both of these affect the performance of VRLA cells.

In a string of cells forming the battery, the net effect of this self-discharge from negative depolarization can vary from cell to cell, leading to uneven performance. A direct evidence of this can be found by measuring the stabilized open circuit voltage (OCV) of individual cells comprising battery strings that are on float for extended periods [4].

Fig. 1 shows typical OCV data for C&D Liberty 2000, cell type HD-700, after 4–6 years on float service. It can be seen that while many cells are at a good state of charge, as depicted by an OCV of 2.12–2.15 V, there are cells that are at about 2.10 V (or lower). This OCV could correspond typically to a state of charge of about eighty percent or lower for the cell.

The concept of recombining hydrogen and oxygen gasses on a noble metal surface to regenerate water is many decades old. Use of such noble metals as catalysts for recombining these gasses has also been in commercial use for a long time, as a further attempt to limit water loss from the lead-acid battery.

These catalysts recombine stoichiometric amounts of hydrogen and oxygen gas and convert them into water vapor, which then condenses and replenishes the cell. Palladium is the material of choice for the catalyst, although other noble metals can be used. The metal, in a finely divided form, is coated on the surface of a substrate such as carbon or ceramic in order to maximize its surface area. The catalyst (comprising the noble metal on its substrate) is then placed in a porous ceramic housing which allows free gas transport but minimizes any liquid contact. This is important since any liquid on a catalyst's surface would limit its ability to recombine [5].

These catalytic recombination devices are routinely offered for standby float applications for flooded lead-acid batteries where the catalyst is used external to the cell [6]. Work geared toward improving the performance and durability of such catalysts has been ongoing for some time, again focusing on the flooded cells. Some work has been reported for VRLA cells also [7,8], but the fact that there is lack of stoichiometry within the headspace as the gasses evolve has deterred concerted effort. Hence, equal attention has been devoted toward recombining the hydrogen gas at an auxiliary electrode.

In 1996, Jones and Feder [9] reported significantly reduced gas loss for VRLA cells on float duty, by placing noble metal catalysts within their headspace. The report succeeded in generating renewed interest on this technology among battery manufacturers. At C&D, we have been performing extensive testing on the impact of these gas-recombining catalysts on VRLA cells [10,11]. After confirming and duplicating some of the main advantages (of the catalyst), C&D introduced and commercialized its version of a gas recombination catalyst in early 1998, initially, incorporating it in our long-life designs and calling it the Maximizer$^{\text{TM}}$.

A patent application is pending for this concept of the catalyst plug forming a special attachment to the vent plug. The effort to understand the role of gas recombination catalysts in VRLA cells (and the means to quantify them) forms the basis for this paper.

2. Experimental

All data generated and reported here use commercially available cells and batteries, specifically the C&D Liberty 1000 and 2000 product lines. The Liberty 2000 is the long-life design with 20-year expected grid life. Liberty 1000 product lines are comprised of multi-cell mono-blocks with thinner grids and correspondingly lower expected life.

The active ingredient of the catalyst is comprised of finely divided palladium metal, dispersed on an inert surface and housed within a porous ceramic cup. The open end of this cup is then sealed with epoxy. The ceramic cup has fine pores to access gas but has flash arresting capability. This ensures safe operation even as gas recombination makes the surface of the palladium-dispersed catalyst extremely hot. It was more convenient at times to house the palladium-dispersed catalyst inside housing made from stainless steel mesh — this was adopted when the effect of 'poisons' was investigated.

Test cells of the Liberty 2000 type were fitted with the catalyst plug that was mounted on the pressure-relief vent assembly (Maximizer$^{\text{TM}}$). The typical venting pressure was about 1–1.5 psig. This design insures that all gas that potentially could escape from the cell must first come into proximity of the catalyst. Work at elevated temperature conditions was generally performed after the cells were fitted with a heating blanket with a low heat density that could be adjusted to maintain the desired temperature.

Table 1
Chemical and electrochemical reactions at the electrodes[a]

Description	Chemical component	Electrochemical component	Remarks
Reactions at the positive plate			
Grid corrosion, followed by charge reaction	$Pb + PbO_2 = 2PbO$	$PbO + H_2O = PbO_2 + 2H^+ + 2e^-$	Grid lead consumes water, PbO_2 formed on charge
	$PbO + H_2SO_4 = PbSO_4 + H_2O$	$PbSO_4 + 2H_2O = PbO_2 + H_2SO_4 + 2H^+ + 2e^-$	Grid lead consumes water, PbO_2 formed on charge
Net reaction: open circuit	$Pb + PbO_2 + 2H_2SO_4 = 2PbSO_4 + 2H_2O$		Grid Pb uses acid, water generated
Net reaction: float charge		$Pb + 2H_2O = PbO_2 + 4H^+ + 4e^-$	Corrosion current, I^+_{corr}
Self-discharge, followed by recharge reaction	$PbO_2 + H_2SO_4 = PbSO_4 + H_2O + (1/2)O_2\uparrow$	$PbSO_4 + 2H_2O = PbO_2 + H_2SO_4 + 2H^+ + 2e^-$	Water used and oxygen available for recombination
Net reaction		$H_2O = (1/2)O_2 + 2H^+ + 2e^-$	Same as overcharge, I^+_{sd}
Standard charge reaction		$PbSO_4 + 2H_2O = PbO_2 + H_2SO_4 + 2H^+ + 2e^-$	Overcomes self-discharge, I^+_{ch}
Float: continuous overcharge		$H_2O = (1/2)O_2 + 2H^+ + 2e^-$	Primary reaction: uses water, I^+_{oc}
		Organic + H_2O = CO & $CO_2 + 2H^+ + 2e^-$	Minor secondary reaction, I^+_{org}
Reaction at the negative plate			
Self-discharge and recharge	$Pb + H_2SO_4 = PbSO_4 + H_2\uparrow$	$PbSO_4 + 2H^+ + 2e^- = Pb + H_2SO_4$	Hydrogen loss from electrolyte
Net reaction: open circuit	$Pb + H_2SO_4 = PbSO_4 + H_2\uparrow$		Hydrogen and electrolyte loss
Net reaction: float charge		$2H^+ + 2e^- = H_2\uparrow$	Hydrogen loss, I^-_{sd}
Standard charge reaction		$PbSO_4 + 2H^+ + 2e^- = Pb + H_2SO_4$	Overcomes self-discharge, I^-_{ch}
Float: continuous overcharge		$(1/2)O_2 + 2H^+ + 2e^- = H_2O$ and/or $2H^+ + 2e^- = H_2\uparrow$	Oxygen recombination and hydrogen loss, I^-_{oc}

