

Balanced Float Charging of VRLA Batteries by Means of Catalysts

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Abstract

The internal-oxygen cycle characterizes the VRLA battery as the main reaction during float charging. When it reaches a high efficiency, almost all the oxygen evolved at the positive electrode is reduced at the negative electrode. But, the two secondary reactions hydrogen evolution and grid corrosion have also to be considered. With an highly efficient internal-oxygen cycle, the rates of these secondary reactions have to be equal. Otherwise, the basic law would not be fulfilled that equal currents must flow through both electrodes. As a consequence, the proportion between hydrogen evolution and grid corrosion determines the polarization of both electrodes. Only if hydrogen evolution and grid corrosion are well balanced, negative and positive electrodes are polarized sufficiently to keep their full charge. With the technical product 'battery' the desired balance is often not reached, and if the hydrogen evolution rate is high compared to grid corrosion, partial discharge of the negative electrodes occurs during float charging.

Increased float voltage would be a remedy, since it increases the corrosion rate and so effects the desired balance. Most applications, however, do not allow an increased float voltage. As an alternative, temporary boost or equalizing charges at increased voltage are occasionally applied, sometimes included in monitoring routines. The use of more corrosive alloys would also be a possibility to balance a too high hydrogen evolution rate. But increased corrosion means reduced service life. A further possibility to stabilize the polarization of the negative electrode would be a reduced efficiency of the internal-oxygen cycle. But it would be difficult to stabilize such a limitation, since the efficiency of the internal-oxygen cycle is automatically increased with progressing water loss of the battery. Common to all these methods is, furthermore, that they cause increased water loss and thus are inconsistent with the demand for a long service life of the VRLA battery.

Incorporation of a catalyst into the unbalanced cell is a promising possibility to solve the problem. It also reduces the efficiency of the internal-oxygen cycle, since the catalyst recombines a certain portion of the oxygen before it can reach the negative electrode. As a consequence, a correspondingly increased amount of hydrogen must be generated at the negative electrode. This again requires an adequate polarization and so ensures full charge. Simultaneously, the positive electrode is less polarized, and grid corrosion reduced. The great advantage, compared to the above mentioned methods is that the oxygen that is lost from the internal cycle, is not lost from the cell, since it is directly recombined by the catalyst into water and so remains within the battery.

1 The General Situation of the Lead-Acid Battery

The lead-acid battery is an unstable system in two aspects:

1. Its cell voltage of 2 V is far above 1.23 V, the decomposition voltage of the water in its electrolyte. Thus water is split by electrolysis into hydrogen and oxygen gas. Fortunately, in the lead-acid battery the rate of these reactions is extremely slow.
2. The high potential of the positive electrode destroys all metals usually applied as current conductors. Lead can be used, since on its surface the corrosion forms a layer of lead dioxide that protects the underlying metal. But this layer is not quite stable and corrosion gradually progresses, and a continually flowing current is required to re-establish the protecting layer.

As a consequence, hydrogen evolution, oxygen evolution, and grid corrosion are unavoidable secondary reactions.

A further secondary reaction is oxygen reduction, the reversal of oxygen evolution. It is a quick reaction at the potential of the negative electrode, and oxygen that reaches its surface, is immediately reduced. In flooded batteries, this reaction is limited to extremely low rates by the slow diffusion of dissolved oxygen. In VRLA batteries, however, the immobilization of the electrolyte allows fast transport of oxygen in the gas-filled space. As a consequence, nearly all the oxygen that is generated at the positive electrode subsequently is reduced at the negative electrode. This is the internal-oxygen cycle that characterizes the VRLA battery. But oxygen that permeates into the cell by a leakage, also reaches quickly the negative electrode and acts as an additional anodic current that causes discharge.

Fig. 1 illustrates the situation. The electrode potential is plotted at the x-axis, the range of the negative electrode on the

left, the range of the positive electrode on the right hand. The two hatched columns represent the equilibrium potentials of the negative and positive electrodes. Their dependence on acid concentration is indicated by the width of these columns. The potential difference of 1.23 V between the beginning of hydrogen and oxygen evolution marks the water decomposition voltage.

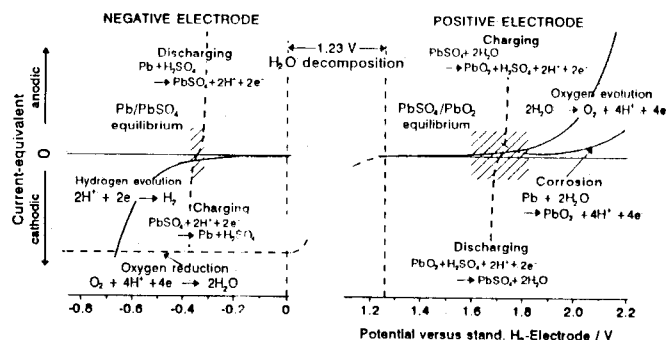


Fig. 1 Reactions that occur in lead-acid batteries vs. electrode potential.

The rates of these reactions are indicated by current potential curves

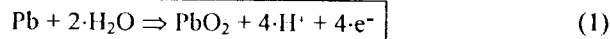
The **charging** and **discharging** reactions are represented by the broken curves. They are very steep, since these reactions are fast, even at a small deviation from the equilibrium potential.

Hydrogen evolution begins at an electrode potential of 0 V which is about 0.3 V above the open-circuit potential of the negative electrode. **Oxygen evolution** begins at 1.23 V which is about 0.5 V below the positive electrode potential. Thus, hydrogen and oxygen evolution already occur at the open circuit potential of the negative and positive electrodes respectively, and gradual self-discharge of both electrodes is

the result. In Fig. 1, both reactions are represented by continuous curves. The gradual increase at their beginning indicates that these reactions occur slowly, as long as the potential difference relative to their origin, the 'polarization' or 'overvoltage', remains fairly small. When, however, this deviation from the equilibrium potential exceeds a certain value, the two curves show a steep increase. This means that hydrogen as well as oxygen generation gain in volume enormously at correspondingly low and high overvoltages.

Corrosion of the positive grid also is an electrochemical reaction. The corrosion rate is at its minimum at about 40 to 80 mV above the PbSO₄/PbO₂ potential. At an electrode potential below this minimum, corrosion increases due to destabilization of the protecting layer. Above this minimum, the corrosion rate follows the usual exponential increase with increasing electrode potential.

