

# VRLA batteries, advances and limitations

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## Abstract

VRLA batteries offer a number of advantages compared to conventional lead-acid batteries. So they can be cycled in a partial state of charge. But limitations have to be observed, e.g., the negative electrode cannot be recharged separately and thus lost capacity cannot be regained. Furthermore, hydrogen evolution and grid corrosion must be in certain balance. At a too high hydrogen evolution rate the negative electrode will suffer gradual discharge. This might cause problem in hybrid-vehicle applications because of the unavoidably strong polarization during recuperation of braking energy.

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*Keywords:* VRLA batteries; Cycling in state of partial charge; Balance hydrogen evolution and grid corrosion

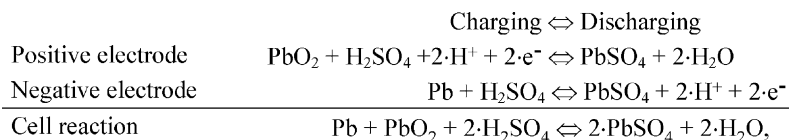
## 1. Introduction

Lead-acid batteries are the most economical electrochemical energy storage system and in widespread use everywhere, the exception being portable applications because of their limited specific energy and unavoidable corrosion problems that prevent the design of suitable small batteries. Their valve-regulated version, the VRLA battery, is characterized by immobilization of the electrolyte. It offers various advantages, e.g., no acid spilling, reduced gassing rates, and the possibility of partial state of charge performance, since acid stratification does not occur. It has, however, to be considered that the secondary reactions hydrogen evolution and corrosion can only be minimized, but they always remain to a certain extent. Furthermore, the internal-oxygen cycle causes a close linkage between positive and negative electrode that does not allow separate charging of the electrodes, and a combination of both effects may cause partial discharge of one of the electrodes that cannot be avoided.

New applications were opened up for lead-acid batteries by the valve regulated design, for example, the use in applications that repeatedly require boost charges, like automatic guided vehicles, and the question is raised about the use of VRLA batteries in hybrid electric vehicles where a battery of an acceptable weight has to accept and deliver a huge number of high current charge and discharge pulses during regenerative braking and acceleration of the car, respectively. Such a capability is mainly determined by the parameters specific energy ( $\text{Wh kg}^{-1}$ ), specific power ( $\text{W kg}^{-1}$ ), and cycle stability, but the electrochemical facts mentioned here could also be very important.

## 2. The electrochemical system

The actual storage system is based in both electrodes on lead. When discharged, in the positive lead dioxide ( $\text{PbO}_2$ ) is converted into lead sulfate ( $\text{PbSO}_4$ ), while in the negative electrode lead ( $\text{Pb}$ ) is converted into lead sulfate ( $\text{PbSO}_4$ ). The result is the reaction scheme



which shows a characteristic feature of the lead-acid battery, namely the electrolyte acts not only as ion conductor but also represents a part of the electrode reaction. As a consequence, the equilibrium cell voltage depends on acid concentration as shown in Fig. 1.

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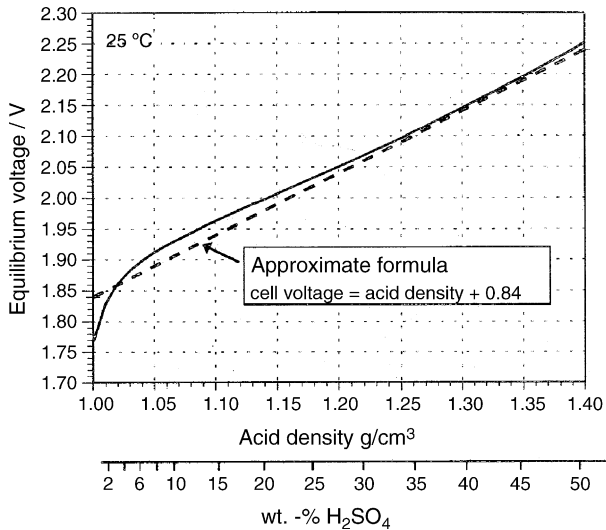


Fig. 1. Equilibrium cell voltage of the lead-acid battery referred to acid density and acid concentration.