[a] The reactions shown as 'chemical component' occur on the background and do not involve current balance shown for the 'electrochemical component'. All electrochemical reactions involve charge transfer at an electrode surface. They use electrons that must be transferred to the other electrode in the cell and balanced. Consequently, the current generated must be balanced — between those occurring at the positive and the negative plates, respectively. The currents associated with self-discharge and oxidation of organic components at the positive can be neglected. Therefore, one has the following current balance on float: $I^+_{corr} + I^+_{ch} + I^+_{oc} = I^-_{ch} + I^-_{sd} + I^-_{oc}$.

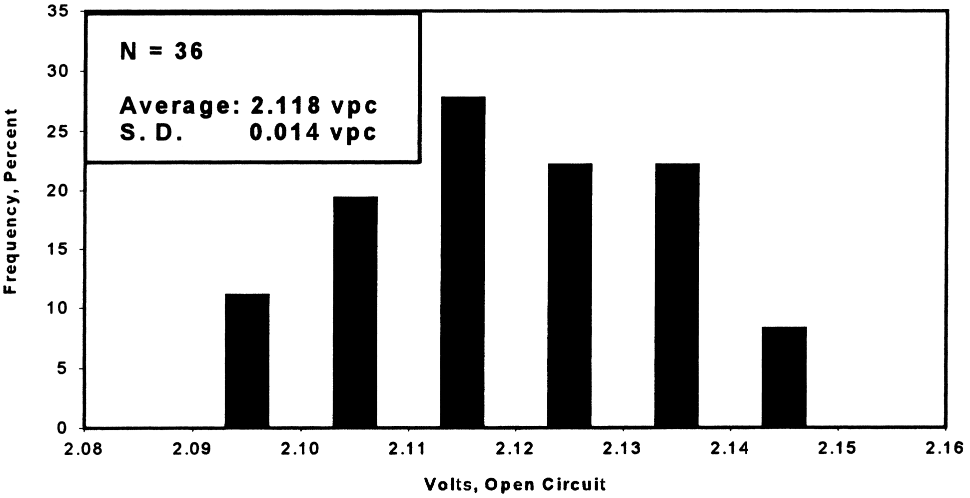

Fig. 1. Open circuit cell voltage measured for battery strings type HD-700: on float for 4–6 years.

Test units of Liberty 1000 multi-cell mono-blocks were fitted with the catalyst plugs through separate ports that were drilled through the cover. PVC pipe fittings of appropriate size were glued to these ports for ease of installing and accessing these plugs. Separate pipe fittings were also glued to the top of the vent area, to which flexible tubings were attached. This allowed any gas escaping the vent to be collected for measurement by directing it to an inverted graduated cylinder. All tubing and other fittings were periodically checked for leaks with a combustible gas detector. Heavy walled Tygon^{TM} tubing was used wherever possible. The actual time for gas collection was adjusted such that the volume evolved could be estimated with some accuracy.

When required, a mercury–mercurous sulfate reference electrode was used to measure plate polarizations. In such cells (with a reference electrode), the catalyst was mounted external to the cell-cover through a modified vent-assembly. Internal pressures were measured by incorporating pressure transducers inside the headspace of the cell.

The effectiveness of catalysts for gas recombination and their efficiencies was measured outside of a cell environment, in special fixtures that incorporated a reaction chamber that housed the catalytic device. It utilized hydrogen and oxygen gas mixtures that were generated in stoichiometric proportions, using an electrolytic cell. A Platinum wire served as the positive electrode and titanium wire the negative electrode. Collection of any gas escaping the reaction chamber was carried out by a method similar to that described above. More details of the devices and test fixtures used are discussed in a later section, together with the results.

2.1. Safety

The generation of hydrogen and oxygen gas, mixed together, can lead to an explosive event. Proper safety precautions must be used at all times. Details of such safety precautions have not been mentioned in this paper since they are both outside its scope and are the complete responsibility of the party doing the tests.

3. Results and discussion

In view of the fact that only minimal amount of oxygen is available within the headspace of VRLA cells, the first set of experiments was directed toward measuring the effectiveness of the catalyst to recombine and minimize gas loss when it is housed within this sealed space.

The primary function of any recombination catalyst is to minimize gas-loss to the environment (which is linked to electrolyte and water loss and consequent cell dry-out). Hence, many tests were performed to quantify any potential benefit in that direction, some of which are described below.

3.1. Gassing tests with long-life, 20-year design VRLA cells

3.1.1. Standard float

Test cells were from the Liberty 2000 product line. Gassing was monitored from 12 RHD-250 (2 V, 250 Ah) cells that incorporated the Maximizer^{TM} catalyst-equipped vent. The cells were arranged as two six-cell strings that were maintained on float at 2.27 V per cell (VPC) and at ambient temperature of the laboratory. No out-gassing could be observed from any of the 12 cells when they were fitted with the catalyst over a 14-day-period. After this (14-day-period) the catalyst assemblies were removed and replaced with standard vent assemblies. The cells began to gas, although at a very low rate, as shown in Fig. 2. While not shown here, the float current was also higher for the test without the catalyst when compared to the value with the catalyst in the headspace.