Corrosion gradually destroys the current conducting elements, but is also a water consuming reaction, since oxygen that is required for the reaction



is taken from the electrolyte.

Parameters that influence corrosion are grid alloy, manufacturing conditions, and also the size of the grid's surface area.

Oxygen reduction, the reversal of oxygen generation, is possible in the acid electrolyte at an electrode potential below 1.23 V vs. SHE (Standard Hydrogen Electrode). Its rate is largely determined by the rate of oxygen transport and therefore does not depend on the potential of the negative electrode. This is characterized by the horizontal curve in Fig. 1.

Oxygen reduction depends on two factors

1. the amount of oxygen that is generated at the positive electrode or penetrates otherwise into the cell, and
2. the portion of it that subsequently reaches the surface of the negative electrode.

In flooded batteries, the transport of dissolved oxygen through the electrolyte limits this reaction rate to very low values.

1.1 Semi-logarithmic Scale, Polarization, TAFEL Lines

For many electrode reactions the current is an exponential function of the electrode potential. This suggests to plot the current in a logarithmic scale to cover the required wide range. Such a semi-logarithmic plot has the further advantage that often the current/voltage curves form straight lines (TAFEL lines), since they are exponential functions. In the lead-acid battery, this is true for the hydrogen and oxygen gas-evolving reactions. Such a linearisation allows quantitative considerations.

Fig. 2 corresponds in principle to Fig. 1, but is drawn in the semi-logarithmic scale. Since negative logarithms do not exist, cathodic currents, like those for hydrogen evolution and oxygen reduction, are also drawn in positive direction. The horizontal axis also shows the electrode potential, but here it is not referred to the standard hydrogen electrode, but to the deviation from the open circuit potential of the positive and the negative electrodes, i.e., the PbSO₄/PbO₂ and the Pb/PbSO₄ equilibrium potential, respectively. Thus the currents which correspond to the reaction rates, are plotted versus the polarization of the concerned electrode.

Polarization is an important parameter, given by the relations

$$\eta_+ = E_+ - E_+^0 \quad \text{or} \quad \eta_- = E_- - E_-^0 \quad (2)$$

with η_+ and η_- : polarization of positive and negative electrodes respectively
 E_+ and E_- : actual potential
 E_+^0 and E_-^0 : equilib. potential of pos. and neg. electrodes

The cell voltage, as the difference E_+ minus E_- is given by

$$E = E^0 + \eta_+ - \eta_- \quad (3)$$

with E^0 : equilibrium or open circuit voltage of the cell
 η_+ and η_- : polarization of the positive and negative electrode respectively

Polarization has the negative sign when the actual electrode potential is below its equilibrium value.

For float charging, polarization is a very important parameter. The negative electrode is only kept fully charged when its polarization is negative or zero ($\eta_- \leq 0$) while for a charged positive electrode a positive polarization is required ($\eta_+ \geq 0$).

The curves for the various reactions, as far as they are linearized, are described by the relation (TAFEL equation)

$$\eta = a + b \cdot \log(|j|) \quad (4)$$

with b : slope of the TAFEL line (mV per decade of current)

a : Intersection of the TAFEL line with $\eta = 0$

The curves for charging and discharging are not shown in Fig. 2. They would not be linearised in the semi-logarithmic plot, but would form nearly vertical lines on account of the low polarization of these reactions.

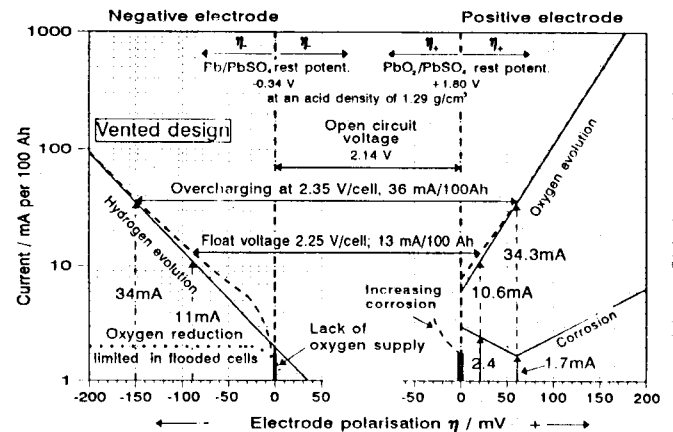


Fig. 2 Secondary reactions in a lead-acid battery vs. electrode polarization in a semi-logarithmic plot. The here assumed open circuit voltage of $E^0 = 2.14$ V/cell corresponds to an acid density of ≈ 1.29 g/cm³. The limited oxygen reduction rate applies to flooded cells

In Fig. 2, hydrogen and oxygen evolution form TAFEL lines that are drawn with their typical slopes of 0.12 and 0.08 V/decade of current respectively. These data depend, of course, on the individual parameters of the considered type of battery such as cell design, used materials and manufacturing methods. The values, used in Fig. 2, were selected for model calculations (1). They are based on experimental data and a larger number of data in the literature and correspond fairly

Summed up for a year's period, it means a coulomb equivalent of 96 Ah ($1 \times 24 \times 365 / 1000$) which corresponds to a water loss of 32 g per year and 100 Ah (*1 Ah decomposes 0.336 grams of water*). It is important to notice that the water loss is proportional to hydrogen escape. Thus water loss can be derived from gas measurements combined with gas analysis. Determination of the weight loss is misleading, since the oxygen lost by corrosion remains in the cell. This applies also for VRLA batteries.

The efficiency of the internal-oxygen cycle would be 18% in this example (2 mA O₂ reduction; 10.6 mA O₂ evolution). This seems to be a high efficiency in a flooded cell, and depends, of course, on the given data. But the internal-oxygen cycle is known to have a considerable influence on the scattering of the individual cell voltage of modern stationary batteries with antimony-free grid alloys that are floated at a low voltage (6).

