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Valve-regulated lead-acid batteries

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Abstract

This paper is the introductory presentation given at the pre conference seminar devoted to a discussion of the oxygen-cycle in valve-regulated lead-acid batteries. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The valve-regulated design of lead-acid batteries offers a number of advantages compared to its flooded counterpart. There are, however, some disadvantages that must be observed. Water loss, for example, is an aging factor that cannot be compensated by refilling. Water loss occurs, even when a perfect internal oxygen-cycle is established, because of the unavoidable secondary reactions that provide hydrogen evolution and grid corrosion. The design of the battery therefore must aim to keep water loss to a minimum, and the user has to be aware that reduced service life of the battery can result from increased operational temperature or too high a float voltage. Beyond that, the rates of hydrogen evolution and grid corrosion have to be in balance, otherwise one of the electrodes, usually the negative one, may not be sufficiently polarized. Then gradual discharge of the electrode concerned occurs and a corresponding loss of capacity will be the consequence, even though the battery is float charged at its specified voltage. Further possible problems with VRLA batteries are: self-discharge of the negative electrode by the intake of air through a leakage, corrosion at the negative plate group, and thermal problems that can be caused by increased heat generation connected to the internal oxygen-cycle when heat dissipation is not ensured and the voltage of the battery is not under adequate control.

2. The electrochemical system “lead-acid battery”

The lead-acid battery is an unstable system, since the decomposition voltage of the water in its electrolyte amounts to only 1.23 V which is far below the nominal cell voltage of 2 V. Furthermore, at the high potential of the positive electrode, all metals are destroyed by oxidation and only lead can be used for the grid and the conducting elements, since the corrosion of lead generates a protecting layer of lead dioxide. Even this layer is not quite stable, and corrosion causes a small continuous current flow. As a consequence, in lead-acid batteries, water decomposition and lead corrosion are to be accepted as unwanted secondary reactions. To illustrate the situation, the possibility of the various reactions is drawn in Fig. 1 versus the electrode potential refered to the standard hydrogen electrode (SHE).

Charge and discharge are the main reactions at both electrodes. The difference between their equilibrium potential determines the open-circuit voltage of the battery. It depends to some extent on acid concentration as indicated in the caption of Fig. 1.

Polarization is a decisive parameter. It means the deviation from the equilibrium potential, caused by current flow. Whether the electrode is charged or discharged, depends on its polarization. The positive electrode is charged when it is positive polarized and discharged at a negative polarization. The reverse applies to the negative electrode: it is charged when negative polarized and discharged when positive polarized. The extent of the polarization determines the rate of the reaction concerned.

The charging/discharging reactions are fast at both electrodes, which means that charging or discharging occurs at a high rate, even at a small deviation from the equilibrium value (small polarization).

2.1. Secondary reactions

Fig. 1 shows that the following four secondary reactions which are inherent in the system since, their equilibrium

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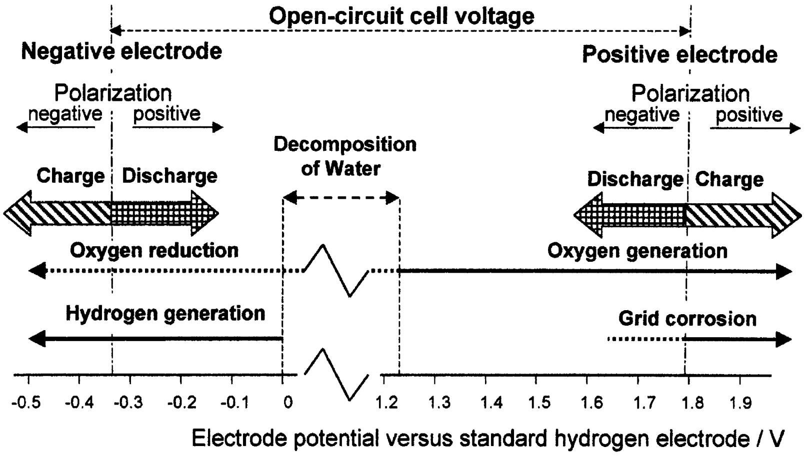

Fig. 1. Possible reactions in lead-acid batteries plotted vs. electrode potential. The origin of the arrows represents the equilibrium potential of the reaction concerned. The open-circuit voltage depends on acid density according to E^0 = acid density (g/cm^3) + 0.84. In this example, the cell voltage of 2.12 V ($E^0_{pos} = 1.79$ V; $E^0_{neg} = -0.33$ V) corresponds to an acid density of 1.28 g/cm^3.

potential lies within the cell voltage:

- hydrogen evolution at the negative electrode;
- oxygen reduction at the negative electrode;
- oxygen evolution at the positive electrode;
- grid corrosion at the positive electrode.

In the following sections they will be described in some detail.

2.1.1. Hydrogen evolution

When two electrode reactions occur simultaneously in opposite directions, they form a mixed potential. This applies, for example, at the negative electrode between hydrogen evolution and the discharge reaction at open-circuit, as illustrated in Fig. 2. Discharge of the negative electrode causes conversion of Pb into Pb^{2+} which is an oxidizing (or anodic) reaction that releases electrons. It is balanced by the reduction of H^+ ions into H_2 that consumes electrons. An internal current flow is thus established directly at the electrode surface, although no outer current is observed.

