

VRLA batteries electrochemical factors affecting life

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Abstract

Valve-regulated lead–acid (VRLA) batteries have been revealed as showing an impressive cycle life performance, which compared with the equivalent flooded type, yields increments as large as three–five times. These impressive results have been achieved even though components, such as lead–calcium alloys, which are not especially adequate for obtaining high cycle lives are used. The report is concerned with the electrochemical factors, that determine such performance. The development of the new ORBITALTM battery, especially the cycling version, has been possible, through an optimisation process of the parameters determining life performance. In this way lives approaching 1000 cycles at 60% depth-of-discharge (DoD) have been achieved, which open the possibility to use such batteries in cycling applications, up to now restricted to other technologies like gel batteries. A review of the electrochemical factors, determining such performance is presented in an attempt to highlight the electrochemical basis of VRLA performance.

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1. Introduction

Valve-regulated lead–acid (VRLA) battery was introduced on a commercial basis at the beginning of the 1980s, first for SLI applications and later for standby use. From the very beginning, it was clear, that the new battery, exhibited some very distinctive characteristics with respect to the flooded equivalent types. Especially significant were the clear differences observed on cycle life performance, with figures doubling the duration of standard batteries from the very beginning. As development of the new battery progressed, new values confirmed initial results, and quantified the differences in performance between the two batteries.

Based on the previous results, specific programs were devoted to the development of the new technology for cycling applications. These programs revealed the exact possibilities of the new technology, with increases around three times with respect to flooded types. These impressive results, are the consequence of a number of factors, some of them affecting the product design and the others being of an electrochemical nature. The first ones include the characteristics of the positive active material, (density, phase composition), and the degree of compression of the separator. The electrochemical factors, are basically related to the potential distribution within the cell, which in turn is

determined by cell macroscopic properties such as the degree of saturation of the separator.

Another very important electrochemical issue, to achieve high cycle life, is the kind of charge that the battery receives during cycling. The degree of overcharge, and especially the type of charge, is of paramount importance to determine life performance. This paper analyses the influence of the electrochemical factors on cycling use.

2. Theoretical foundation

The basic electrochemical reactions, of VRLA batteries, are essentially the same as the ones of the flooded types. The only difference, is that on VRLA batteries, reactions leading to the recombination of oxygen take place, and on flooded batteries these are not operative. The occurrence of these reactions, has important consequences in terms of battery characteristics, allowing a completely maintenance-free operation, as well as on electrochemical performance, due to the modification of the potentials within the cell.

Once the transformation of the active materials is complete and charge enters the Tafel region, in which $I-U$ relationships in the battery are determined by oxygen and hydrogen evolution, the influence of the recombination reactions, begins to take place. Fig. 1 gives the $I-U$ relationship in the Tafel region for both the flooded and VRLA batteries [1].

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LEAD ACID BATTERY, FLOAT CHARGING CURRENT FLOW IN VENTED AND SEALED VERSION

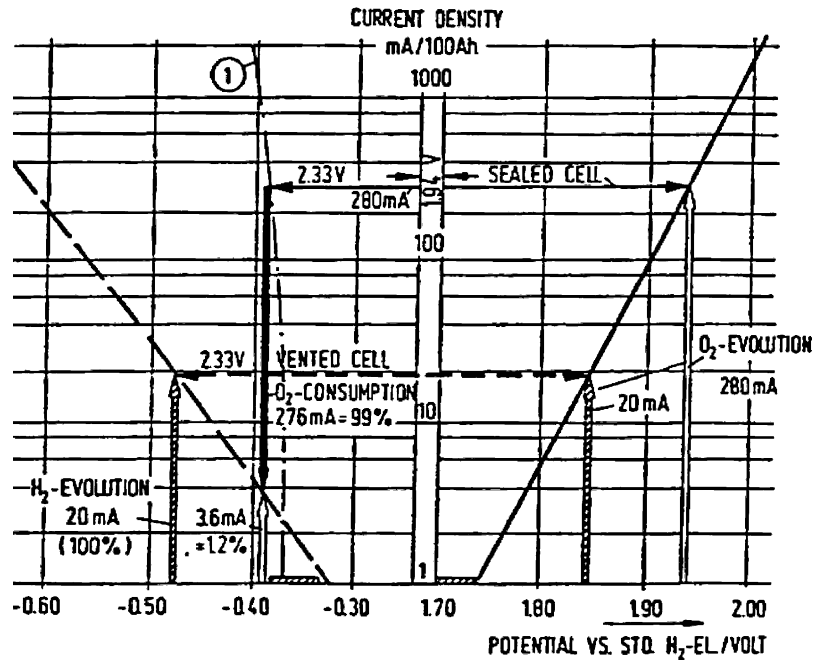


Fig. 1. Polarisation characteristics of sealed and vented cells: plate potential is shifted in the anodic direction by the oxygen recombination reaction.