An advantage of the lead-acid battery system is that all reacting components are well defined, and there are no intermediate states of oxidation. As a consequence, any voltage above the open circuit voltage results in complete charge, keeps the battery fully charged, and thus makes this battery system ideal for standby applications.

### 2.1. Acid as reacting component

The participation of acid in the cell reaction causes a number of drawbacks compared to other storage systems, e.g., nickel–cadmium or nickel/metal hydride batteries:

- The concentration of the electrolyte does not remain constant when the battery is charged or discharged. This effects the open cell voltage that depends on acid concentration. Furthermore, specific resistance of the electrolyte and its freezing point depend on the state of charge.
- There must be sufficient acid between the electrodes, which requires a certain spacing and means that the internal resistance of the battery cannot fall below a certain minimum.

#### 2.1.1. Acid stratification

When the battery is discharged,  $\text{SO}_4^{2-}$  ions are absorbed by both electrodes, and at the positive electrode in addition, water is generated that further dilutes the acid. Acid consumption occurs at the surface and in the pores of the active material, and thus reduces the specific weight close to the electrode surface. This causes an upward flow of the so formed more diluted acid that mixes the bulk of the electrolyte between and above the electrodes, except for the share that is located below the electrodes as shown in the left part of Fig. 2. Complete uniformity of the acid would only be reached after a prolonged period of time by diffusion.

When the battery is discharged, the reversed process causes downward movement with the result that the acid at the bot-

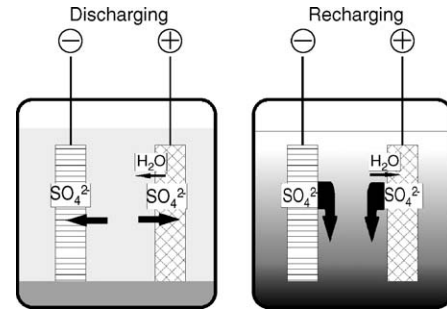


Fig. 2. The origin of acid stratification when lead-acid battery is discharged and recharged without gassing or other means of mixing the electrolyte (ref. [1], Fig. 4.9, p. 121).

tom becomes increasingly concentrated. When such discharging/charging cycles are repeated without acid mixing, the acid at the top is more and more diluted, while at the bottom the concentration may significantly exceed the initially specified value with the consequence that in the upper part of the electrodes the active material is only partly utilized due to the lack of  $\text{H}_2\text{SO}_4$ , while it is over used in the lower zone. Thus, in the bottom part of the positive electrode disintegration of active material may occur, while in the negative electrode sulfatation of active material is to be expected.

As a consequence, flooded lead-acid batteries, used in cycling applications, must regularly be overcharged to mix the electrolyte by heavy gassing, unless they are equipped with forced acid agitation. Because of acid stratification, conventional lead-acid batteries cannot stand cycling in a partially state of charge.

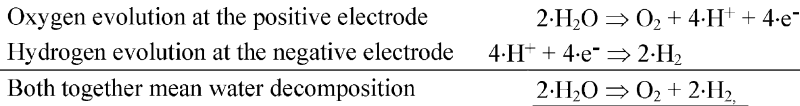
VRLA batteries do not show these drawbacks, provided that the electrolyte is strongly immobilized to suppress the influence of gravity that causes the downward movement indicated in Fig. 2. A corresponding fine pore system of the AGM separator is required or the electrolyte must be gellified [2].