		2.25 V/cell	2.35 V/cell
Negative electrode	H ₂ evolution	11 mA	34 mA
	O ₂ reduction	2 mA	2 mA
Positive electrode	O ₂ evolution	10.6 mA	34.3 mA
	Corrosion	2.4 mA	1.7 mA
Lost equivalents	Hydrogen (H ₂)	11 mA	34 mA
	Oxygen (O ₂) *	11 mA	34 mA
	Ah per year	96	297
	Water g/year	32	100

Table 1 Values of Fig. 2

*) O₂ evolution minus O₂ reduction plus O₂ loss by corrosion.

When this battery is overcharged at 2.35 V/cell, the polarization of both electrodes is automatically increased until the situation is reached that equal currents flow through positive and negative electrodes. In this example, then the potential of the positive electrode would be close to that of minimum corrosion. Thus, the corrosion rate would be reduced to its minimum of 1.7 mA. But water loss is now increased to an equivalent to 34 mA or 297 Ah per year which means 100 g of water is lost per year and 100 Ah. This approximately is a factor 3 compared to the voltage of 2.25 V/cell. The efficiency of the internal-oxygen cycle is reduced to 5.8% (2 mA reduction, 34.3 mA escape), since the limiting transport rate of oxygen is not changed with charging voltage.

2.2 Float Charging of the Valve-regulated Design

In the valve-regulate design, the electrolyte is immobilized, and thus the hindrance of the oxygen transport to the negative electrode is nearly nullified, since oxygen transport mainly occurs through the gaseous phase and only a thin wetting layer on the surface of the negative electrode has to be penetrated by dissolved oxygen. Thus nearly all the oxygen that is evolved at the positive electrode, reaches the surface of the negative electrode.

Fig. 3 illustrates the situation under the assumption that the efficiency of the internal-oxygen cycle is 100%. I.e., all the oxygen that is generated at the positive electrode, subsequently is reduced at the negative electrode (*In practice, values very close to 100% are usually reached*). Since oxygen evolution is completely compensated by oxygen reduction,

also the equivalents of hydrogen-evolution and corrosion must equal each other. Otherwise, the fundamental rule would be infringed, that equal currents have to flow through both electrodes. Consequently, polarization of both electrodes is now determined by the balance between hydrogen evolution and grid corrosion, as indicated by the dashed horizontal double arrows. At the float voltage of 2.25 V/cell, the required balance is reached at a polarization $\eta_- = -11$ mV and $\eta_+ = 99$ mV of negative and positive electrodes respectively.

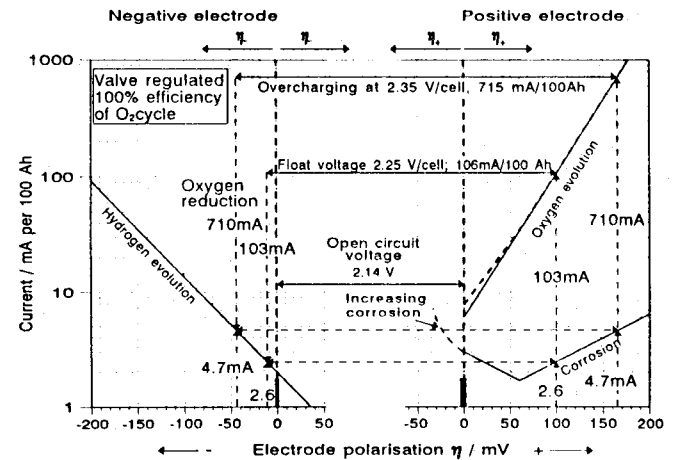


Fig. 3 Float charging of a valve-regulated battery based on the data of Fig. 2, under the assumption that the internal-oxygen cycle has an efficiency of 100%

Compared to Fig. 2 the situation in Fig. 3 is quite different, although both Figures are based on the same data. In the vented design (Fig. 2), the polarization of the electrodes is mainly determined by the balance between hydrogen and oxygen evolution. In the valve-regulated design, polarization of the electrodes depends on the balance between hydrogen evolution and grid corrosion, although both reactions contribute only a small portion of the current.

Fig. 3 indicates the typical situation that in the VRLA battery the polarization of the negative electrode is small compared to that of the positive electrode. If in this example, hydrogen evolution should slightly be increased, or the cell voltage be decreased, the required balance to corrosion possibly could only be achieved at a positive polarization of the negative electrode, but this means discharge.

The advantage of the reduced polarization of the negative electrode is the correspondingly reduced hydrogen evolution. Only an equivalent to 2.6 mA is evolved, i.e., only 24% compared to the vented design in Fig. 2. Water loss is correspondingly reduced, since oxygen is not lost from the cell and only an equivalent of 2.6 mA is consumed by corrosion. 2.6 mA correspond to 23 Ah per year that is equivalent to 8 grams of water. The initial water content of a VRLA battery is about 1000 g per 100 Ah. So, in this example 0.8% of the water content would be lost per year.

At a higher charging voltage, as shown by 'overcharging at 2.35 V/cell', the situation at the negative electrode is less critical, since the positive electrode is polarized to values with an increased corrosion rate. The so increased deficit between float current and oxygen evolution requires a correspondingly increased hydrogen evolution. This again causes a more negative polarization of the negative electrode, and insures so that it remains fully charged.

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Fig. 3 illustrates the situation under the assumption that the efficiency of the internal-oxygen cycle is 100%. I.e., all the oxygen that is generated at the positive electrode, subsequently is reduced at the negative electrode (*In practice, values very close to 100% are usually reached*). Since oxygen evolution is completely compensated by oxygen reduction,

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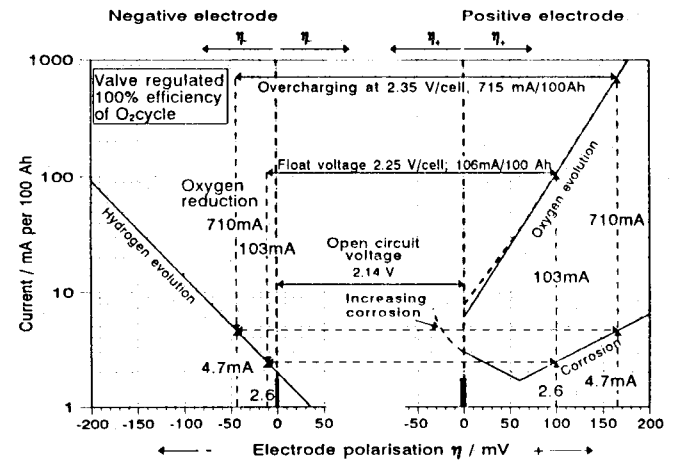


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At a higher charging voltage, as shown by 'overcharging at 2.35 V/cell', the situation at the negative electrode is less critical, since the positive electrode is polarized to values with an increased corrosion rate. The so increased deficit between float current and oxygen evolution requires a correspondingly increased hydrogen evolution. This again causes a more negative polarization of the negative electrode, and insures so that it remains fully charged.