Three main facts become evident from this diagram:

- the dramatic increase of final charging current;
- the different effect of cathodic current;
- the modification of electrode potential.

Let us review each of them in more detail.

2.1. Charging current

For the same charging voltage, the current flowing through the cell experiments a 10-fold increase in VRLA batteries. This is a consequence of electrode potential modifications, the cathodic current being no longer determined by the line defining hydrogen evolution, but by the line defining the $I-U$ relationship for reduction of the negative active material, which has a much higher slope (recombination reactions, keep the negative plate slightly discharged).

2.2. Effect of cathodic current

Most of the cathodic current is used to maintain operative the oxygen recombination cycle. In fact about 99% of this current is used to reduce the oxygen generated on the positive plate that reach the negative, and only about 1% to hydrogen evolution. This fact is quite important because it allows a totally maintenance-free operation with only marginal amounts of water consumption due to hydrogen evolution.

2.3. Modification of electrode potentials

This is the key point for the purpose of this paper. As it is clearly seen, electrode potentials have been modified with respect to the flooded battery. Both potentials are shifted in the anodic direction. As a consequence, the negative plate becomes less polarised, whereas polarisation increases for the positive plate becoming more positive. This fact is the essential point to explain why all the facts affecting the degree of recombination efficiency are so important in determining the cycle life of VRLA batteries.

Lead-acid batteries performance on cycle life, is normally determined by the positive plate. On the other hand, charge acceptance of the positive is significantly lower than that of the negative, because competitive reactions like oxygen evolution begin to take place before total transformation of the positive active material has occurred. In VRLA batteries and due to the potential modification, a more complete recharge is essential for increasing cycle life performance.

3. Experimental

3.1. Cycling application

3.1.1. Influence of separator degree of saturation

In order to study the influence of the degree of separator saturation on cycle life, six VRLA batteries of the Golf Car

type were tested, four batteries with a separator saturation of 97%, leaving the other two with a saturation of 100%.

3.1.1.1. Battery characteristics.

- Technology: VRLA;
- rating: 6 V/180 Ah;
- plates: pasted type, with lead–calcium alloy grids.

The batteries were assembled, and container formed obtaining, after formation, the saturation values indicated above.

3.1.1.2. *Cycling test.* The test profile selected, includes a partial-state-of-charge cycling with periodic recharges. The particular conditions were:

- cycling between 60 and 80% SOC, charging and discharging exactly the same amount on each cycle;
- complete recharge every 25 cycles;
- control discharges every 50 cycles.

3.1.1.3. *Results.* Fig. 2 gives the evolution of the capacities of the control discharges with cycling. The four batteries with 97% saturation, show similar behaviour all with cycling, with an initial stabilisation for the first 400

cycles, followed by a steady decline until reaching the end of life.

On the other hand, the two batteries with 100% saturation, shows a clearly distinctive performance. Just from the very beginning, a marked decline of capacities is evident.

At 350 cycles, both batteries were submitted to a controlled gasification charge to eliminate the excess of electrolyte and adjust the degree of saturation to the same level as the other batteries.

3.1.1.4. *Gasification charge.* Gasification charge was made at a rate of $0.02 C_{10}$, for 150 h, which make a total of 525 Ah. During charge, weight, and voltage of batteries were taken at regular intervals, as shown in Fig. 3.

For most of the time the voltages of both batteries remain high reaching values as high as 2.7 V per cell indicating that the batteries perform as a flooded type, but when the batteries lose 3% of water, there is a sharp decline of the voltages reaching, values of 2.4 V per cell, indicating a sharp increase of the recombination efficiency.

From this point on, the electrical performance of the batteries changes sharply, with a marked increase of capacity, and a totally similar evolution to the other batteries. This fact, demonstrates the key importance of the degree of separator saturation on cycle life performance.