### 2.2. Secondary reactions

The lead-acid battery is an unstable system, since its open cell voltage of 2 V is much higher compared to the decomposition voltage of 1.23 V of water that forms one component of the electrolyte. Corrosion of the positive grid and conducting elements that are connected to the positive electrode represents a further problem because of the high positive electrode potential of about 1.75 V (cf., e.g., ref. [1], Table 4.9, p. 109). Metals such as copper or nickel that in general are used as conducting material would be destroyed. Lead can be applied, since its corrosion forms a protecting layer of  $\text{PbO}_2$  that conducts the electronic current and thus makes possible that the charge/discharge reactions occur at the so protected surface. But this layer is not quite stable and gradual corrosion always proceeds.

#### 2.2.1. Water decomposition

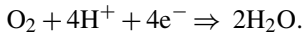
The unavoidable water decomposition occurs according to the following equations:



Oxygen and hydrogen evolution are always present secondary reactions. Fortunately, both reactions are extremely hindered at the lead and the lead-dioxide surface, respectively. This makes both secondary reactions so slow that they do not really disturb the function of the battery, but they always occur in parallel to charge and discharge, and at open circuit they cause gradual self-discharge of the electrodes.

### 2.2.2. Oxygen reduction

Oxygen reduction is the reversal of oxygen evolution:



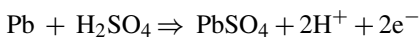
It is a fast reaction at the negative electrode. However, oxygen transport through liquid electrolyte is a very slow process due to a low diffusion rate and limited solubility. Therefore, oxygen reduction usually can be neglected in flooded cells. But in VRLA batteries oxygen can easily reach the negative electrode by fast diffusion in the gaseous phase that is present in void space within larger pores in absorbent–glass–mat separators, in cracks within the gelled electrolyte, or around the separators. Thus, almost all the oxygen that is generated at the positive electrode is reduced at the negative one, and thus the formed internal-oxygen cycle constitutes the main secondary reaction in VRLA batteries.

### 2.2.3. Corrosion

Although lead is protected by a layer of  $\text{PbO}_2$ , the situation of the current-conducting elements in the positive electrode is not stable and corrosion gradually penetrates further into the underlying lead, and under current flow metallic lead is converted into lead dioxide according to:



or, at a potential below the  $\text{PbO}_2$  equilibrium, e.g., at open circuit:



The rate of corrosion depends on the lead alloy being used and is lowest for pure lead. It also depends on a number of additional parameters, such as electrode potential, temperature, grid surface area, and also the grid manufacturing process. In any case, grid corrosion finally ends the service life of each lead-acid, assuming no other failure modes.

Corrosion is an electrochemical reaction that contributes to current flow through the electrode. In flooded cells, corrosion is not noticed as current consumer, since its contribution is small compared to hydrogen and oxygen evolution. In VRLA batteries, however, current balance between hydrogen evolution and grid corrosion gains importance when the internal-oxygen cycle reaches high efficiency.

In general, the unavoidable corrosion reduces the possibilities of grid design, since one requires a “corrosion reserve”. This means that the material must have a certain thickness, otherwise service life would severely be limited. An example of such a

limitation is the “BOLDER TMF-battery” that uses lead–tin foils of 0.05 mm thickness as support for 0.13 mm thick electrodes and corresponding thin separators. This valve regulated design offers power output up to  $800 \text{ W kg}^{-1}$  (cf., e.g., ref. [3], Fig. 5, p. 219), but life time is limited by corrosion to about one year.

## 3. Rate of the secondary reactions

The rate of an electrochemical reaction depends on polarization referred to its equilibrium potential. Usually the rate of the reaction, expressed as an equivalent current, is a complex exponential function of polarization that can be simplified at a sufficient high polarization. The results are TAFEL lines as shown in Fig. 2 for the above secondary reactions.

The curves in Fig. 3 are, of course, generalized and actually will be influenced more or less by individual parameters of the battery type under consideration. Hydrogen evolution especially is prone to be increased by contaminating metals that decrease the hindrance of this reaction at the negative electrode. In that case the TAFEL line in Fig. 3 would be shifted upwards. The rate of oxygen evolution is less sensitive to contamination due to the high potential of the positive electrode that converts metals into their oxidized form, which thereby lose their electrochemical effectiveness.