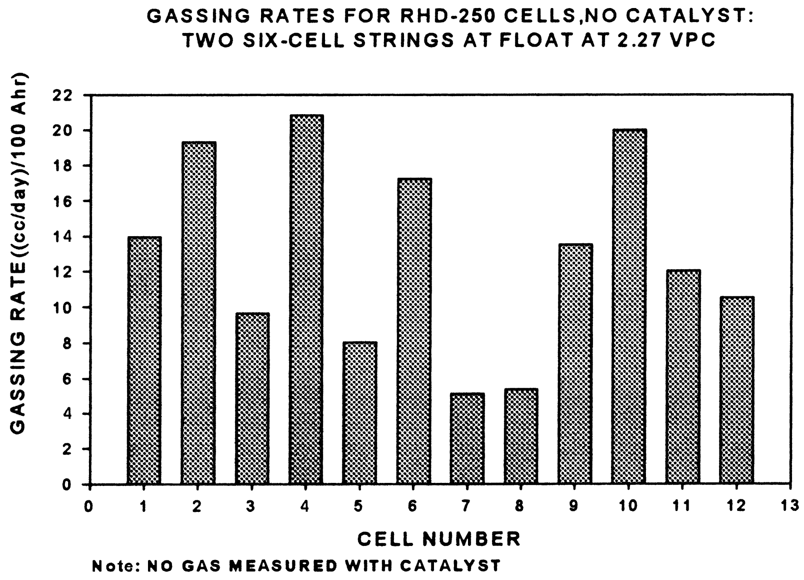

Fig. 2. Two six-cell RHD-250 strings at 2.27 VPC.

3.1.2. Float at elevated voltage

The above test sequence was repeated at an elevated voltage level of 2.45 VPC. The result (with and without catalyst) is seen in Fig. 3. This higher voltage level simulates the presence of two shorted cells for a 24-cell string on float, or the typical charging voltage used on cycle service. At this higher voltage, the Maximizer$^{\mathrm{TM}}$ catalyst allowed some gas to escape, although considerably less than the same cell without the catalyst.

Reduction in gassing certainly implies a longer life battery, at least in cases where dry out (as distinct from grid corrosion) is the primary failure mode. Besides, less water loss should also provide greater protection against thermal runaway.

These results show the ability of the Maximizer$^{\mathrm{TM}}$ catalyst to offer additional protection for the remaining 'good' cells in a string even when two cells are shorted, as compared to the standard product without the catalyst.

3.1.3. Elevated temperature

The effect of an elevated temperature on performance of the Maximizer$^{\mathrm{TM}}$ catalyst was also investigated. Fig. 4 shows cumulative gassing for cells of the same size, on float at 2.27 VPC and at 95°F (35°C). This higher temperature is more typical of not only some plant installations, but also for cells that must be placed close to rectifiers due to space limitations or inadequate air circulation. As can be seen, use of the Maximizer$^{\mathrm{TM}}$ catalyst resulted in a six- to eight-fold reduction in gas evolution.

3.2. Gassing tests with multi-cell mono-block design VRLA cells

Gassing tests, done with batteries from the Liberty 1000 product line, have produced similar results. Typical data generated with LS 6–125 battery units, fitted with catalyst plugs used in modified assemblies and at various voltages, is presented in Table 2.

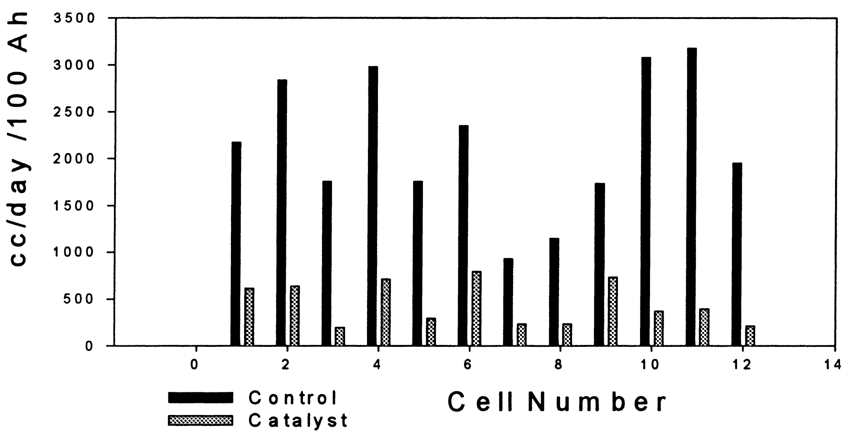

Fig. 3. Two six-cell RHD strings at 2.45 VPC.

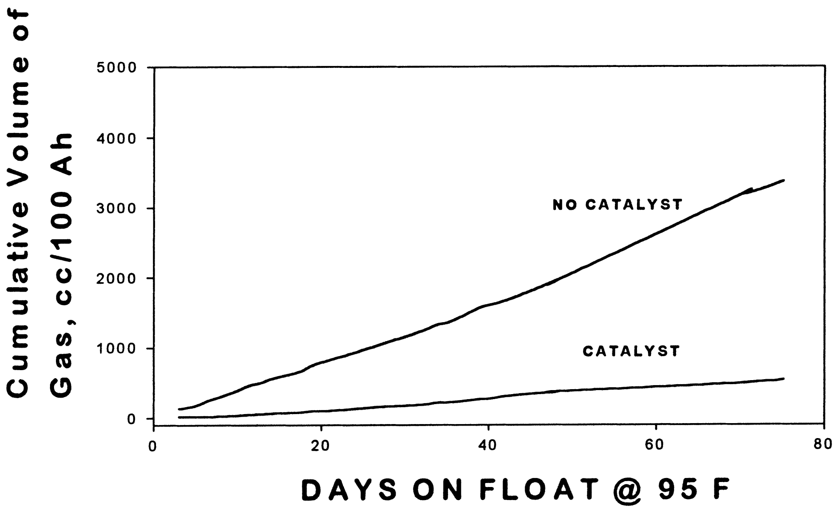

Fig. 4. Test on RHD-250 cells at 2.27 VPC.