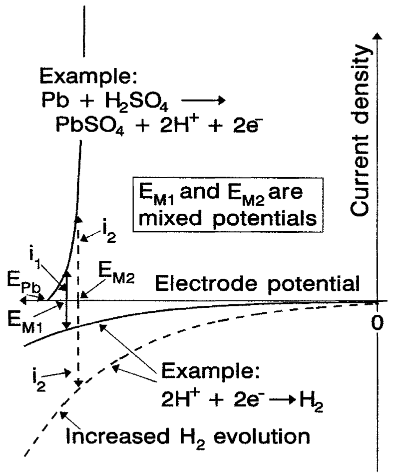

Fig. 2. Mixed potential between discharge of the lead electrode and hydrogen evolution resulting in self-discharge. Horizontal axis: electrode potential vs. hydrogen electrode; vertical axis: reaction rate as current equivalent; E_{Pb}: Pb/PbSO$_4$ equilibrium potential; E_{M1} and E_{M2}: mixed potentials; i_1, i_2: rates of self-discharge. The dashed curve represents reduced hydrogen overvoltage (cf. Figs. 2 and 9 on p. 31 in [1]).

Fig. 2 shows that the position of the mixed potential is largely determined by the faster of the two reactions, while the rate of the reaction, the self-discharge of the negative electrode in this example, is determined by the slower reaction. The continuous curve of hydrogen evolution represents a fairly high hydrogen overvoltage; the broken curve characterizes the situation when hydrogen can be evolved more easily. The position of E_M is close to the equilibrium potential of the lead electrode and its position is only slightly changed between the two examples, but the rate of the self-discharge, the current i_2, is much larger than i_1 in the second case.

The sum of the two reactions in Fig. 2 is

$$Pb + H_2SO_4 \Rightarrow PbSO_4 + H_2 \qquad (1)$$

Fig. 2 illustrates that the rate of self-discharge approximately represents the lowest hydrogen evolution rate of the charged negative electrode. When the electrode is polarized to more negative values, hydrogen evolution is increased according to the curves, shown in Fig. 2. Polarization to more positive values than the equilibrium potential reduces hydrogen evolution, but simultaneously causes discharge of the electrode.

In flooded batteries, self-discharge of the negative electrode usually is equated with Eq. (1), since other reactions can be neglected. In VRLA batteries, however, oxygen intake can also cause considerable self-discharge of the negative electrode due to the easy access of oxygen to the electrode surface. In the mixed potential of Fig. 2, then oxygen reduction forms an additional discharging current.

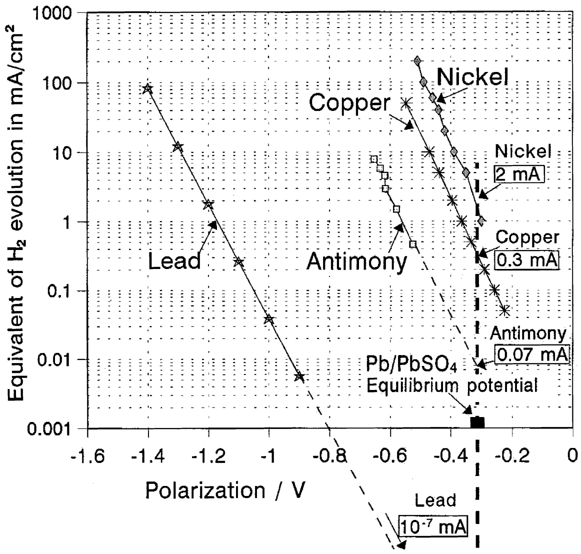

Fig. 3. Hydrogen evolution in sulfuric acid at various metal surfaces in a semilogarithmic plot vs. electrode potential (polarization). The origin of the horizontal scale is the equilibrium potential of the hydrogen electrode. The enframed figures represent the gassing rates at the open-circuit potential of the lead electrode. (Data: lead [2]; antimony [3], copper [4], nickel [5]).

Hydrogen evolution is extremely hindered at the lead surface. This is pointed out in Fig. 3, where the hydrogen evolution rate is compared for several metals as a function of the electrode potential.

In this semilogarithmic plot, the hydrogen evolution curves represent TAFEL lines. The figure indicates the outstanding situation of lead. The position of its TAFEL line is far to the left, and hydrogen evolution at a faster rate than 0.001 mA/cm^2, the beginning of the current scale in this figure, is only possible at a polarization more negative than 0.8 V refered to the standard hydrogen electrode or -0.5 V compared to the open-circuit potential of the negative electrode ($Pb/PbSO_4$ equilibrium potential). Of all metals only mercury shows a similar hindrance of hydrogen evolution. This is emphasized by the enframed figures for hydrogen evolution at the equilibrium potential of the lead electrode (in equivalents (mA/cm^2)). At nickel, copper and antimony, hydrogen is evolved at the rate of 2, 0.3, and 0.07 mA/cm^2, respectively. At the lead surface this value, which approximately corresponds to the rate of self-discharge, shown in Fig. 2, is about six orders of magnitude smaller than hydrogen evolution at the other metals. That self-discharge by hydrogen evolution is noticed in the lead-acid battery despite this small rate, is due to the large surface area of the active material of about 500 m^2/100 Ah of nominal capacity. Multiplied by this surface area, the 10^{-7} mA/cm^2 in Fig. 3 results in 0.5 mA/100 Ah as a reference figure for self-discharge of pure lead.

W.E.M. Jones concludes from practical experience that hydrogen gassing of the negative active material in VRLA batteries should be a maximum at 12 ml/100 Ah per day to achieve a "balanced cell" [6]. This corresponds to 1.09 mA/100 Ah and comes very close to the above value for pure lead.

Extreme hindrance of an electrochemical reaction is always in danger of being released by contaminants. Thus, hydrogen evolution would enormously be increased by the precipitation of traces of other metals, like those shown in Fig. 3, on the lead surface. Such a contamination shifts the TAFEL line to the right and degrades the exceptional situation of lead.