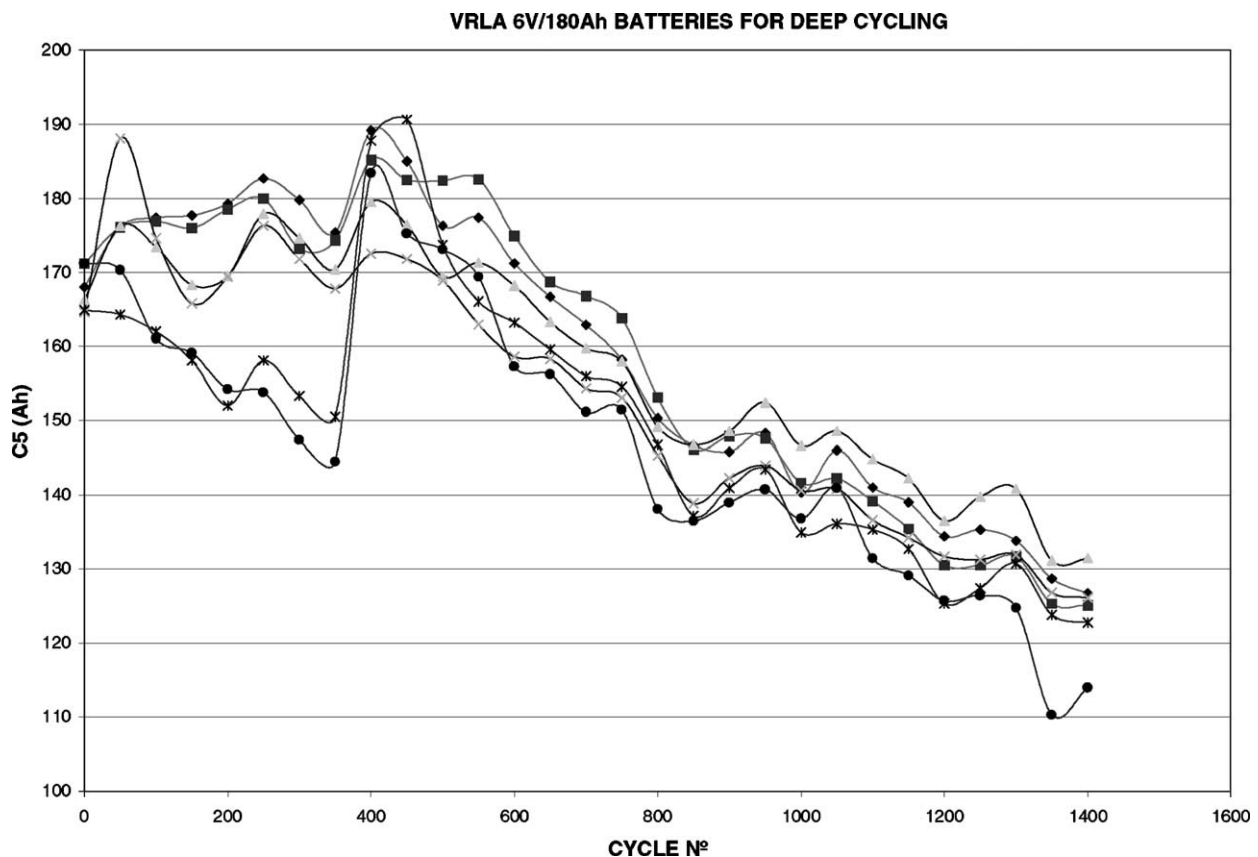


Fig. 2. Cycling characteristics of VRLA batteries with different separator degrees of saturation. Batteries with 100% saturation, falls prematurely, and once adjusted, they perform like the rest.