Practically, no out-gassing was observed in batteries fitted with the catalyst under float conditions. The impact of catalyst on other products from this family is the subject of a recent publication [12]. The results mirror those obtained with the 20-year products fitted with the Maximizer^{TM} catalyst presented earlier.

To summarize, placing a recombination catalyst like the Maximizer^{TM} within the headspace of VRLA cells minimizes out-gassing under normal float, float at higher voltages and at higher temperatures. As mentioned earlier, use of a recombination catalyst also results in a lowering of the float current. Some results are shown in the following section.

3.3. Effect of recombination catalysts on float current of VRLA cells

An unexpected outcome of placing recombination catalysts within the headspace of the VRLA cell is the significant lowering of float current. The data that follow is from Liberty 2000 cells in the field and is reproduced from our earlier publications, referred earlier.

These data are from three separate battery strings that were in operation for several months. They were at a slightly higher ambient temperature (85–90°F, or 29–32°C). Float current and ac conductance was measured on the three 24-cell strings of HD-1300 cells, nominal capacity 1430 Ah. The standard vents were replaced with the Maximizer^{TM} vent assemblies and the current and ac conductance re-measured after stabilization. The results are shown in Figs. 5 and 6.

The float current in a traditional VRLA cell is typically higher than its flooded equivalent due to oxygen recombination and the associated parasitic current. The recombination catalyst, however, influences the traditional recombination mechanism. This lowers the float currents (and any associated heat) as seen in Fig. 5.

The ac conductance (measured with a Midtronics ‘Celltron Plus’ meter) also increased, as seen in Fig. 6. This is attributed to reduced sulfating of the negatives as well as more intimate contact between the AGM separator that contains the electrolyte and the plates that comprise the cell element, due to the creation of a lower pressure within the headspace.

These specific cells were perfectly functional and the increased conductance did not result in any significant capacity improvement.

3.4. Effect of recombination catalysts on the internal pressure of VRLA cells

Presence of a gas recombining catalyst in the headspace of VRLA cells lowers the equilibrium pressure on float. Typically, the C&D Liberty 2000 cells on float operate at about

Table 2
Gassing rates for LS6-125 batteries with and without catalyst assemblies

Description		Set voltage		
		2.27 VPC (ml/day/100 Ah)	2.35 VPC (ml/day/100 Ah)	2.45 VPC (ml/day/100 Ah)
Control: no modification	Battery 1	17.9	322.6	Very high
	Battery 2	26.9	149.8	Very high
With catalyst	Battery 3	0	11.9	42.2
	Battery 4	0	0	0

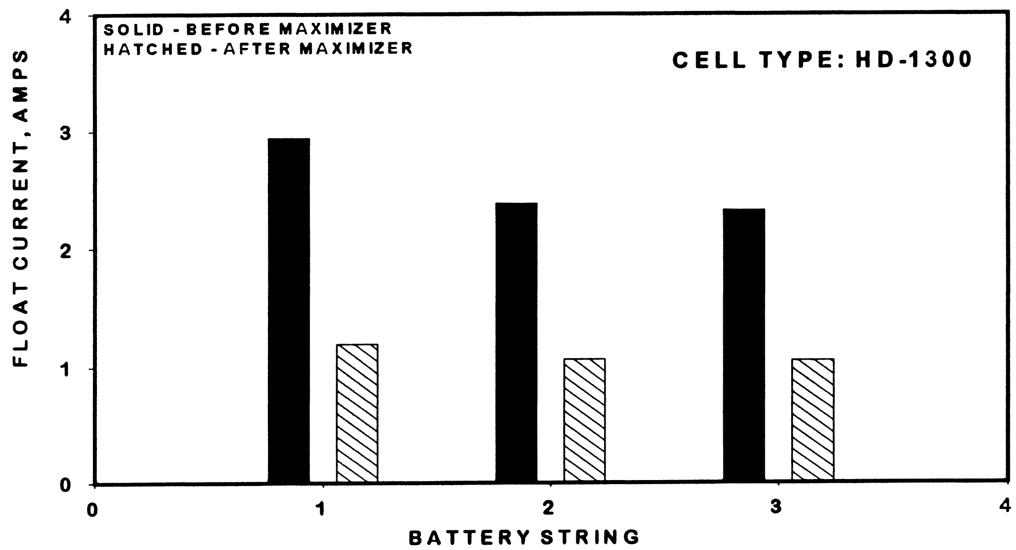

Fig. 5. Float current comparison: cell type HD-1300, before and after installing catalyst — solid: before Maximizer^{TM}; hatched: after Maximizer^{TM}.

1.0–1.5 psig. Since a low-pressure vent is necessary for stability of the large plastic containment of these cells, there is some out-gassing through these vents. With catalyst, however, the out-gassing is substantially reduced. The following set of experiments quantifies the operating pressure of these cell types when equipped with the catalyst.

The internal (headspace) pressures of four HD-900 cells, each of which was equipped with the catalyst, were monitored over a period of about 5 weeks. The cells were fitted internally with pressure transducers and maintained on float at 2.27 VPC. The measured pressures are shown in Fig. 7. In general, these cells (that are equipped with the catalyst) show around 0.5 psig or lower operating pressure. This pressure is much less than the opening pressure of the vent and explains the lack of out-gassing under normal float operation.

Some variability (in headspace pressure) is seen with time, which may be partly due to variations in the ambient temperature conditions in the laboratory. A slight negative pressure (or vacuum) was observed part of the time for all four cells.