Consequently, a low hydrogen evolution rate can only be achieved by the use of extremely purified lead and stable materials. This concerns mainly the active material and the grid in the negative electrode. However, all the other components of the cell, may also become involved since critical substances may be leached out and migrate to the negative electrode where they are precipitated when their equilibrium potential is more positive than that of lead. The demand for highly purified materials, however, leads to a penalty in terms of price which grows considerably with increasing purity. In the near future, this question may gain in importance since, due to growing recycling efforts, secondary lead has increasingly to be used for the active material in batteries. In the US, nowadays already 75% of the lead on the market is secondary lead and this fraction is increasing [7]. Secondary lead, may contain quite a number additives which in their entirety determine the hydrogen evolution rate [8], and it is a question of economics how far the various smelters can purify the lead at an acceptable price. Thus, it may become more and more expensive to purchase "highly purified lead".

Additives, like organic expanders are often considered as a possibility to increase hydrogen overvoltage and thus reduce hydrogen evolution. However, the intrinsic extraordinarily strong hindrance of hydrogen evolution at the lead surface makes it unlikely that substances will be found which further increase this effect without simultaneously blocking the charging/discharging reactions.

2.1.2. Oxygen evolution

Oxygen evolution starts at 1.23 V, refered to the SHE and thus is always present as a secondary reaction at the positive electrode. The corresponding reaction is

$$H_2O \Rightarrow \tfrac{1}{2}O_2 + 2H^+ + 2e^- \qquad (2)$$

Oxygen evolution and the discharge reaction of the positive electrode also form a mixed potential, similar to the situation of the negative electrode shown in Fig. 2. But oxygen evolution at the open-circuit potential is small and therefore self-discharge due to oxygen evolution is not usually noticed. However, oxygen evolution increases more rapidly than hydrogen evolution with increasing potential, and the slope of the corresponding TAFEL line is steeper. For this reason, considerable rates of oxygen evolution are observed at a higher potential of the positive electrode. This is important, since oxygen evolution determines the rate of the internal oxygen-cycle in VRLA batteries, which is important in deciding the rate of the float current as shown below.

2.1.3. Oxygen reduction

Oxygen reduction is the reversal of the oxygen evolution reaction described by Eq. (2). It occurs according to

$$\tfrac{1}{2}O_2 + 2H^+ + 2e^- \Rightarrow H_2O \qquad (3)$$

at an electrode potential below 1.23 V versus SHE (in acid solution). Thus, oxygen reduction is always thermodynamically possible at the negative electrode, and oxygen is immediately reduced when it reaches the surface of the negative electrode. The rate of this reaction is largely determined by the rate of oxygen transport to the negative electrode surface. Data that determine this transport are shown in Table 1.

The transport rate of the oxygen in air is proportional to the diffusion coefficient, while that in the liquid is proportional to the product of the solubility and the diffusion coefficient. The resulting ratio is

$$\frac{\text{Transport rate in the air}}{\text{Transport rate in the liquid}} = \frac{0.18}{0.02\,2 \times 10^{-5}} = 4.5 \times 10^5 \qquad (4)$$

Thus, oxygen transport in the gaseous phase is half a million times faster than that in the liquid.

This great difference between the transport rates explains why oxygen reduction is hardly noticed at a charged negative plate that is submerged in water or acid, while a moist charged plate reacts readily with oxygen according to $Pb + \frac{1}{2}O_2 \Rightarrow PbO$ when exposed to the air (burning of the plate). In the latter case, oxygen in the dissolved state has to permeate only the thin wetting layer on the surface.

The slow transport also explains why in flooded batteries, self-discharge by oxygen reduction usually is limited to a few mA/100 Ah. When such batteries are float charged at very low voltages with resulting low float currents, varying efficiency of the internal oxygen-cycle in the individual cells may split the battery into groups of deviating float voltages [9].

An increased rate of oxygen reduction is observed when flooded batteries have lost so much water that the connecting elements or even parts of the negative electrodes are no longer immersed in the electrolyte and can easily be reached by the oxygen gas.

Table 1
Diffusion coefficient and solubility of oxygen at room temperature

Diffusion coefficient of oxygen in air D_{air} (cm^2/s)	0.18
Diffusion coefficient of oxygen in 20% H_2SO_4 D_{liq} (cm^2/s)	2×10^{-5}
Solubility in sulfuric acid (Bunsen coefficient, α)	0.02

2.1.4. Grid corrosion

Corrosion of lead in principle starts at the equilibrium potential of the negative electrode. At a more positive potential lead (Pb), is no longer stable as a metal but is converted into Pb^{2+} that forms lead sulfate ($PbSO_4$) according to

$$Pb + H_2SO_4 \Rightarrow PbSO_4 + 2H^+ + 2e^- \qquad (5)$$

which is equivalent to the discharge.

In flooded batteries, the conducting elements are submerged in the electrolyte or covered by a wetting layer of acid that is connected to the electrolyte by ionic conductivity, and this layer is re-concentrated by acid fumes continuously. During float charging, at the more negative potential of the electrode, corrosion according to Eq. (5) is not possible and corrosion is prevented. This also applies to the conducting elements (“cathodic corrosion protection”). In VRLA batteries, however, the plate lugs and the other conducting elements cannot be submerged in the electrolyte and the wetting film is diluted by the formation of water according to Eq. (3). Then the potential of the wetting layer may be shifted to more positive values and the cathodic corrosion protection may be lost (cf. [1], p. 164 f). Severe corrosion problems have occasionally been observed at the conducting elements in the negative plate group for this reason.

Above the potential of the positive electrode, the fourvalent ion (Pb^{4+}) is the stable state and this forms lead dioxide (PbO_2). Thus, grid corrosion in the positive electrode results in the conversion of lead (Pb) into lead dioxide (PbO_2) according to

$$Pb + 2H_2O \Rightarrow PbO_2 + 4H^+ + 4e^- \qquad (6)$$

The lead dioxide produced forms a rather dense layer that protects the underlying lead from further corrosion. The situation at the lead/lead dioxide, phase boundary however, is not stable. The protecting layer obviously breaks open again and again and the corrosion process starts. As a result, the corrosion front gradually permeates further into the bulk of the metal at a quasi linear rate.