The linear course of the corrosion curve at low polarization values is a rough approximation, but the combination of two curves with reversed slope reflects an always observed minimum corrosion rate at 50–80 mV of polarization. The negative slope of the curve is caused by increased corrosion rate close to the equilibrium potential due to destabilization of the  $\text{PbO}_2$  layer that protects the metal.

Compared to the seriously hindered secondary reactions, charging and discharging are very fast reactions at both elec-

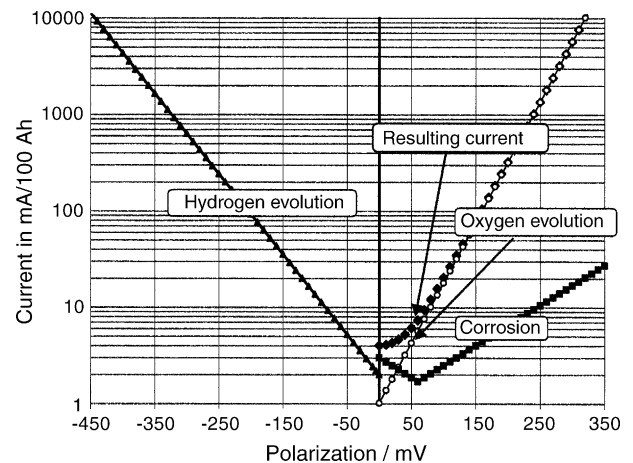


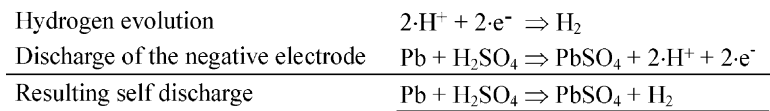
Fig. 3. Secondary reaction in lead-acid batteries. Generalized dependence of their rates on polarization (TAFEL lines) [4]. Polarization referred to an equilibrium cell voltage of about 2.12 V ( $\approx$ acid density  $1.28 \text{ g cm}^{-3}$ ).

trodes, and thus charging would be represented by almost vertical lines in Fig. 3.

#### 4. Self-discharge

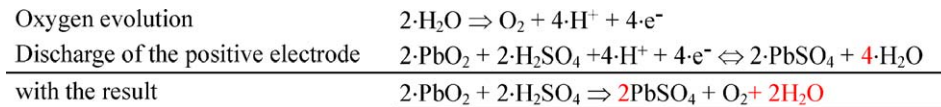
Self-discharge characterizes the situation at open circuit, i.e. when current does not flow through the cell. Then, polarization is zero and positive and negative electrodes are at their rest potential. Hydrogen and oxygen evolution are then at their lowest value for a charged battery. A more positive potential of the negative electrode or a more negative potential of the positive electrode would cause further reduction of the gassing reaction, as extension of the TAFEL lines in Fig. 3 would indicate, but simultaneously this would cause discharge of the concerned electrode.

At the negative electrode, at open circuit hydrogen evolution and the discharge reaction form a couple, that forms a mixed potential and gradually discharges the negative electrode:

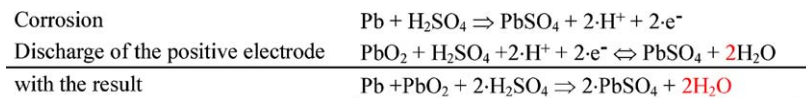


where the rate of this discharge is determined by the rate of hydrogen evolution as the slower reaction.

Self-discharge of the positive electrode is caused by two reactions, namely oxygen evolution and corrosion that independently from each other occur as parallel reactions according to the following scheme:



and



Self-discharge of positive and negative electrodes is independent from each other and occur at rates that are determined by the concerned reacting couple.