3.5. *Positive and negative polarization in VRLA cells with recombination catalyst*

The traditional oxygen recombination in a VRLA cell depresses the negative over-voltage and thus may result in partially discharged negatives. Consequently, minimizing

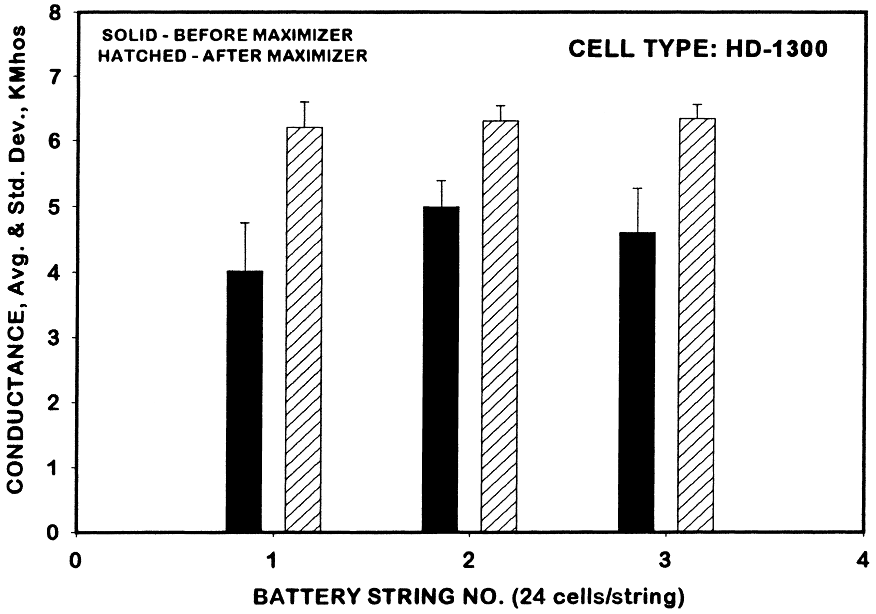

Fig. 6. Conductance before and after Maximizer^{TM}, 6-month-old installation, about 85–90°F — solid: before Maximizer^{TM}; hatched: after Maximizer^{TM}.

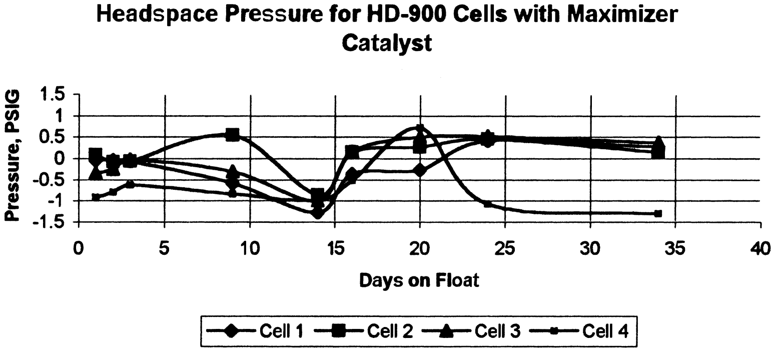

Fig. 7. Headspace pressure for HD-900 cells with Maximizer^{TM} catalyst.

this reaction (at the negative plate) should result in non-sulfated and therefore "healthier" negative plates. The next series of tests [10,11] were designed to show the impact of a recombination catalyst on both positive and negative polarization.

Reference electrode measurements are commonly used to determine the magnitude of polarization. An RHD-250 cell was fitted with a reference electrode and recombination catalyst. For convenience, a modified vent assembly was used such that the catalyst resided just outside the conventional headspace of the cell. Positive and negative polarization was measured over a 6-month-period. A standard RHD-250 cell, without catalyst, served as control. The results are shown in Fig. 8A.

Clearly, the introduction of a recombination catalyst has significant influence over both the positive and negative polarizations. While the magnitude of this influence may vary from cell to cell, presence of a gas-recombining catalyst will always have some impact. On cells with catalyst, the negative polarization is increased with a corresponding reduction in positive polarization. Both are positive influences on cell life. The increase in negative polarization assures a fully charged negative electrode that will not limit capacity or life. The reduction in positive polarization for the cell fitted with catalyst (in the current test) brings it down to a level that is characteristic of that observed in flooded products. Both accelerated life tests and actual field experience with flooded cells have demonstrated a 20-year life for properly designed grids at these polarization levels.

The observed shifts in polarization could occur only if the traditional oxygen recombination mechanism was greatly reduced due to the action of the catalyst. As a further test of the system dynamics, the vent assembly with the catalyst was removed from the RHD-250 cell and replaced with a standard vent assembly. After it stabilized, the polarization at the negative plate and the associated float current were noted. Several days later the standard vent assembly was again replaced by the catalyst-equipped vent-assembly and the system allowed to reach stability.

A measured capacity discharge (8-h rate) followed. After the discharge (and subsequent recharge) the system needed several days to re-stabilize. The influence of all these situations on float current and polarization at the negative plate is shown in Fig. 8B.

3.5.1. Impact of catalyst on mechanism of recombination

Removal of the catalyst obviously caused the float current to increase and the negative polarization to decrease. The system appears to stabilize quickly in this mode. Negative polarization increased again when the catalyst was re-introduced. Stabilization in this mode is a long process. Probably, increased hydrogen generation at the negative and changes to the internal compression characteristics are involved that take more time to equilibrate. However, it is clear that presence of a catalyst in the headspace is changing the entire dynamics of the oxygen recombination process.

Presumably, oxygen evolved at the positive is diverted away from the negative plate and recombined (on the surface of the catalyst) with the hydrogen available in the headspace. With the depolarizing forces from recombination not present, the normal charging and gassing reactions at the negative will now proceed, generating more hydrogen in the process. Mechanistically, this is similar to the operation of a flooded cell; but the evolved gasses are recombined and hence water loss minimized.

3.6. Stability and quality control aspects of recombination catalysts

With all these positive results, it is reasonable to ask about the limitations to catalyst use in VRLA cells. Performance limits must also exist for any catalyst, due simply to the practical consideration of the catalyst that can be placed in a cell's headspace. In addition, it is well-known that certain gaseous compounds can greatly reduce or make a catalyst totally non-functional; i.e. "poison" the catalyst.