General parameters that determine this corrosion current are

- electrode potential, and temperature.

Two further parameters specific to the batteries concerned are

- specific corrosion rate of the employed alloy, and surface area of the grid.

The specific corrosion rate of alloys is a complex quantity that is not only influenced by the composition of the alloy but also by a number of further parameters, like metallographic structure. In general, pure lead has the lowest corrosion rate. Some examples observed in practice are shown in Table 2.

Table 2
Penetration rates of grid corrosion under float charging published for various alloys

Battery	Alloy	Manufacturing process	Penetration (mm per year)
GNB absolyte [10]	1.5% Sb; 1.5% Cd	Gravity casting	0.05
VARTA OPzS ([1], p. 153)	1.6% Sb (Se)	Pressure casting	0.03
HAWKER cyclon [11]	PbSn	Punched	0.01[a]
HAWKER cyclon [11]	Pb	Punched	0.005[a]

[a] Derived from [11] under the assumption that the design of the grids corresponds to those of battery #2 in Table 3.

Table 3
Rough comparison of grid weight and surface area of two extreme types of plate design

No.	Type of positive grid	Grid weight (g/100 Ah of nominal capacity)	Surface area (cm^2/100 Ah of nominal capacity)
1	Tubular (8 mm thick plate)[a]	≈1100	≈800
2	Punched thin grid[b]	≈1100	≈4000

[a] VARTA OPzS 100, 19 spines of the diameter 3 mm and the length 435 mm.

[b] GATES cyclon (1980), cylindrical 5 Ah cell with spirally wound electrodes, grid thickness 0.8 mm; rectangular mass fields 6 mm × 2.2 mm, bar width between them 0.8 mm (values converted to 100 Ah).

The surface area is given by the grid design and can markedly vary as shown in Table 3 by two extreme samples.

The values shown in Table 3 mark the wide variety of grid surface that can be expected. In both grids about the same amount of lead is used per Ah of capacity, but the specific surface area (per Ah) of the thin punched grid is about five times that of the tubular one.

The gradual penetration of the corrosion front into the bulk of the grid material requires a current to re-establish the corrosion layer. With the values in Tables 2 and 3 this current can be estimated.

Table 4 shows the great variety that can be expected for the corrosion current due to specific corrosion rate and surface area. To achieve a balanced cell, these values have to be matched to the hydrogen evolution rates (cf. Section 3.2).

3. The internal oxygen-cycle

During float charging, in flooded batteries, oxygen and hydrogen evolution are the main overcharging reactions, and both electrodes are polarized so that hydrogen and oxygen are generated (nearly) equivalent to the float current at the negative and positive electrodes, respectively. A (nearly) stoichiometric ratio of hydrogen and oxygen escapes from the cell, and a corresponding water loss is observed. Oxygen reduction can be neglected because of the slow transport of oxygen, and the corrosion current can be neglected compared to the float current.

In the VRLA battery, the internal oxygen-cycle characterizes the float situation, i.e. the oxygen, generated at the positive electrode according to Eq. (2), subsequently is reduced at the negative (Eq. (3)), and the partial pressure of oxygen is kept fairly low. The reaction at the positive electrode is thus reversed at the negative electrode. This internal oxygen-cycle is the same principle that characterizes the sealed nickel/cadmium battery. In lead-acid batteries, however, it can only be approximated, since a certain hydrogen evolution at the negative electrode and grid corrosion at the positive electrode are always present as secondary reactions (cf. Fig. 1).

Hydrogen evolution and grid corrosion cause water loss, since the sum of both reactions

$$\text{Hydrogen evolution} \quad 4H^+ + 4e^- \Rightarrow 2H_2$$

$$\text{Grid corrosion (Eq. (6))} \quad Pb + 2H_2O \Rightarrow PbO_2 + 4H^+ + 4e^-$$

$$\text{In total is} \quad Pb + 2H_2O \Rightarrow PbO_2 + 2H_2 \tag{7}$$

Table 4
Corrosion currents under float charging derived from the values in the Tables 2 and 3

Penetration (mm per year)	Weight of Pb (per year) (g/cm^2)	Coulombic equivalent (mAh/cm^2)	Current equivalent (mA/cm^2)	Current per 100 Ah of nominal capacity	
				800 cm^2/100 Ah (mA/100 Ah)	4000 cm^2/100 Ah (mA/100 Ah)
0.005	0.00567	2.93	0.000335	0.268	1.34
0.01	0.01134	5.86	0.000698	0.536	2.68
0.03	0.03402	17.6	0.00201	1.61	8.04
0.05	0.0567	29.3	0.00335	2.68	13.39

Hydrogen that is generated at the negative electrode must escape from the battery. An "internal hydrogen-cycle" is not established, since hydrogen oxidation at the positive electrode is an extremely hindered reaction. For this reason, a lead-acid battery cannot be sealed hermetically but must have a valve that opens from time to time for gas escape, even under normal operational conditions.

3.1. Immobilized electrolyte

The internal oxygen-cycle requires fast oxygen transport that can only be achieved by diffusion in the gaseous phase, as indicated by the ratio shown in Eq. (4). To provide void volume for such a fast transport, the electrolyte must be "immobilized". This can be achieved by two methods.

1. Addition of about 6 wt.%. of silica (SiO_2) that converts the acid into a stiff gel.
2. Application of absorbent-glass-mat separators (AGM) that are soaked by the acid so that liquid acid is not left within the cell.

In the gel, a certain amount of acid is released on account of shrinkage during the solidification process. This liquid can be removed, and void cracks remain within the gel that allow fast gas transport.