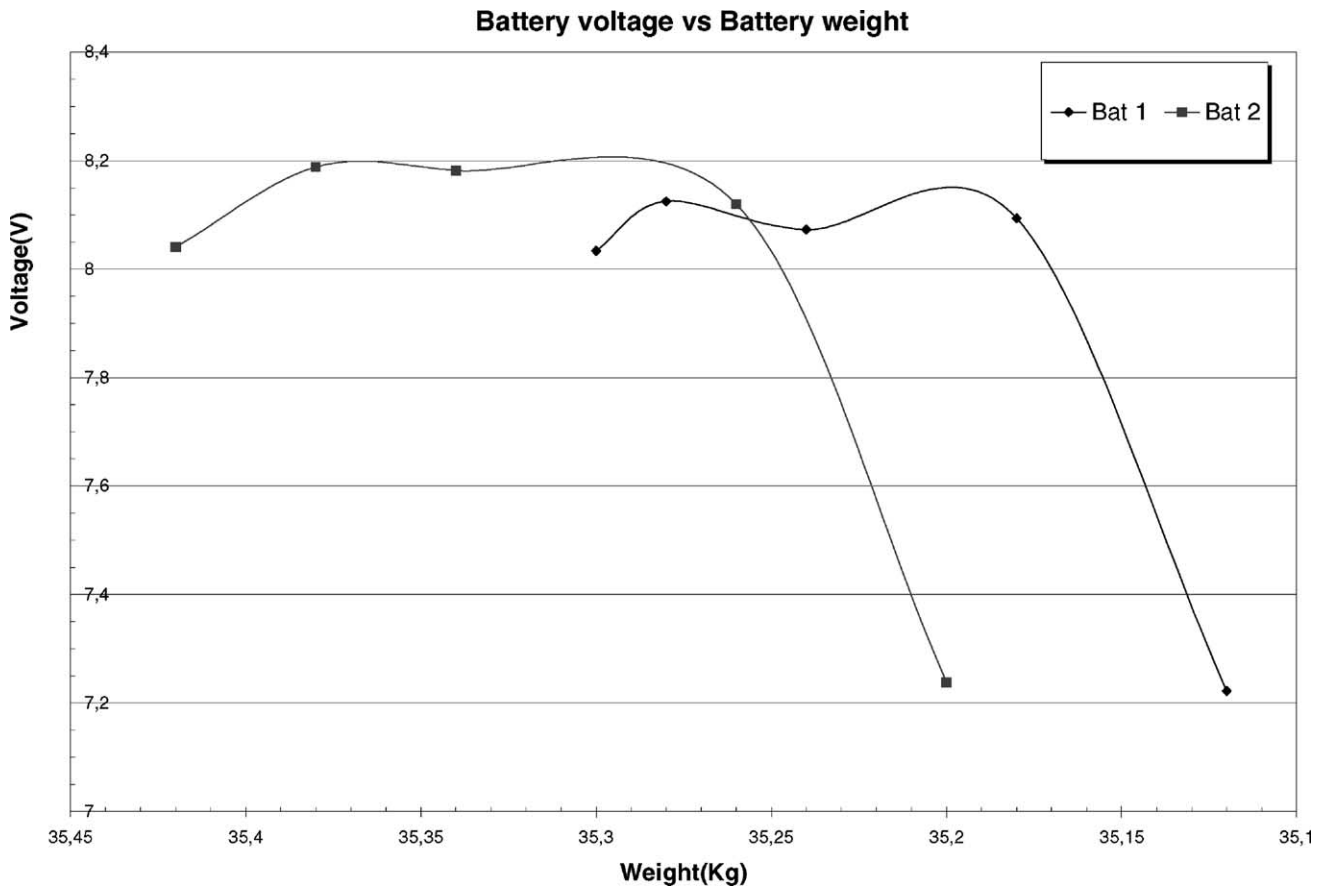


Fig. 3. Gassing characteristics of VRLA batteries. Voltages remains stable and high while saturation is high. Once saturation falls to around 97%, there is a sharp decrease, indicating that the oxygen recombination reaction is operative.

3.1.2. Influence of charging conditions

VRLA batteries are more prone to develop imbalances between cells, resulting in different charging voltages at the end of charge. From the $I-U$ diagram it is clear that there is a potential modification within the cell, as the recombination efficiency changes, but this modification depends on the particular condition of each cell. It is quite difficult to adjust exactly the degree of saturation of all the cells to the same value, and hence differences are unavoidable. Battery performance reflects the imbalances, being limited by the cells with the lowest final charging voltages. Because these cells do not reach complete recharge, the situation becomes worse as the cycling progresses, finally resulting in battery failure.

In order to try to overcome this situation, a series of cycling tests with different charging conditions, have been made as described below.

3.1.2.1. Tests. To try to study the influence of charge, a batch of ORBITAL deep cycle batteries were cycled according BCI specification (25 A, 10.5 V), using three different charging profiles:

- *IU* charge (15 V): constant current charge, 20 A, with voltage limitation at 15.0 V, recharging 110% of previous discharge.

- *IU* charge (15.6 V): constant current charge, 20 A, with voltage limitation at 15.6 V, recharging 120% of the previous discharge.
- *IUI* charge (14.4 V + 1 A, 2 h): constant voltage limited charge at 14.4 V, until 100% of previous discharge is recharged, followed by a final constant current equalisation step at 1 A, 2 h, without voltage limitation.

Every 50 cycles, all the batteries were completely recharged according to EN 50342 (20 A, 14.4 V, followed by constant step at 1.25 A, 4 h).

3.1.2.2. Results. Results are included in Fig. 4, in which it is clearly seen the enormous difference between the group charged with *IUI* profile and the other two. The two charging profiles at constant voltage without final charging step, are unable to sustain the performance of the batteries, no matter how high the recharging factor. Increasing charging voltage from 15 to 15.6 V, the charging factor increased from 110 to 120%, but even this high factor is unable to maintain the battery capacity, allowing only an initial increase. On the other hand, the use of such high charging voltages can have very deleterious effects on the batteries. In fact charge acceptance is strongly modified, undergoing a sharp increase, as evidenced by the time needed to achieve the