Float charging at an increased voltage would thus be a remedy against the critical situation of the negative electrode. But in practice, this usually is not possible since the gap between charging and discharging voltage would be increased. Further disadvantages are increased hydrogen escape and increased corrosion rate, as shown in Table 2. But terminated boost charging or equalizing charging is occasionally included in monitoring routines for valve-regulated lead-acid batteries to recoup the full capacity of the negative electrodes (7). The effect of such boost charges is, of course, only a temporary one, since they do not change the basic situation in the cell. The increased water loss may be critical, if such boost charging is repeated too often.

The values of Fig. 3 are listed in Table 2

		2.25 V/cell	2.35 V/cell
Negative electrode	H ₂ evolution	2.6 mA	4.7 mA
	O ₂ reduction	103 mA	710 mA
Positive electrode	O ₂ evolution	103 mA	710 mA
	Corrosion	2.6 mA	4.7 mA
Lost equivalents	Hydrogen (H ₂)	2.6 mA	4.7 mA
	Oxygen (O ₂) *	2.6 mA	4.7 mA
	Ah per year	23	41
	Water g/year	8	14

Table 2 Values of Fig. 3

*) Only O₂ loss by corrosion, since O₂ evolution is compensated by O₂ reduction

Table 2 indicates the characteristic situation of a VRLA battery. Compared to the vented design (Table 1), the float current is high, but most of the current is consumed by the internal-oxygen cycle, while hydrogen evolution and thus water loss is low. Even at the increased float voltage, hydrogen evolution and water loss are less than doubled, although the internal-oxygen cycle and so the float current is increased by a factor of 7.

Fig. 3 shows that a certain hydrogen evolution remains, even at zero polarization of the negative electrode (2 mA/100 Ah in this example). This figure represents the self-discharge rate of the negative electrode and simultaneously stands for the minimum of water loss that can be reached with a fully charged negative electrode. The value of 2 mA in this example corresponds to an equivalent of 17.5 Ah per year, or a water loss of 6 grams per year and 100 Ah. This is less than one per cent of the water content in such a battery. Nevertheless, this water loss is one reason for the slight decrease of the capacity with proceeding service life, usually observed with VRLA batteries. To keep this effect as small as possible, hydrogen evolution must be kept as low as possible.

2.2.1 Rates of Hydrogen Evolution and Grid Corrosion

Water loss of a VRLA battery is proportional to hydrogen evolution. Fig. 3 shows, furthermore, that at a high efficiency of the internal-oxygen cycle, balance between hydrogen evolution and grid corrosion determines the polarization of positive and negative electrodes. Thus in VRLA batteries, two conditions have to be observed for these reactions:

1. The rates of hydrogen evolution and grid corrosion should be as small as possible to minimize water loss.

2. An appropriate balance between these rates is also required to ensure that both electrodes are sufficiently polarized.

The rate of hydrogen evolution is influenced by a number of parameters. It is markedly increased by foreign metals, like nickel or antimony, that are precipitated on the negative electrode. The state of charge of the negative electrode is a further parameter that influences hydrogen evolution, since the rate of self-discharge decreases with progressing discharge. Thus a partly discharged negative electrode generates less hydrogen than the same electrode when fully charged. This is of great importance in regard to the above described problem that the polarization might not be sufficient to keep the negative electrode fully charged. The effect of a reduced hydrogen evolution is illustrated Fig. 4. The continuous line corresponds to that in Fig. 3, the dashed one represents a hydrogen evolution rate that is reduced to 50%. In the logarithmic scale this means a corresponding shift in parallel.

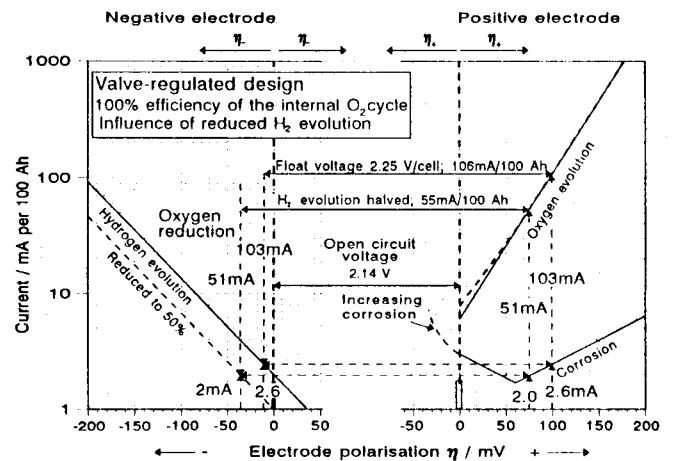


Fig. 4 Influence of a reduced hydrogen evolution on float charging. The Figure is based on Fig. 3 and shows how the situation would be changed at a hydrogen evolution rate reduced to 50%. As in Fig. 3, 100% efficiency is assumed for the internal-oxygen cycle.

Fig. 4 shows that with reduced hydrogen evolution, the polarization of the negative electrode is increased. As a consequence, in a battery with a too high hydrogen evolution rate, balance between hydrogen evolution and grid corrosion will be reached after a certain amount of negative capacity has been lost. The partly discharged negative electrode remains then at zero polarization, but is not further discharged.

It depends on the extent of the initial imbalance, how far the negative electrode must be discharged until this balance is reached. If the initial imbalance is small, a discharge of a few percent of the negative electrode already may re-establish balance. Then the capacity of the battery may hardly be influenced. But a larger imbalance between hydrogen evolution and corrosion will cause a significant loss of the available battery capacity after a period of float charge.

Since the balance between hydrogen evolution and grid corrosion is the decisive quantity, an increased corrosion rate would also increase the polarization of the negative electrode. But the increased corrosion would be balanced by a correspondingly increased hydrogen evolution. Thus, balance would be reached, but at an increased water loss.