Common examples are gaseous compounds of sulfur, lead And stibine gas. Of course, gaseous compounds from the first two elements would only be generated after total deterioration of the battery. Stibine (a compound of antimony) is not generated in cells that utilize lead–calcium grid alloys. The latter is the alloy of choice for most recombinant battery manufacturers.

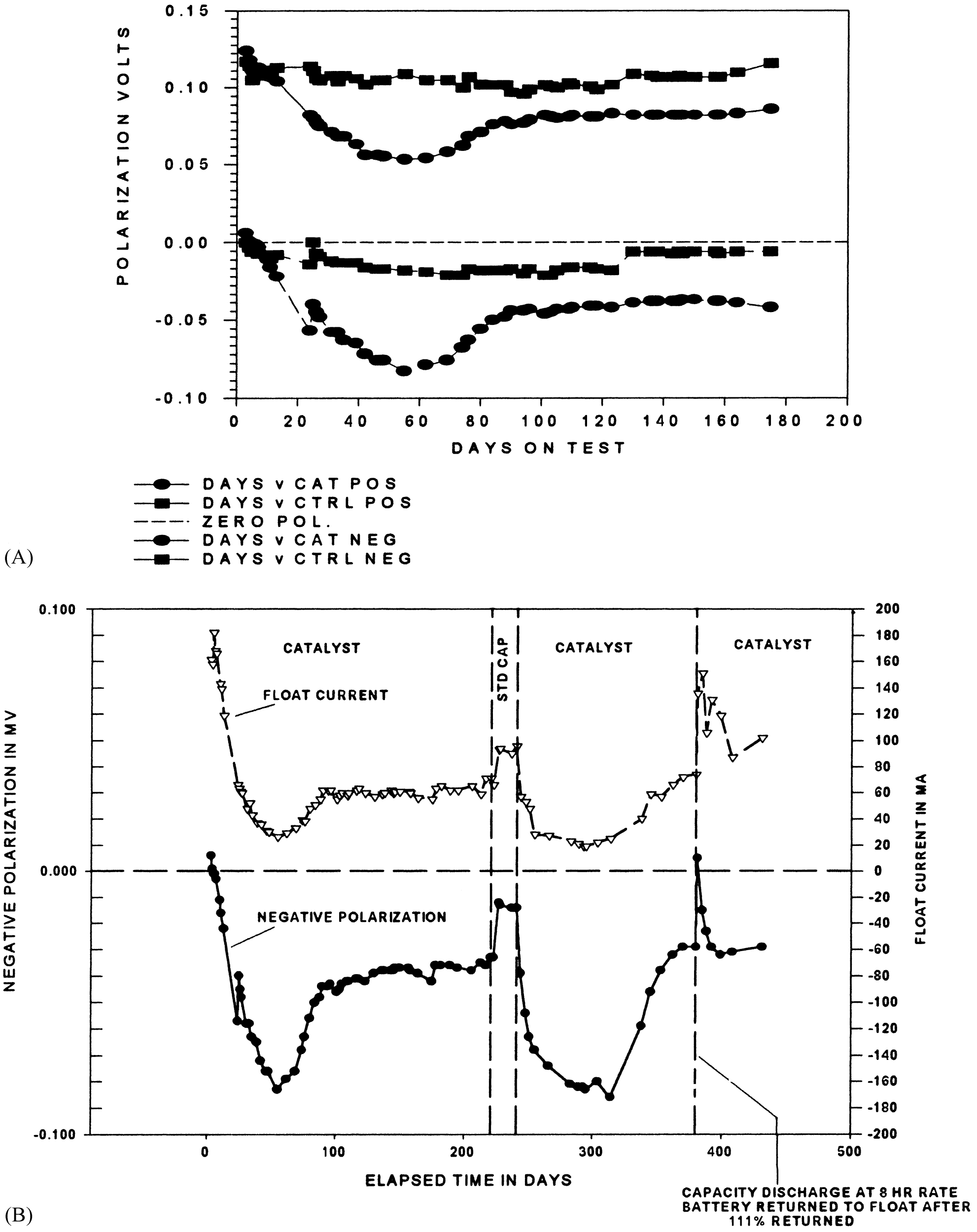

Fig. 8. (A) Polarization vs. days on float RHD-250 cells at room temperature. (B) Float current and negative polarization for RHD-250 with catalyst.

Recombination catalysts can also be poisoned by volatile organic components released by certain adhesives and plastics — they can be found even in the air itself. Although internal catalysts come into contact only with the headspace gasses, it is still critical to test the ability of any material to "poison" a catalyst it contacts. It is also reasonable to expect that the recombination efficiency be related to the amount of catalyst present. For these reasons, methods have been developed to check the activity and quantify the recombination efficiency of the catalyst plugs used in the VRLA cells.

A generalized schematic of the test fixtures used to determine catalyst activity and the recombination efficiency is shown in Fig. 9.

The schematic shows a power supply connected to an electrolytic cell that generates a Faradaic-equivalent amount of hydrogen and oxygen gas. The current utilized for electrolysis determines the volume of each gas evolved. The gas mixture first passes through a safety trap and then to a test chamber where it is exposed to the catalyst assembly. The amount of hydrogen and oxygen gas, which is not recombined, is collected in an inverted graduated cylinder and measured. The percentage recombination efficiency is calculated, utilizing Faraday's law.

Two test chambers were utilized for these measurements. Details and sketches of these two are available in a recent publication [13]. The first (of the two test chambers) is a non-pressurized chamber made from a battery jar and cover.