In glass-mat separators, the capillary forces fill the smaller pores while the larger ones remain void for gas transport. Such separators usually are mixtures of "coarser" types of fibers with diameters slightly above 1 μm and "fine" types with a diameter of about 0.5 μm, to achieve both, sufficient stiffness and absorptive capacity. "Hybrid separators" contain plastic fibers to increase stiffness and effectuate a certain void pore volume by "controlled wetting" [12]. Separators that consist of two or more layers of different fibers are also on the market (a survey is given in [13]). Such layered separators offer advantages for special applications, and they can also be helpful for the filling process, since layers of coarse fibers are more quickly soaked. On the other hand, mats of fine fibers are superior in regard to the wicking height, which is advantageous in tall cells and also reduces stratification problems in cycling applications [14].

In both versions of immobilization, sufficient void space is left that allows fast diffusion of oxygen through the gaseous phase. Only a thin wetting layer at the negative electrode surface has to be permeated by dissolved oxygen, and the efficiency of the internal oxygen-cycle comes close to 100%. Even when a battery initially contains too much liquid that hinders fast oxygen transport, increased water loss of such a "wet" cell finally yields an efficient internal oxygen-cycle.

For most applications, the differences between the two immobilization methods are marginal. When batteries of the same size and design are compared, the internal resistance of the gel battery is slightly higher, mainly due to the conventional separator that is required with the gelled electrolyte, since the gel itself does not prevent the penetration of lead dendrites that can cause short-circuits between the electrodes. As a consequence, AGM batteries are prefered for high load applications, because of the possibility to achieve a very low internal resistance. In gelled electrolyte, on the other hand, the acid is more strongly bound and therefore the influence of gravity is almost negligible. Thus, gel batteries do not show acid stratification. In general, they are superior in cycle applications, and tall gel cells can be operated also in an upright position, while with tall AGM batteries operation in horizontal position is usually recommended to limit the height of the separator to about 30 cm.

In gelled electrolyte, most of the oxygen must surround the separator. This is one of the reasons that the maximum rate of the internal oxygen-cycle is lower in gel cells. Another reason may be, that a certain portion of the surface is masked by the gel. Rough figures for this maximum rate are 10 A/100 Ah in AGM batteries and 1.5 A/100 Ah in gel batteries. A charging current that exceeds this maximum causes gas escape as in a vented battery. But this limitation normally does not influence charging or float behavior, since lead-acid batteries are charged at constant voltage, and overcharging rates are far below, 1 A/100 Ah, even at 2.4 V per cell. The more limited maximum rate of the internal oxygen-cycle in gel batteries even offers the advantage that gel batteries are less sensitive to thermal runaway when overcharged at too high a voltage.

3.2. Electrochemical consequences

To gain an insight into the mutual dependence of the involved reactions, their characteristics have to be considered.

- Charge/discharge reactions, hydrogen and oxygen evolution, and also grid corrosion occur independent from each other, and their rates are only determined by the potential of the electrode concerned.
- For oxygen reduction, the situation is different, since its rate is determined by the amount of oxygen that is evolved at the positive electrode and subsequently reaches the negative electrode, provided that oxygen intake from the surroundings is precluded by proper sealings and a properly operating valve. Due to the high transport rate, usually a high efficiency of the internal oxygen-cycle is achieved, and the amount of reduced oxygen closely corresponds to the rate of oxygen evolution at the positive electrode.

A strong relation between these reactions is given by the primary rule, **"the same current must flow through both electrodes as soon as the charging or discharging current circuit is closed"**.

Fig. 4 illustrates the resulting situation of a cell that is float charged at 2.27 V per cell. The figure is based on model calculations by U. Teutsch [15,16]. The horizontal axis shows the polarization of the positive and negative

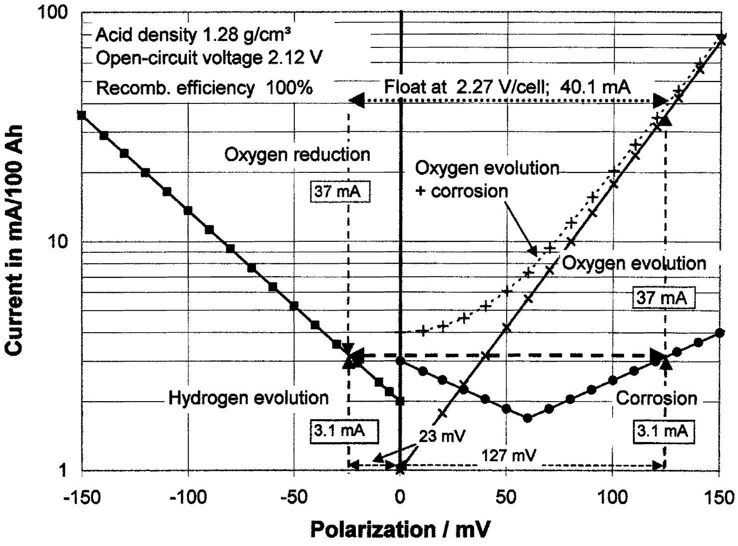

Fig. 4. The float charging situation of a VRLA battery. Current voltage curves as current equivalents in a semilogarithmic scale vs. polarization, refered to the open-circuit potential of the negative and positive electrodes.

electrodes. The zero point of the horizontal axis is the open-circuit voltage of the cell, i.e. zero polarization of positive and negative electrodes. The rates of oxygen and hydrogen evolution rise exponentially with increasing polarization. In this semilogarithmic plot they are represented by TAFEL lines. Fig. 4 shows the typical slopes per decade of current increase of −120 and +80 mV for hydrogen and oxygen generation, respectively. At open-circuit, i.e. zero polarization, oxygen and hydrogen evolution in this example correspond to 1 mA/100 Ah and 2 mA/100 Ah, respectively. The latter would be equivalent to a self-discharge of the negative of 1.44 Ah per month or 1.44% per month.