In general, the use of less corrosion resistant grid alloys is inconsistent with a long service life of the battery, and such

an alloy might cause additional problems, like grid growth or release of critical additives. A too high corrosion rate would even provoke a very critical situation. It would reduce the polarization of the positive electrode below the value of corrosion minimum, and a reduction to $\eta_+ \leq 0$ would cause accelerated disintegration of the positive grid. Both aspects underline the necessity for the use of highly corrosion resistant alloy in valve-regulated lead-acid batteries.

So, a decrease of the hydrogen evolution rate should be the choice to achieve the desired polarization of the negative electrode. But this may be hindered by technical and financial problems, since the purification of the available raw materials may be too expensive.

2.2.2 Reduced Efficiency of the Internal Oxygen Cycle

The condition that hydrogen evolution must equal grid corrosion depends upon the 100% efficiency of the internal-oxygen cycle. Only then all the oxygen that is generated at the positive electrode, subsequently is reduced at the negative electrode, and only then oxygen generation and reduction are completely balanced. At a lower efficiency, a portion of the generated oxygen is lost, and a corresponding additional hydrogen evolution is required to balance this oxygen loss. Such a reduction of the efficiency can, e.g., be caused by too much electrolyte in the cell that hinders the rapid oxygen transport by filling a larger portion of the pore system. Fig. 5 shows an example, where the efficiency of the internal-oxygen cycle is only 98%.

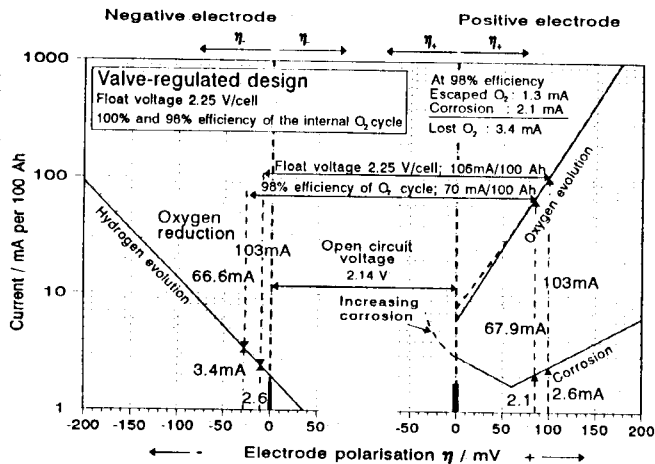


Fig. 5 The consequence of a reduced efficiency of the internal-oxygen cycle. The Figure is based on the data of Fig. 3, but only 98% of efficiency is assumed for the internal-oxygen cycle.

In this example, an equivalent of 1.3 mA of oxygen does not reach the negative electrode surface but escapes together with the hydrogen from the cell. Since this amount of oxygen is not available for reduction, a corresponding increase of the hydrogen evolution rate is required. This causes a corresponding negative polarization, as shown in the Figure.

Compared to Fig. 3, the corrosion rate is slightly reduced, since the positive electrode is less polarized. The situation of the negative electrode is improved, since its polarization is increased from -11 to -29 mV. But water loss is increased too, since the lost oxygen is automatically compensated by a correspondingly increased hydrogen evolution.

Furthermore, such a situation would not be stable. The gradual water loss increases automatically the efficiency of the

internal-oxygen cycle, since more and more of the pore system is opened for rapid oxygen transport. From practice it is known that, after a certain service life, usually more than 99% of efficiency is reached, even if the battery started at a comparatively low efficiency.

2.2.3 The Use of a Catalyst within VRLA batteries

The idea to use catalytic recombination in batteries is very old. So in 1912 a patent was granted to Edison (8) to remove gases from storage batteries by using an electrically heated platinum wire in the gas phase for the recombination of hydrogen and oxygen. A great number patent claims to minimize the water loss of lead acid batteries with the aid of such recombinators are also known (cf., e.g., (9)), and with vented lead-acid batteries they are used to some extent where they are inserted instead of the vent plug (cf., e.g. (3), p. 260). The possibility to improve the float situation of VRLA batteries with the aid of an inserted catalyst was initiated at Philadelphia Scientific International (10). The effect of such a catalyst is demonstrated in Fig. 6:

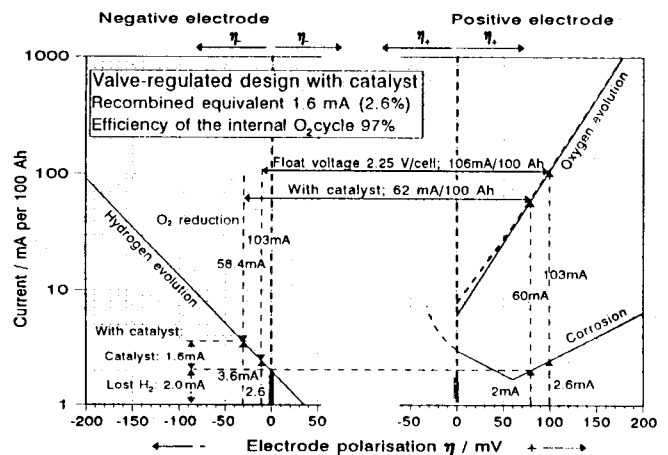


Fig. 6 The effect of a catalyst in a valve-regulated battery. The Figure is based on the data of Fig. 3.

The catalyst reduces the efficiency of the internal-oxygen cycle, since it recombines a portion of the generated oxygen directly with the surplus of hydrogen that mainly fills the gaseous space of the cell. The consequence is a reduction of the efficiency of the internal-oxygen cycle, and, as in Fig. 5, an increased amount of hydrogen must be evolved at the negative electrode to fulfill the fundamental rule that equal current has to flow through both electrodes. In this example, the polarization of the negative electrode is increased to -28 mV, and corrosion is reduced to an equivalent of 2.1 mA.

The main advantage of this method is that the reduced efficiency of the internal-oxygen cycle does not cause water loss. The oxygen that is 'stolen' from the internal-oxygen cycle and the corresponding equivalent of hydrogen are converted by the catalyst into water that remains in the cell. For this reason water loss corresponds to hydrogen escape which again equals the corrosion rate when the efficiency of the internal-oxygen cycle is 100%. In the example of Fig. 6 hydrogen escape equals 2 mA which amounts to 17.5 Ah or 6 g of water per year and 100 Ah.