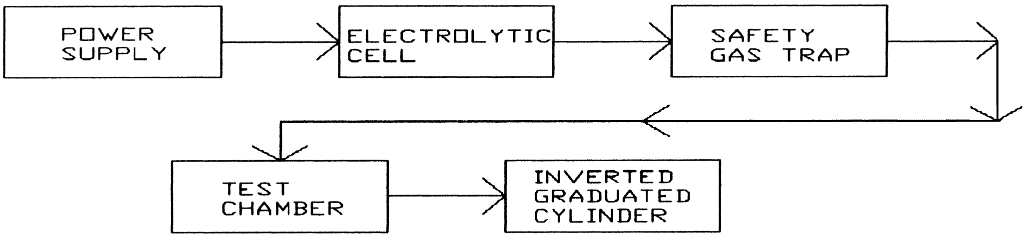

Fig. 9. Catalyst test system schematic.

Holes cut into the cover allowed for both the entry and exit of gas as well as a thermocouple lead. Gas could easily escape from the chamber after coming into only passing contact with the catalyst or Maximizer^{TM} assembly, which is the main difference between this system and a pressurized battery. The only pressure in this system is the small water pressure-head associated with the inverted graduated cylinder. The second (test chamber) is pressurized. This chamber differs from the previous one in that gas must exit through a pressure release vent to escape from the chamber. This vent is a commercially available valve that can be procured with a pre-determined venting pressure. A Maximizer^{TM} assembly is mounted within the chamber such that the incoming gasses will come in intimate contact with the catalyst.

Small holes available around the assembly, however, allow the gasses to by-pass this standard battery vent. In both chambers, a bayonet type opening is provided to assure proper seating of the assembly.

Table 3 gives the test results from both chambers. Tests in the pressurized chamber were performed at 1.45 and 2.7 psig.

For each test, gas was generated for 30 min and at 3 A. The temperature was at the laboratory ambient — it was generally in the range of 72–79°F (23–25°C). Column 3 gives the results from the pressure-free chamber while measurements in the pressurized chamber are shown in Columns 4 and 5.

Ideally, the tests designated "no catalyst" should show 100% of the theoretical gas generation in all the three columns (Columns 3–5). Obviously, the pressure of the vent interferes with free transport of the gas to the inverted graduated cylinder (Columns 4 and 5). "no catalyst" tests in the pressure-free chamber shows the volume of gas collected to be close to the theoretical values. Conversely, tests in the pressurized chamber gave higher but more inconsistent recombination efficiencies. However, efficiencies measured under pressure are more indicative of catalyst performance in batteries.

A comparison of results from tests with and without catalysts, performed in the pressure-free and the pressurized chamber leads to the conclusion that the pressure-free chamber is more consistent and hence superior for evaluating catalyst performance. Consistency of results is critical to discriminate performance even as the catalyst degrades under the influence of potential "poisons" or to differentiate between catalyst designs.

The pressure-free chamber was used to determine the potency of catalyst plugs and as a quality control measure.

In separate tests, different weights of catalyst were exposed to 3 A for 30 min in the test chamber. The results are shown in Table 4.

The results show that the extent of gas recombination is broadly controlled by the amount of base catalyst present in the catalyst plug. Specifically, in this test. 40% less catalyst weight resulted in a 39.5% loss of recombination efficiency.

Ideally, the weight of the base catalyst should be sized with the battery or application. The higher the current and the amount of gas it is expected to recombine, the greater amount of catalyst should be provided.

The chamber can also be used to determine if introducing a new battery material (adhesive, plastic, etc.) will negatively impact catalyst performance.

Table 5 gives the recombination efficiencies of catalyst, which was separately exposed for fixed periods to three different materials, designated, respectively, as A, B, and C, each of which was identified as potential "poisons". For this test, the catalyst was placed inside a cage made from

Table 3
Comparison of gas generated (no catalyst) vs. gas recombined (with catalyst): volume (ml) of gas, generated at 3 A and 30 min, collected at various pressures

	Test no.	Atmosphere (psi)		
		~0 (Column 3)	1.45 (Column 4)	2.7 (Column 5)
No catalyst	1	975 (95% of theoretical)	930 (91% of theoretical)	790 (77% of theoretical)
	2	1027 (100% of theoretical)	940 (92% of theoretical)	
With catalyst	3	580 (43.5% of theoretical)	200 (80.5% of theoretical)	100 (90.3% of theoretical)
	4	590 (42.5% of theoretical)	110 (89.3% of theoretical)	80 (92.2% of theoretical)
	5	610 (40.6% of theoretical)	140 (86.4% of theoretical)	110 (89.3% of theoretical)

Table 4
Effect of catalyst weight on recombination efficiency, %: pressure-free; 30 min at 3 A

Normalized weight (%)	Recombination efficiency (%)			
	Sample 1	Sample 2	Sample 3	Average
100	27.9	28.9	28.9	28.6
60	16.2	20.1	15.5	17.3

stainless steel wire mesh. This allowed a more intimate contact with the incoming gas compared to the porous ceramic containment. That explains the much higher recombination efficiency when compared to the values reported in Column 3 of Table 3 in the pressure-free chamber.

Table 5
Potential "poisons" — effect on catalytic activity

Material	Recombination efficiency (%)
A	2.6
B	74.6
C	71.7

Presence of material "A" has clearly poisoned the catalyst. Use of this as an internal component in the VRLA battery could be detrimental to the functioning of the recombination catalyst. While benefit of using the test fixture to screen materials is obvious, other tests not reported here have allowed us to improve and optimize the catalyst itself.