The corrosion behavior is represented in Fig. 4 by the combination of two TAFEL lines. This is a rough approximation, but it corresponds to the practical experience and describes an always observed minimum of corrosion at 40–80 mV above the open-circuit potential of the positive electrode. At lower potentials, the protecting layer of PbO_2 is destabilized. At polarization values more positive than this minimum, the corrosion rate increases also exponentially with respect to polarization. The slope of this TAFEL line is 240 mV per decade which is in accordance with the general experience in practice.

The curves for charge and discharge would be represented by nearly vertical lines due to their low polarization. They are not drawn in Fig. 4, since they do not occur in a normal float situation.

Fig. 4 of course is based on generalized values, and in actual batteries deviations are to be expected depending on electrode materials and cell design.

The inserted double arrow shows the situation that results at a float voltage of 2.27 V per cell which means a polarization of 150 mV in total at the open-circuit voltage of 2.12 V. The above mentioned demand, that the sum of hydrogen evolution and oxygen reduction at the negative electrode, in electrochemical equivalents, must equal the sum of oxygen evolution and grid corrosion at the positive electrode, is only fulfilled at a polarization of +127 and −23 mV of the positive and the negative electrodes, respectively. At the positive electrode, such a polarization causes oxygen evolution equivalent to a current of 37 mA and corrosion equivalent to 3.1 mA (always refered to 100 Ah). Both together form the total float current of 40.1 mA. At the negative electrode, oxygen reduction (37 mA) and hydrogen evolution (3.1 mA) cause the corresponding result.

In this example, 100% of recombination efficiency is assumed, i.e. all the oxygen (O_2) that is evolved at the positive electrode is subsequently reduced at the negative. Thus, oxygen evolution is completely compensated by oxygen reduction, and this means that the current equivalents for oxygen evolution and oxygen reduction must equal each other. As a consequence, also the current equivalents of hydrogen evolution and grid corrosion must equal each other, since they are the required supplements for the current in total. This is indicated by the lower double arrow in Fig. 4. *(In practice, 100% of recombination efficiency can only be approximated, since a small partial pressure of oxygen always exists within the cell and a corresponding small portion of oxygen is lost together with the escaping hydrogen).*

The result, shown in Fig. 4 is typical for many VRLA batteries: the polarization of the negative electrode is small and the hydrogen evolution rate is close to the self-discharge rate at open-circuit. But this is only a question of the balance between hydrogen evolution and grid corrosion. When the hydrogen evolution is small compared to grid corrosion, balance will be achieved at an increased polarization of the negative electrode (cf. Figs. 5 and 6).

In Fig. 4, hydrogen evolution and grid corrosion are equivalent to 3.1 mA which corresponds to 27 Ah per year. Since 1 Ah decomposes 0.336 g of water, the water loss

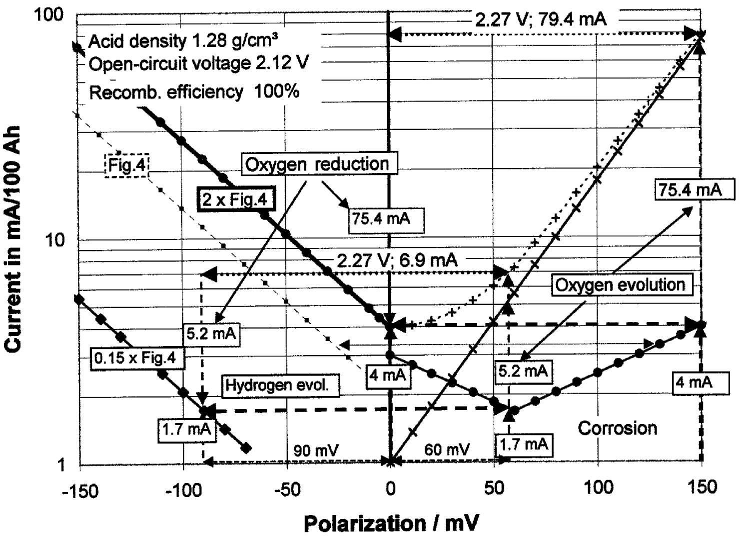

Fig. 5. Float charging situation at varying hydrogen evolution rates. Cell data as in Fig. 4, except the hydrogen evolution rates that are assumed doubled (the TAFEL line 2× Fig. 4) or reduced by a factor 6.5 (the line 0.15× Fig. 4).

would be 9.1 g per year which means about 1.0% per year, since usually 9 g of water are contained per 1 Ah. Such a water loss would be just tolerable for a 10 years service, since the battery should not lose more than 10% of its initial water content. Otherwise, the performance data may be affected.

1 Ah is equivalent to 456 cm^3 of hydrogen (at 25°C). Consequently, 3.1 mA correspond to a gassing rate of 1.4 cm^3 of H_2 per hour or 33.7 cm^3 per day and 100 Ah. *(The practical experience [6], mentioned in Section 2.1.1, that only 12 ml of H_2 per 100 Ah and day can be tolerated in balanced cells, indicates that corrosion rates in modern VRLA batteries might be smaller than assumed in Fig. 4).*

Three important statements given below, can be derived from Fig. 4.

1. The polarization of the negative and positive electrodes is determined by the balance between hydrogen evolution and grid corrosion, expressed in current equivalents.
2. Water loss is equivalent to the hydrogen evolution rate, which together with corrosion results in $2H_2O + Pb \Rightarrow 2H_2 + PbO_2$ (Eq. (7)).
3. The float current is determined by the sum of the internal oxygen-cycle and grid corrosion and has no direct relation to water loss.