2.3 Oxygen Intake by a Leakage

Oxygen intake by a leakage is dangerous in VRLA batteries, since the gas channels within the immobilized electrolyte allow easy access of oxygen to the surface of the negative electrode. The additional amount of oxygen depolarizes the electrode and acts as an additional anodic current. At the usual thickness of the container wall of about 4 mm, even a small leakage of the area of 0.1 mm² causes an oxygen diffusion rate equivalent to about 1 mA. Fig. 7 illustrates the influence of such a leakage.

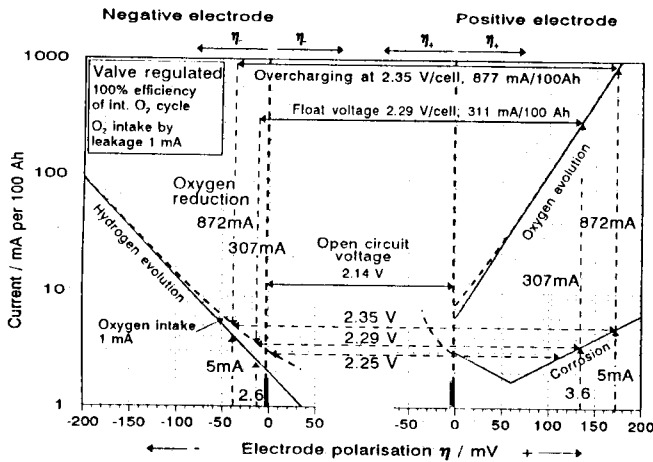


Fig. 7. Influence of oxygen intake equivalent to 1 mA

Since the oxygen intake acts like an additional anodic current at the negative electrode, corrosion must now balance hydrogen evolution and the equivalent of the oxygen intake.

Fig. 7 shows that float charging at 2.25 V/cell would no longer be possible, since the required balance between hydrogen evolution and grid corrosion would only be reached at a positive polarization of the negative electrode ($\eta_- > 0$). But this means discharge of the electrode.

A negative polarization of $\eta_- = -11$ mV, corresponding to the situation at 2.25 V/cell in Fig. 3, is now only reached at a voltage of 2.29 V/cell. Then the polarization of the positive electrode would be increased to about 170 mV. Oxygen loss by corrosion would be increased to 3.6 mA. This oxygen loss, however, is compensated by 1 mA due to the amount of oxygen that additionally is reduced at the negative electrode. Thus, water loss corresponds to 2.6 mA and so equals hydrogen evolution. Also in this situation the escape of hydrogen corresponds to water loss, and this is the only parameter which can be used to determine water loss.

For cycling applications, controlled oxygen intake with the aid of a double acting valve has been occasionally considered as a measure to reduce water loss (11). In stationary applications it would make no sense, since the internal pressure always is slightly above that of the surroundings. For this reason, the valve would not open.

3 Experimental Results

The given explanations will be illustrated by the results of a test that is running at the PSI laboratories since the end of 1996. The used cells are so called 'Premium cells' designed for long service life. Their nominal capacity is 125 Ah at the

10hour rate. (For comparison, all the following figures are referred to 100 Ah). The 'catalyst cells' are equipped with the catalyst, the 'control cells' are as delivered by the manufacturer. Both groups are run in different strings. One cell in each string was equipped with a mercury sulfate reference electrode. For gas measurements fine bore thick wall Teflon tubes were inserted with a pressure relief valve having a stainless steel spring set at 1.5 psi (103 mbar). The cells were standing in a common water tank with the water flowing around each cell. The escaping gas was separately collected for each cell.

The gassing rate of the of the control cells was rather uniform, at the beginning about 80 ml/day and 100 Ah, after 64 weeks of continual float charge reduced to about 60 ml/day. Assumed that it is only hydrogen that escapes from the cells, 1 ml/day would be equivalent to 0.09 mA (1 Ah corresponds to 0.448 l of H₂ at 20 °C). So the gassing rate means that an equivalent of 7.2 mA/100 Ah escapes at the beginning which later was reduced to 5.6 mA/100 Ah.

The gassing rate of the catalyst cells was less uniform and amounted to less than 10 ml/day. This can be explained by a correspondingly low corrosion rate, provided that all the evolved oxygen is recombined by the catalyst. 10 ml/day are equivalent to 0.9 mA.

Fig. 8 shows the float situation according to the experimental values at the beginning of the test, compared to the data used in Fig. 3. In this Figure, a hydrogen loss of 1.5 mA is assumed which is increased by 0.6 mA compared to the measured value. According to former experience (e.g., (4), Section 4.2), this seems to be a plausible figure, since despite all precautions a certain amount of hydrogen is always lost, which gains in significance at such low rates.

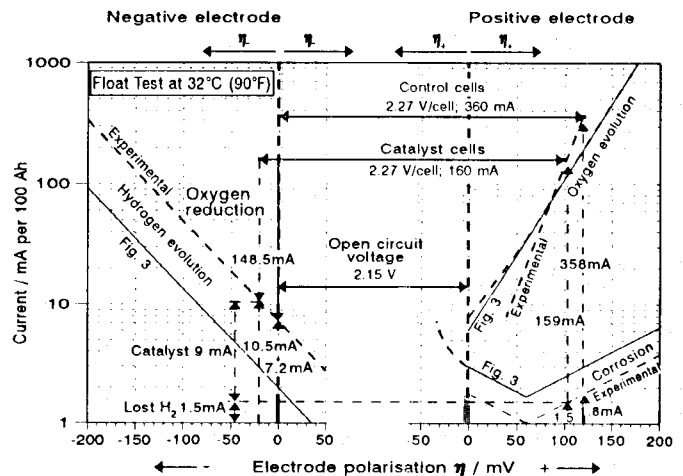


Fig. 8 Float charging of cells without and with catalysts. VRLA batteries with AGM separation. Float charging at 2.27 V/cell at 32°C (90°F).