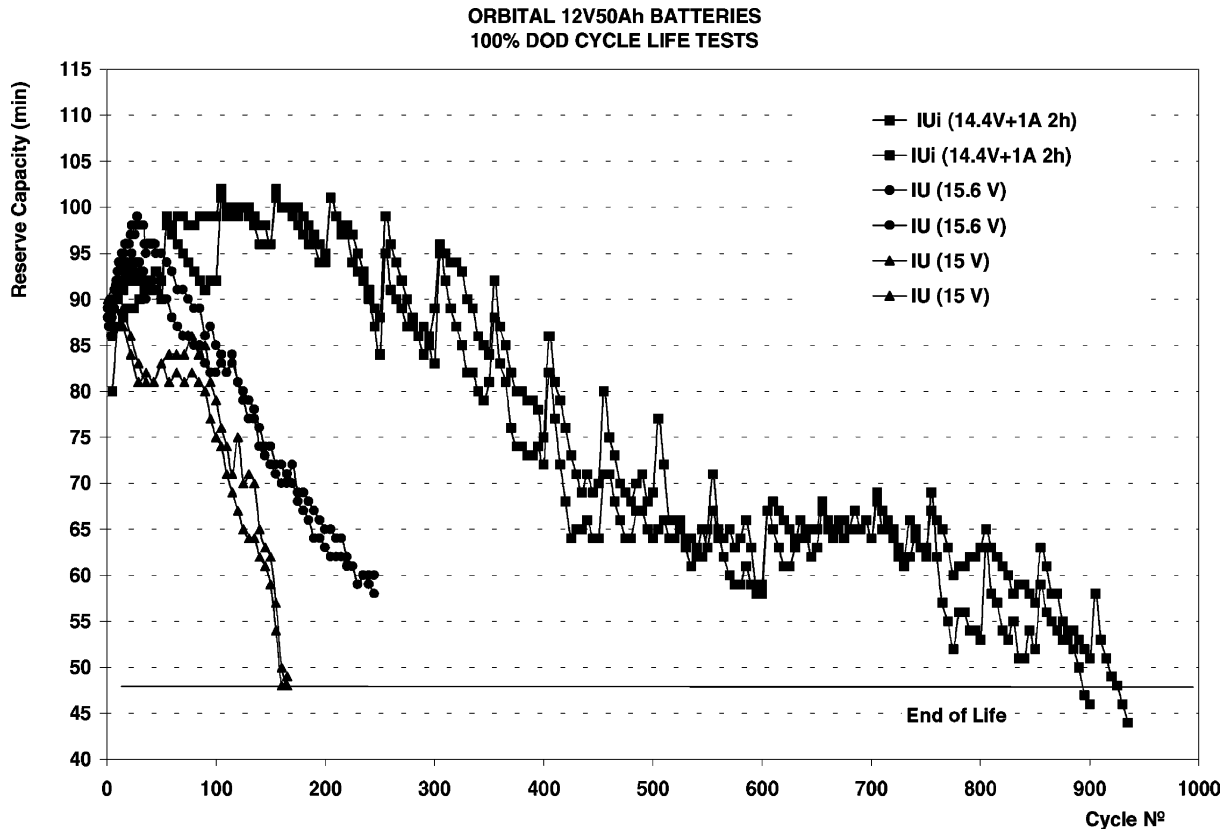


Fig. 4. Influence of charging procedure on VRLA cycling performance. There is a dramatic increase when charging profile is changed from *IU* to *IUI*.

recharge factor (110–120%), that varies from 10 to 20 h at the beginning, to 2–4 h at the end of test. This fact, reflects the increase of the final current due to the increase of the recombination efficiency, which in turn is a consequence of the progressive dry out, due to the relative long time that the battery is submitted to the high charging voltages. This current increase, is used to sustain the recombination reactions, and does not contribute to charging of the active materials, and the net final effect, is the heating of the battery due to the exothermic nature of the recombination reaction.

On the other hand, the use of an *IUI* charging profile, results in a quite different situation. Previously discharged capacity, can be recovered in as little as 1 h, with the overcharge factor (5–10%), obtained at a low current value (1 A), at which the recombination efficiency, achieves significant values, in this way minimising water losses.

The absence of voltage limitation in the final step, has a regulating effect with respect to the imbalance of the cells [2–4]. Each cell according to its particular condition regarding acid saturation, will achieve a different potential level. Cells with a high degree of saturation, will get high charging voltages, because they perform essentially like flooded ones. These high voltages enhance gasification, that together with the low recombination efficiency of the cell, results in progressive dry out, until achieving the correct degree of saturation. Cells with lower degrees of saturation, achieve lower voltages, but the shifting of electrode voltages due to

the recombination reactions, increases charge polarisation of the positive plate, contributing in this way to maintaining the electrical performance of the battery.

The net effect of all of these facts is to increase the life of the battery by a factor of 5, changing from 150 cycles for *IU* charges, to 750 for *IUI* profiles.

3.1.3. Influence of recovering discharges

Capacity evolution with cycling, generally shows a marked evolution: a sharp decrease at the beginning of cycling, let us say during the first 50 cycles, followed by a quasi stabilisation for the rest of the cycling, until the battery reaches the end of life, the point at which a sharp and irreversible capacity decay occurs.

This general trend is nevertheless altered, with capacity fluctuations up and down throughout cycling. In order to try to stabilise battery performance cycling profiles, including deep discharges, have been made, and have shown a marked effect on stabilising battery performance [6,7].