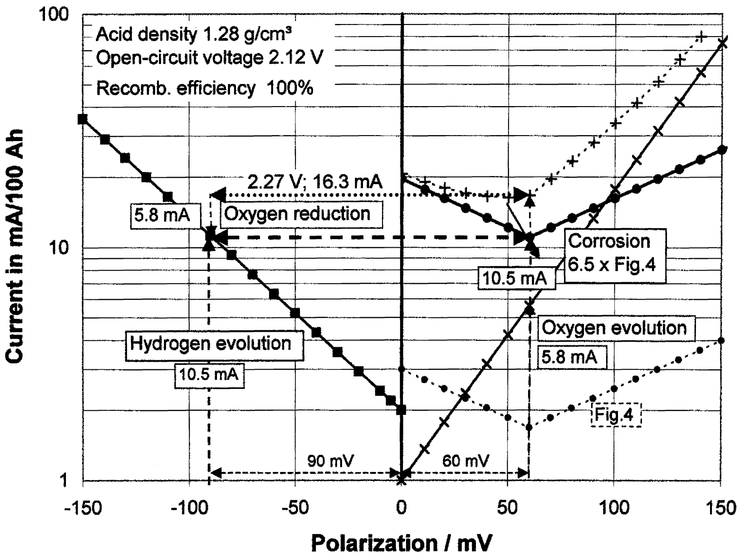

Fig. 6. Float charging situation at an increased grid corrosion rate. Cell data as in Fig. 4, except that the grid corrosion rate is increased by a factor 6.5.

Strictly speaking these relations are valid only at 100% of efficiency of the internal oxygen-cycle. But they can be transferred to most VRLA batteries, since usually such a high efficiency is closely approached

Note. *In regard to water loss attention has to be drawn to the fact that water loss in VRLA batteries can only be determined by measurement of the escaped hydrogen. Due to the fugacity of hydrogen such measurements have to be carried out very thoroughly and it has to be observed that only suitable tubing and sealing materials are used. Otherwise, the permeation of hydrogen disturbs the results too much. Water loss cannot be determined by loss of weight, since oxygen that is consumed by corrosion remains in the cell, and only the low weighty hydrogen escapes.*

3.2.1. Effect of varying hydrogen evolution rates

The fact that the polarization of both electrodes is determined by the balance between hydrogen evolution and grid corrosion turns this balance into a decisive parameter. This is illustrated in Fig. 5 which is based on the same data as Fig. 4, but in addition the float situation is shown when the hydrogen evolution is doubled or is reduced by a factor 6.5 (the line 0.15× Fig. 4).

At the low hydrogen evolution rate, balance between hydrogen evolution and grid corrosion is established at a more negative polarization of both electrodes. It amounts to −90 and +60 mV for the negative and the positive electrode, respectively. The corresponding equivalents for hydrogen evolution and grid corrosion are 1.7 mA. Based on the above calculation, water loss would now correspond to 14.9 Ah per year or 5.0 g per year. Water loss is thus reduced to 0.55% per year, when again 9 g of water are assumed as the initial content for 1 Ah. The reduced potential of the positive electrode reduces the oxygen evolution to a rate which controls the internal oxygen-cycle at 5.2 mA. As a consequence float current is reduced to 6.9 mA. Grid corrosion also is reduced and would be close to its minimum. On the whole, the reduced hydrogen evolution rate would improve the float situation markedly and increase the service life of the battery.

The doubled hydrogen evolution rate, on the other hand, requires a shift of the electrode polarization to more positive values to balance the increased hydrogen evolution by a correspondingly increased corrosion rate. This balance is reached when the current equivalents of hydrogen evolution and grid corrosion correspond to 4 mA/100 Ah. This balance, however, requires a polarization of 150 mV for the positive electrode, while that of the negative electrode is reduced to zero. The float current is increased to 79.4 mA, and water loss amounts to 35 Ah per year equivalent to 11.7 g per year or 1.3%.

Zero polarization of the negative electrode evokes a very critical situation, since now the negative electrode is discharged as soon as the slightest shift of its potential in the positive direction occurs. Then hydrogen evolution can no longer can compensate for grid corrosion and discharge of the negative electrode appears as an additional reaction required to make the same current flow through both electrodes. Gradual discharge of the negative electrode will be the result, although the cell is float charged at 2.27 V per cell.

Thus, increased hydrogen evolution aggravates the float situation in several aspects: the most critical point is the lost polarization of the negative electrode that can jeopardize proper float charging.

Fig. 5 shows that a considerable range exists for hydrogen evolution rates to achieve a "balanced" battery at a given grid corrosion rate.

3.2.2. Balance by increased grid corrosion

Since it is the balance between hydrogen evolution and grid corrosion that determines the polarization of the electrodes, an increased corrosion rate would have the same effect as a decreased hydrogen evolution rate. Fig. 6 illustrates the situation that results when corrosion is assumed to be increased by a factor of 6.5 compared to Fig. 4 grid.

To compensate for the much higher corrosion rate, the negative electrode must now be polarized to more negative values. The result is that the polarization of both electrodes is similar to that shown in Fig. 5 for the low hydrogen evolution rate. However, besides the very high corrosion rate, water loss would be much higher, namely equivalent to 92 Ah per year (and per 100 Ah) which corresponds to 30.9 g per year or about 3.4% per year. On the whole increased corrosion would be beneficial with respect to the polarization of the negative electrode. But it would markedly reduce the service life of the battery.

3.3. Unbalanced cells

Failure of VRLA batteries due to discharged negative electrodes has been reported repeatedly [17,18]. Obviously, it mainly concerns high quality batteries which employ corrosion-resistant alloys with a corrosion rate that is too low, compared to the self-discharge rate of the active material in the negative electrode. Then a situation appears similar to that shown in Fig. 5 with the doubled hydrogen evolution. As soon as the polarization of the negative electrode attains positive values, a corresponding discharging current of the negative electrode appears to balance the current flow through the positive electrode. Controlled experiments with commercial batteries showed that within a period of 64 weeks, up to 50% of capacity was lost although the cells had been on float charging at 2.27 V at 32°C [19].