Compared to Fig. 3, the hydrogen evolution obviously is markedly increased. Partly this is due to the elevated test temperature, but in Fig. 3, this should have caused an increase to only about 4 mA/100 Ah at $\eta_- = 0$. The grid corrosion rate, on the other hand, seems to be very low in these premium cells, despite the increased temperature. On the whole, the experimental curves indicate a strong imbalance between hydrogen evolution and grid corrosion, which is confirmed by the results shown in the following Figures 9 to 12.

Table 3 summarizes the determined values

	Control cells	Catalyst cells
Float current	360 mA	160 mA
Polarization of the neg. el. (η_-)	0 mV	-20 mV
Polarization of the pos. el. (η_+)	120 mV	100 mV
Hydrogen escape	7.2 mA	1.5 mA ^(*)
Loss of oxygen by corrosion	1.8 mA ^(*)	1.5 mA ^(*)

Table 3 Data for control cells and catalyst cells in Fig. 8.

^(*) experimental value 0.9 mA; ^(*) arbitrary estimation

According to Fig. 8, the catalyst reduces the efficiency of the internal-oxygen cycle to 93% (O_2 evolution equivalent to 159 mA, O_2 reduction 148.5 mA). The recombined equivalent of 9 mA or 5.6% of the evolved oxygen is a small share. Nevertheless it is quite effective, since the polarization of the negative electrode is only determined by the difference between evolved and reduced oxygen, since this difference requires a correspondingly increased hydrogen evolution.

Fig. 9 shows the current that was drawn by both groups of cells. It remained approximately constant for the catalyst cells. The last value is put in parentheses, since it was taken after the insertion of a new type of catalyst.

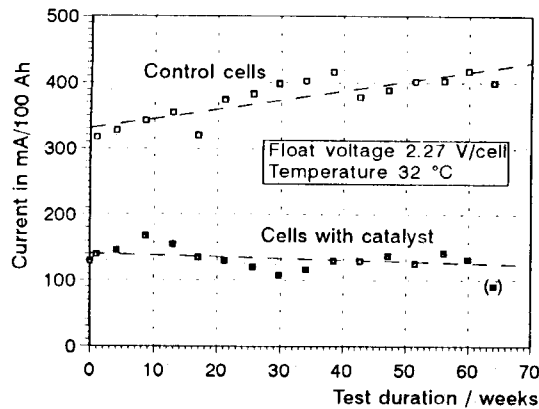


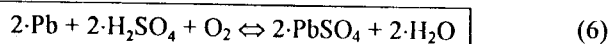
Fig. 9 Current consumption during float charge.

With the control cells, a steady and significant increase of the float current is observed that indicates a gradual change from the very beginning of the test. The reason is the dilution of the acid due to progressing discharge of the negative electrodes, as was confirmed by a capacity test after 64 weeks and a number of simultaneous measurements.

Acid dilution influences the equilibrium potential of the oxygen electrode



In the experiment, the float voltage of 2.27 V/cell was kept constant, and since the negative electrodes of the control cells were not polarized ($\eta_- = 0$) their potential remained at the Pb/PbSO₄ potential. For this reason, changes of the potential of the oxygen electrode referred to the Pb/PbSO₄ electrode would be equivalent to changes referred to the float voltage. The equilibrium voltage of the oxygen electrode versus the Pb/PbSO₄ electrode is given by



and the corresponding Nernst equation is

$$E = E^0 - \frac{RT}{2F} \ln \frac{a_{H_2O}}{a_{H_2SO_4}} = E^0 + 29.5 \cdot \log \frac{a_{H_2O}}{a_{H_2SO_4}} \text{ mV} \quad (7)$$

The acid concentrations at the beginning and the end of the test period of 64 days can be derived from the open-circuit voltages shown in Fig. 10.

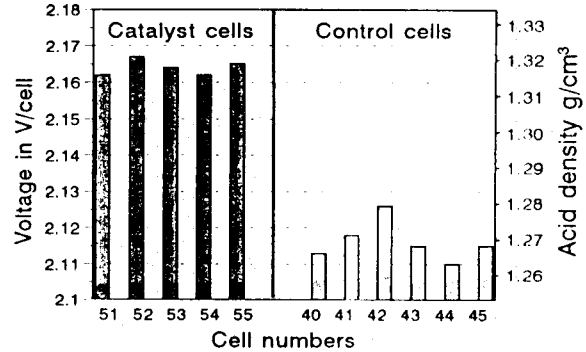
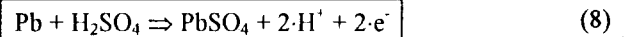


Fig. 10 Open-circuit voltage and corresponding acid densities after 64 weeks of float charging at 2.27 V/cell and 32°C (90°F)

Activities a_{H_2O} and $a_{H_2SO_4}$ and their dependence on acid concentration are listed in (12). With the aid of these values, the result of Equation 7 is a reduction of the oxygen electrode vs. the Pb/PbSO₄ electrode by $\Delta E = E_{\text{initial}} - E_{\text{end}} = 7 \text{ mV}$. It means that the polarization of the oxygen electrode is correspondingly increased. With the usual slope of the TAFEL line for oxygen evolution of 80 mV per decade, 7 mV mean a factor of 1.22 for the current. The initial current of 360 mA/100 Ah should be increased to 440 mA/100 Ah, which is in good agreement with the values shown in Fig. 9. It confirms that acid dilution caused by discharge of the negative electrodes started at the beginning of the test.

Fig. 10 indicates the significant reduction of the acid concentration. If the positive electrode remains charged and only the negative suffers discharge, the acid consuming reaction is:



This reaction would consume 98.1 g H₂SO₄ and require 53.6 Ah

The initial acid density of 1.305 g/cm³ corresponds to 40 wt% of H₂SO₄. At the end, the acid density was reduced to 1.27 g/cm³ which corresponds to 36 wt% of H₂SO₄. The amount of H₂SO₄ that was consumed, depends on the initial content within the cell. This is not known exactly and can only be guessed. Normally, VRLA batteries contain between 800 and 1000 g of water per 100 Ah. In Table 4 figures are listed for both values.