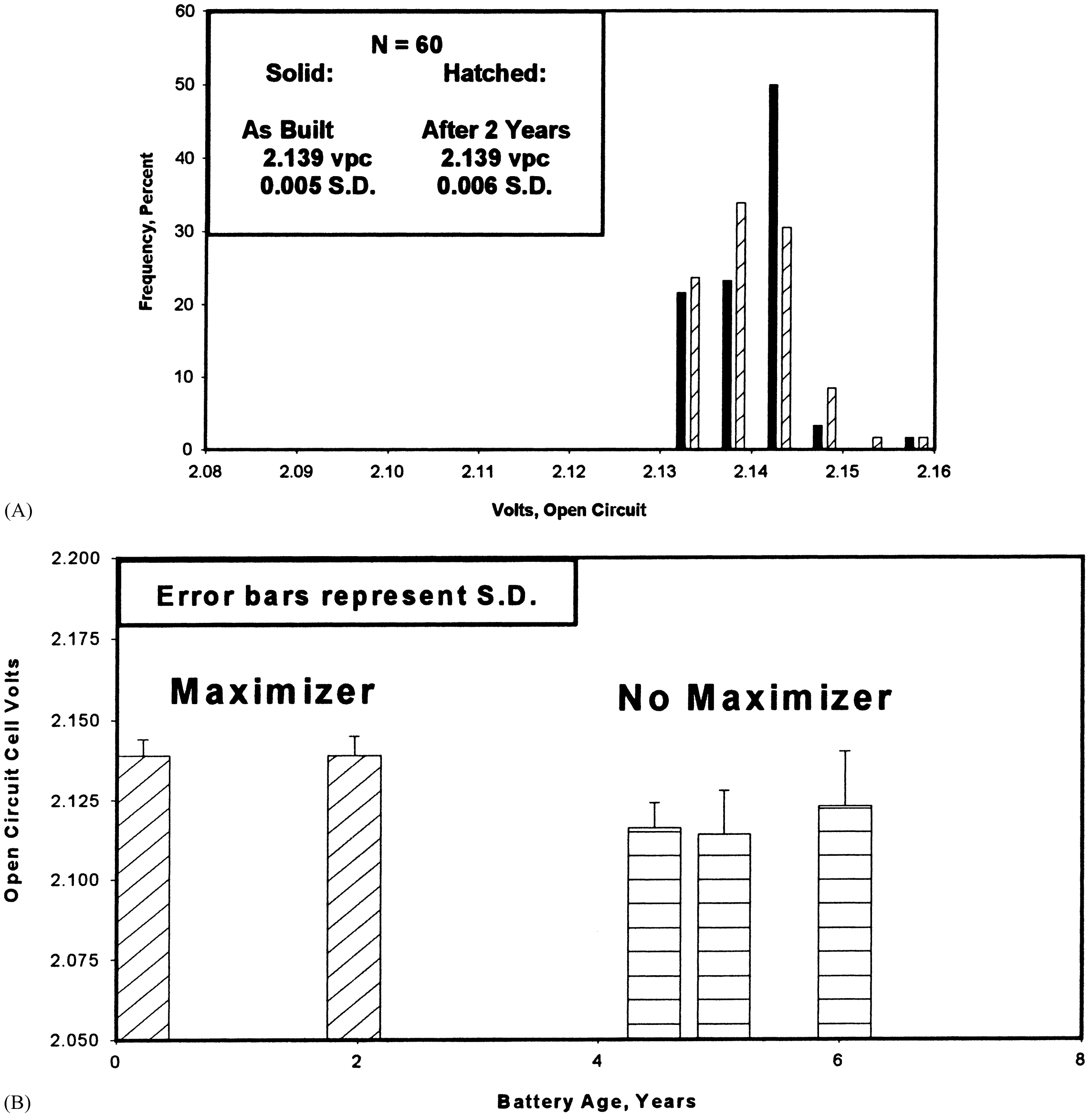

Fig. 10. (A) Open circuit voltage distribution of Liberty 2000 cells with Maximizer^{TM} catalyst 2 years in an UPS installation, floating at 2.26 VPC. (B) Comparison of OCV of Liberty 2000 type battery strings on float at 2.26 VPC.

3.7. Impact of catalyst on the stability of long-life cells in field installations

The Maximizer^{TM} catalyst has been in commercial operation for more than 2 years in C&D long-life designs and all the survey results have been generally positive.

One example of a recent survey is shown graphically in Fig. 10A. It shows the OCV data for a sixty-cell battery string after 2 years of float operation in an UPS installation. The open circuit data for the same set of cells at the time it was installed is also presented and compared with the 2-year OCV data in the same figure. This contrasts favorably with the OCV data for 4–6-year-old installations, presented earlier in Fig. 1. All these data can be seen together in Fig. 10B, spaced apart as it relates to time. This figure incorporates error bars for each battery string together with the average voltage as a function of age. Granted, the older cells (which are without catalyst) have more time in which to degrade and hence show a lower OCV. However, information from the field [4] has shown recovery of the OCV of cells of similar maturity when the Maximizer^{TM} catalytic vent is installed and substituted for the standard vent with catalyst. Therefore, indications are that the catalyst arrests voltage walk-down, which is indicative of gradual performance degradation.

4. Conclusions

Presence of gas recombination catalysts in the headspace of VRLA cells, as done in our long-life cells fitted with the Maximizer^{TM} vents, adds another dimension to the longevity and stability of this still-maturing product.

In spite of the lack of stoichiometry for hydrogen and oxygen gases in the headspace that could affect efficient recombination, catalysts still appear to offer immense benefits. These benefits include:

- potential for reduction in water loss because of hydrogen recombination,
- a reduction in the release of explosive gasses into the atmosphere,
- increased negative polarization, resulting in ''healthier'' negatives,
- reduced positive polarization that reduces grid corrosion,
- reduced float current that has the potential of reducing runaway thermal effects, and
- better cell balance across a string of cells.

All of these benefits should have a positive impact on battery life. However, these devices will not compensate for poor battery design such as inadequate compression or other manufacturing defects. In addition, care must be taken so that the noble metal catalyst is not inadvertently ''poisoned'' by volatile ingredients that may be released by battery components.

This comprehensive review of the work carried out in the laboratory and field by C&D engineering staff is being followed by introduction of multi-cell mono-blocks that also incorporate catalysts. The product line features common headspace, which allows sharing of catalyst plugs by neighboring cells. This technology is the subject of a pending patent application.

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