The problem of impurities that may contaminate the materials employed, especially the active material in the negative electrode, has been mentioned in Section 2.1.1. In this regard it is very important to develop standards for tolerable values of hydrogen evolution and the corresponding measuring methods (cf. [6]).

3.3.1. Possibilities to improve the balance of a cell

If by design, and with the raw materials used, the balance between hydrogen evolution and grid corrosion cannot be achieved, a number of remedies are possible.

Increased float voltage would be a simple method. The increasing float voltage causes an increased polarization of the positive electrode and hence an increased corrosion rate. Consequently, an increased hydrogen evolution is required for compensation, and this means increased polarization of the negative electrode (cf. Fig. 3 in [20]). In practice, however, increased float voltage usually is not possible for technical reasons, and, furthermore, is not advisable because of the increased hydrogen escape and increased corrosion rate. But terminated boost charging or equalizing charging are occasionally included in monitoring routines for valve-regulated lead-acid batteries in order to recoup the full capacity of the negative electrodes [21]. The effect of such boost charges is, of course, only temporary.

Reduced efficiency of the internal oxygen-cycle would also improve the situation of the negative electrode at too high a hydrogen evolution rate. Then a portion of the oxygen generated is not recombined but escapes with the gas, and a corresponding additional amount of hydrogen evolution is required to balance this loss. Actually, the development of special separators is planned that would allow a controlled diffusion rate of oxygen through the separator and thus, simultaneously, prevent thermal runaway (cf. Fig. 8 in [12]). But the high rate of oxygen diffusion in the gaseous phase would probably nullify the effect of such a separator with advancing water loss, by-passing the separator, as occurs in gel batteries.

Incorporation of a small catalyst into the VRLA battery is a further method, if balance is not achieved by design. The catalyst reduces the efficiency of the internal oxygen-cycle, since it recombines a portion of the oxygen generated directly with the surplus of hydrogen that fills the gaseous space of the cell. The consequence is a reduction of the efficiency of the internal oxygen-cycle, and a discrepancy is caused between oxygen evolution at the positive electrode and oxygen reduction at the negative. Consequently, an increased amount of hydrogen must be evolved at the negative electrode and its polarization must be correspondingly increased [19,20]. Such a catalyst must not be efficient, since it only has to "disturb" the oxygen-cycle. The recombined equivalent of oxygen can be small compared to the float current, so that problems of heat dissipation do not arise. The main advantage of this method is that the reduced efficiency of the internal oxygen-cycle does not cause increased 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. Such catalysts are already in practical use [22].

4. Cycling of VRLA batteries

The demand to minimize water loss does not allow the use of antimony alloys, with the consequence, that a certain inferiority of cycle performance has to be expected with VRLA batteries. This disadvantage, however, is compensated to some extent by the immobilized electrolyte that reduces or prevents shedding of the active material. The gelled electrolyte automatically fixes the active material, and AGM separators have to be compressed to a certain degree. Nowadays, VRLA batteries designed for cycle applications, e.g. in electric vehicles, reach up to a thousand full cycles (80% DOD).

A general problem of a cycling regime is the necessity to reach full charge of all cells of a battery within a limited period of time. Differences between the charge acceptance of the positive electrodes in the various cells cause corresponding variations of the rate of the internal oxygen-cycle. A higher rate of the internal oxygen-cycle, however, means that a correspondingly smaller portion of the charging current that flows through the battery, is left for charging this cell. As a consequence, after a certain charging time, the individual cells of the battery reach a different stage of charge. Even if these differences are marginal, they add up with increasing number of charge/discharge cycles.

To avoid this effect, a certain overcharging has to be employed in cycling applications, although this leads to increased water loss. Charging methods for cycling applications of VRLA batteries therefore usually include terminated periods of charging at increased voltage. They always represent a compromise between charging time, charging efficiency, and water loss (cf. [1], pp. 421).

5. Conclusions

The reactions described and the conditions that characterize VRLA batteries, simultaneously indicate where problems are to be expected.

Hydrogen evolution and grid corrosion are approximately doubled by a temperature increase of 10°C. Since both reactions cause water loss according to Eq. (7), operation of the battery at elevated temperature will correspondingly increase water loss and reduce the service life, e.g. the service life of a battery that is continuously operated at 40°C, will be reduced to 25% compared to the service life at 20°C. This has to be accepted. As a remedy, in hot countries, batteries are often installed together with the electronic equipment in air conditioned containers.

Water loss has especially to be considered in high load applications of AGM batteries, since water loss mainly involves the separator due to its larger pore sizes compared to the active material, and the dry-out of the separator may cause a considerable increase of the internal resistance of the battery. High loads are then connected with a corresponding voltage drop (cf. [1], p. 150).

Heat problems, including thermal runaway, are often discussed in connection with VRLA batteries, since all the electrical energy that is consumed by the internal oxygen-cycle is converted into heat. Excessive overcharging therefore generates much more heat in a VRLA battery than in the flooded version, where a large portion of the energy escapes from the cell together with the generated oxygen and hydrogen gases. However, as long as float charging occurs at the usual voltage of less than 2.4 V per cell and the float current does not exceed 400 mA/100 Ah, heat generation is less than 1 W/100 Ah. Even in large cells with a comparatively small surface area, this heat is easily dissipated at a few degrees of temperature above the surroundings, provided that the installation of the battery allows heat dissipation at all. Serious thermal problems are mostly caused by too high a voltage, when for example, some cells in a battery string are short-circuited by grown positive grids that contact the negative bus bar. Regular control of cell or block voltages and their temperatures is the best remedy.

The problem of unbalanced cells, as described in Section 3.3 is now known and understood, and remedies are available. So it should no longer cause serious problems.

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