Fig. 5 shows such effect. The dashed line shows the C_5 capacity evolution after recovering deep discharges. In all cases, it is above the one without recovering deep discharges, with a capacity increase of around 10%. The reason seems to be related to the structural evolution of the active material. During cycling, there is a tendency to develop what is called a coralloid structure [5], characterised by a more open structure, an increase of the particle size, from 0.02 to 0.1 μm , as well as

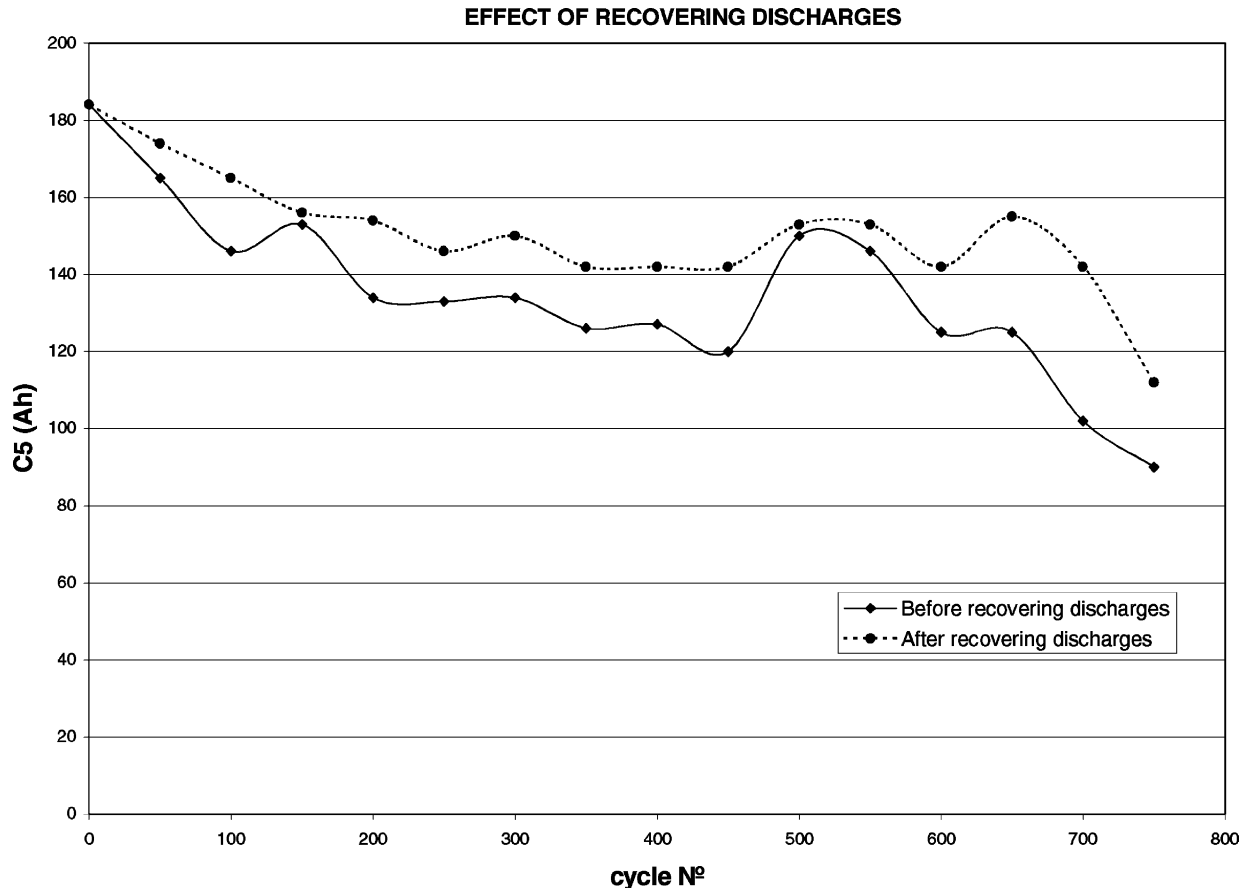


Fig. 5. Influence of recovering discharges on cycling. Periodic deep discharges recovers usable capacity, that otherwise would be lost.

a decrease of the specific surface area, that changes from 5 to 3 m²/g in the positive plate [6,7]. These changes, indicate a more compact and less accessible active material. Deep discharges, as they make use of most of the active material, contribute to open the structure of the compact particles, making them more accessible for the electrochemical reaction.

3.2. Floating applications

Standby use, in which the battery is maintained on permanent charge at the floating voltage until power failure occurs, is at present the most important use of the VRLA batteries. Applications like UPS, alarm systems and the like, consume the majority of VRLA battery production.

This type of service is characterised by the use of low float charging voltages. Voltage levels are limited to the values necessary to maintain the battery fully charged, but avoiding at the same time any undesirable side reaction, like corrosion or water consumption that can adversely influence the expected life of the battery.

To achieve this, very low float values are used. Values for VRLA batteries are of the order of 2.27 V per cell (13.6 V per battery). As battery OCV is around 12.9 V (2.15 V per cell), this leaves a charging overpotential of only 120 mV for each of the cells.