Initial content		Content at the end		$\Delta(H_2SO_4)$	$\Delta(Ah)$
H ₂ O	H ₂ SO ₄	H ₂ O	H ₂ SO ₄		
g	g	g	g	g	Ah
1000	666	977	549	117	63
800	533	777	437	96	52

Table 4 Amount of charge that has been lost from the negative electrodes in the control cells according to Equation 6. The evaluation is based on an initial density of 1.305 g/cm³ (40 wt%) and 1.27 g/cm³ (36 wt%) at the end

The water loss was derived from the mean gassing rate of 70 mA which corresponds to 67 Ah or a water loss of 23 g within the 64 weeks of test.

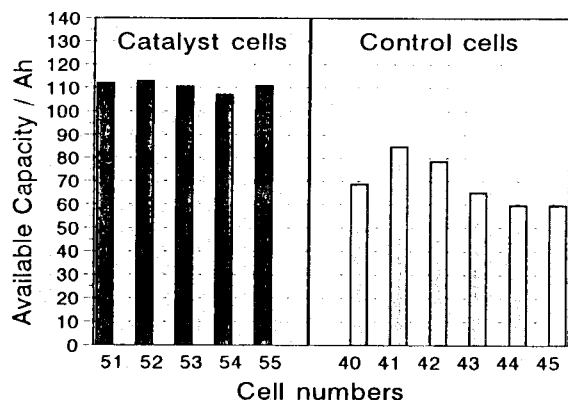


Fig. 11 Capacity test after 64 weeks of float charging at 2.27 V/cell and 32°C. Discharge at 32°C; discharge at 25 Ah to 1.75 V/cell

This estimation is only approximative, since the correct water content of the new batteries is not known, and the usual oversize of the negative electrodes would furthermore distort the result. Despite these limitations, the result of these calculations is supported by the result of the capacity test, shown in Fig. 11. In the average, the control cells reached only 64% of the capacity of the catalyst cells, and two of them had been reduced to 55% of that value. The correspondence between the calculation and the capacity loss confirms that only the negative electrode suffered discharge. Otherwise, e.g. in the case of a short circuit, twice the amount of H_2SO_4 would have been consumed.

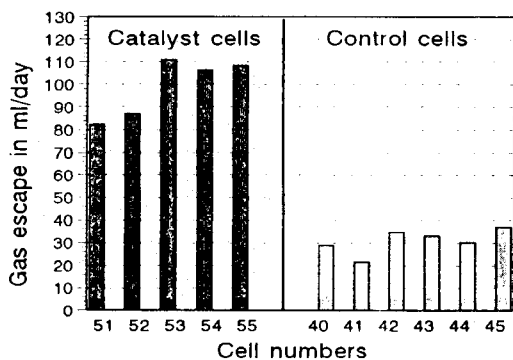


Fig. 12 Open-circuit gassing after 64 weeks of charging at 2.27 V/cell and 32°C and two weeks at open circuit

Open circuit gassing was also measured at the end of the float charging. The result is shown in Fig. 12. Due to the immobilized electrolyte, nearly all of the oxygen that is evolved by self-discharge of the positive electrode will reach the surface of the negative electrode and be reduced and gradually discharge this electrode. So the gassing rate reflects mainly hydrogen evolution at the negative electrode. Fig. 12 shows that the gassing rate of the catalyst cells corresponds to the gassing rate of the control cells at the beginning of the float test (70 ml/day and 100 Ah correspond to 6.75 mA/100 Ah). This confirms that the negative electrodes in the catalyst cells are still fully charged, as was stated by the capacity measurements (Fig. 11). On the other hand, the reduced hydrogen evolution of the discharged control cells supports the arguments mentioned in connection with Fig. 4, namely that the

float charge situation may be stabilized and further discharge stopped, if the initial imbalance had not been too large.

4 Summary and Outlook

When VRLA batteries were introduced to the market, the fundamental idea was that the internal-oxygen cycle had to be as effective as possible to reduce water loss, and so allow a long service life without water refill. In today's VRLA batteries such a desired high efficiency of the internal-oxygen cycle is reached. But this causes the further requirement that hydrogen evolution and grid corrosion have to balance each other, otherwise one of the electrodes will not be sufficiently polarized and gradually lose its charge. Alloys of extremely high corrosion resistance have been developed, but hydrogen evolution cannot be reduced arbitrarily at reasonable expense. As a result, it is usually the negative electrode that is endangered to be partly discharged after certain periods of float charge.

The insertion of a catalyst into the gas space of the cell seems to be the most effective method to overcome this problem, since it does not affect the charging or performance data and does not cause increased water loss. A question that still has to be answered is the service life of such a catalyst. This can only be done by experience, but the prospects are favorable: The VRLA battery is a 'clean' system that does not contain substances like antimony that are known as 'poisons' for a catalytic surface. Furthermore, its internal atmosphere is rather dry and due to the usually higher acid density of the acid, the vapor pressure of the electrolyte is low and the formed water will easily evaporate from the catalyst.

References:

- (1) U.Teutsch, Proc. 1st Telescon Meeting, Berlin 1994, ©IEEE Communications Soc., p.89
- (2) F.J.Vaccaro, J.Rhoades, and B.Le, Proc. 19th Intelec Meeting, Melbourne 1997, © IEEE Communications Soc., p.230
- (3) D.Berndt, Maintenance-Free Batteries, RSP Ltd and John Wiley & Sons Inc., 1997, p.53
- (4) D.Berndt, R.Bräutigam and U.Teutsch, Proc. 17th Intelec Meeting, The Hague, 1995, © IEEE Communications Soc., p.1
- (5) S.S.Misra, T.M.Noveske and A.J.Williamson, Proc. 16th Intelec Meeting, Vancouver 1994, © IEEE Communications Soc., p.250
- (6) W.B.Brecht, Proc. 9th Intelec Meeting, Stockholm, 1987, © IEEE Communications Soc., p.99
- (7) K.E.White, Proc. 18th Intelec Meeting, Boston 1996, © IEEE Communications Soc., p.624
- (8) T.A.Edinson U.S.Pat. 1,016,874 (1912)
- (9) A Winsel and K Ledjeff, German Pat. Appl. DE 3029244 (1980)
- (10) W.E.M.Jones and D.O.Feder, Batteries International, Issue 33, October 1997, p.77
- (11) Batteries International, Issue 17, January 1994, p.86
- (12) K.R.Bullock, J. Power Sources, 35 (1991) 197