3.2.1. Potential distribution on a floating cell

Potential distribution between positive and negative plates is given by the polarisation curves, that represent positive and negative plate voltages with respect to the current flowing through the cell. The general shape of these curves is shown in Fig. 6, from which is evident the different performance, in terms of potential, of the positive and negative plates. In fact, at low charging currents, the positive plate, shows a potential increase, whereas the negative plate remains almost at the rest potential. Values in the graph, show polarisations of close to 100 mV for the positive, and only around 10 mV for the negative. This overpotential distribution, occurs in the potential region in which the battery operates in real applications.

This situation is a consequence of the oxygen recombination reactions, that provoke a marked depolarisation of the negative plates. In a flooded battery, the situation is exactly the reverse. Tafel slopes in a flooded battery, are of the order of 120 mV per decade for the negatives, and 90 mV per decade for the positives. This means that negative plates are more easily polarizable than positives. These facts indicate that control of the plate polarisations can be done in some way, through controlling the oxygen recombination reactions, or what is the same through the control of the cell

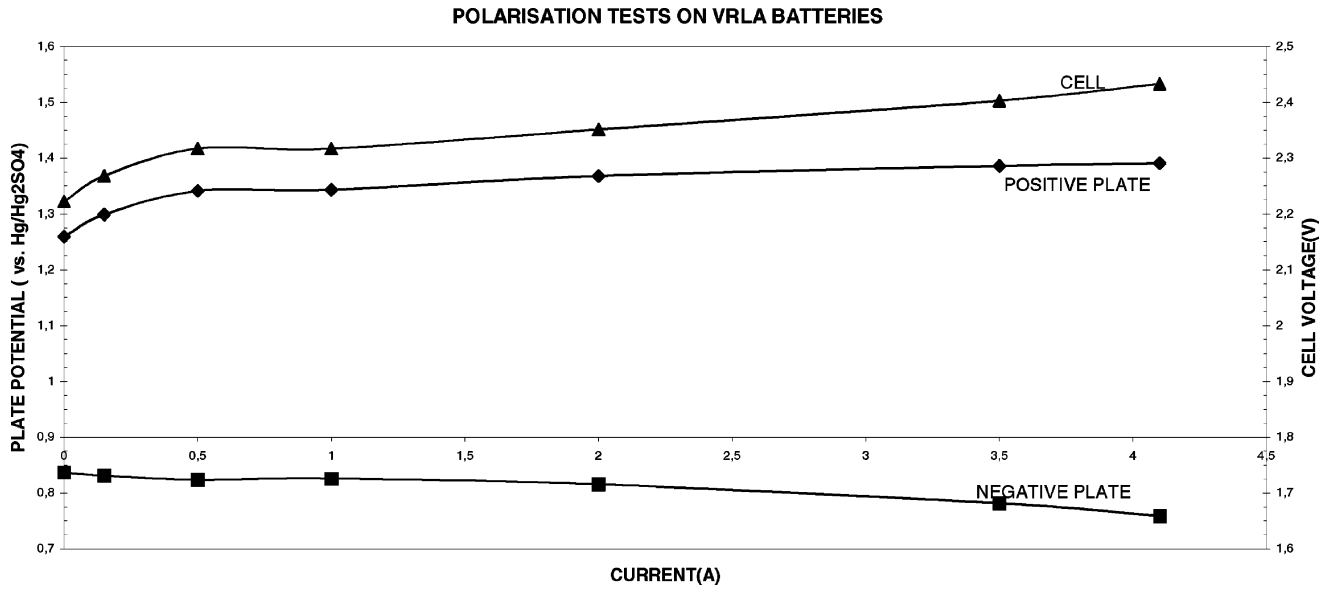


Fig. 6. Cell polarisation characteristics on float charge: negative plate potential remains almost unchanged provoking, in some cases, lack of charge or even discharge that can lead to failure.

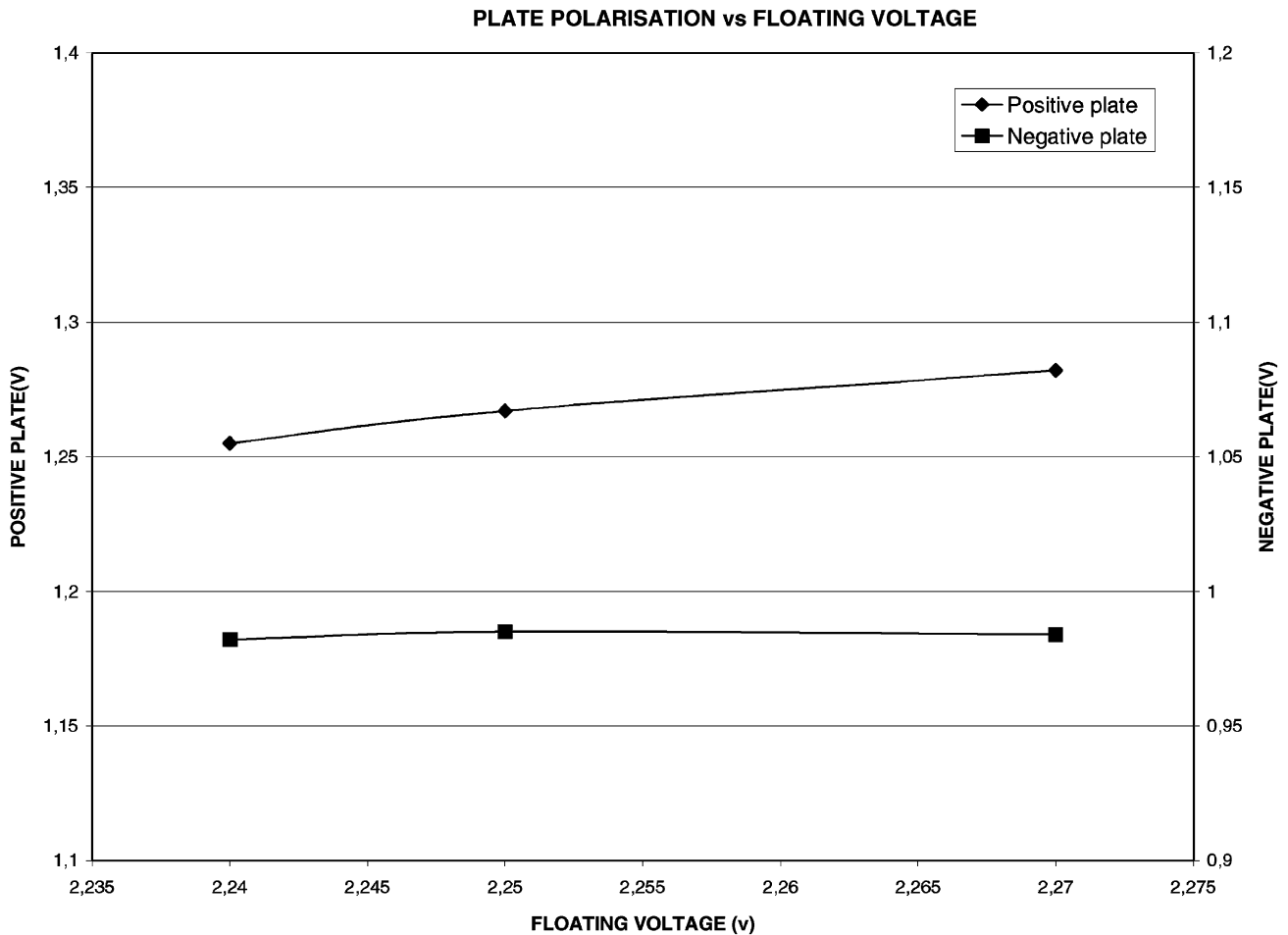


Fig. 7. Plate polarisation vs. float voltage: again it can be seen that negative plate potential, remains essentially unchanged.

recombination efficiency by changing the degree of saturation of the separator.

3.2.2. Practical implications

The changes in plate polarisation, that occur in VRLA batteries as a consequence of the operation of the recombination reactions, have important consequences in terms of battery performance in floating applications.

Essentially, what occurs, is that on float charge, negative plate potential remains at open circuit value, or very close to it. This lack of polarisation, inhibits the negative plate from being totally charged, thus remaining in a partial state of charge, whose value, depends on the polarisation characteristics of the cell.

Plate polarisation as a function of the floating voltage, can be seen in Fig. 7, which covers the usual range of floating voltages for VRLA batteries. On changing the floating voltage from 2.24 to 2.27 V, the positive plate potential increases 27 mV, whereas the negative, remains almost unchanged. The absence of polarisation for charge, can result in a situation in which floating charge is even unable of taking care of self discharge resulting in a slow, but progressive discharge of the negative plate [8].

As stated before, the main factor responsible for the absence of polarisation of the negative plates, is the oxygen recombination reaction, but this is not the only one. Any fact increasing hydrogen evolution, or self discharge contributes to depolarise the negative plate. In this sense the use of alloys with high hydrogen overvoltage, and the absence of any impurities that decrease hydrogen overvoltage and promote self discharge is quite important in order to maintain the adequate plate polarisation characteristics.

4. Conclusions

Electrochemical factors play a capital role in determining VRLA performance and life, contributing to achieve the impressive values already obtained. Some of these

electrochemical factors, are determined by manufacturing processes, and others by the operating conditions through life.

Among the first is the degree of saturation of the separator, that strongly effects oxygen recombination efficiency, and the potential distribution within the cell. Results from Fig. 2 show clearly the strong influence on battery performance.

Operating conditions are basically determined by charging conditions. The results presented, clearly show that elimination of imbalance between cells is of paramount importance in VRLA batteries. To eliminate these differences, it is necessary to allow a free evolution of cell voltages, a situation that is achieved by using final constant current steps at low current rate.

Finally, recovering discharges help in maintaining battery capacities at higher level throughout along life and hence to increase it.

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