#### 5. Current flow

Under current flow, the described reactions occur in parallel, during charging as well as discharging, and in principle they occur independent from each other at a rate that is determined by polarization of the concerned electrode. But this polarization again is determined by the general rule that in the closed circuit equal currents must flow through both electrodes. Thus,

Reaction rates, i.e. current equivalents	
at the negative electrode	at the positive electrode
Charging/discharging reaction, + Hydrogen evolution + Oxygen reduction	Charging/discharging reaction, +Oxygen evolution, + Corrosion
must equal each other as current equivalents when the circuit is closed.	

At a given cell voltage or a given charging current, this relation determines polarization of positive and negative electrodes, and there always exists only one current/voltage couple that fulfills this condition and automatically is accomplished at a given voltage or current.

As a consequence, at a given cell voltage single electrode potential of positive and negative electrodes attain values that fulfill the above rule, and thus polarization of both electrodes is unambiguously determined. At a given current, the same applies to the resulting cell voltage.

##### 5.1. Charging and overcharging of flooded lead-acid batteries

The charging situation of a flooded lead-acid battery is reflected by the following scheme:

Reaction rates, i.e. their current equivalents	
at the negative electrode	at the positive electrode
Charging reaction, + Hydrogen evolution (+ Oxygen reduction)	Charging reaction, +Oxygen evolution, + Corrosion
form the charging current that flows through both electrodes.	

As long as the charging reactions dominate, polarization remains small due to the high current acceptance of both electrodes. As a consequence, the rates of the secondary reactions

are small. A certain oxygen evolution is observed from the very beginning of the charging process, because of the slightly inferior charge acceptance of the positive electrode. Charge acceptance of the discharged negative electrode is excellent and thus hydrogen evolution remains closely to its open circuit value until the electrode is nearly fully charged. Then, the onset of hydrogen evolution is connected to a sudden increase of polarization that causes the characteristic increase of cell voltage at the end of charge.

Hydrogen and oxygen, generated at the negative and positive electrode, respectively, escape from the cell, except a small amount of oxygen that reaches the negative electrode by (very slow) diffusion through the liquid electrolyte.

When the battery is overcharged, only the secondary reactions remain and determine polarization of positive and negative electrodes.

Reaction rates, i.e. their current equivalents	
at the negative electrode	at the positive electrode
+ Hydrogen evolution (+ Oxygen reduction)	+Oxygen evolution, + Corrosion
form now the overcharging current	

Hydrogen and oxygen are generated close to their stoichiometric mixture, since the current equivalents of corrosion and oxygen reduction are small compared to that of the gassing reactions and usually can be neglected. As a consequence, water loss of flooded lead-acid batteries that are on float charging, corresponds fairly well to current consumption.

5.2. Charging and overcharging of VRLA batteries

The charging situation of a VRLA battery differs from the above described one, since now oxygen can easily reach the negative electrode by fast diffusion through void space within the AGM separator or the gelled electrolyte, where it is reduced, and oxygen evolution and oxygen reduction form the internal-oxygen cycle as indicated in the following scheme. Furthermore, the cell is equipped with a valve that causes a slight internal overpressure and prevents a too easy escape of gasses. It opens from time to time to allows escape of mainly hydrogen that is not oxidized within the cell and has to leave. Thus, charging of a VRLA battery means:

Reaction rates, i.e. their current equivalents	
at the negative electrode	at the positive electrode
Charging/discharging reaction, + Oxygen reduction	Charging/discharging reaction, +Oxygen evolution,
+ Hydrogen evolution	+ Corrosion
represent current flow through positive and negative electrodes.	

Now oxygen reduction is the main secondary reaction at the negative electrode. Since the equilibrium potential of oxygen reduction amounts to +1.23 V, this reaction “depolarizes” the negative electrode with the result that in VRLA batteries negative electrodes are only polarized to reach a hydrogen-evolution rate that compensates for the current deficit at the positive electrode caused by corrosion and oxygen loss, whereby the latter can be neglected when the efficiency of the internal-oxygen cycle approaches 100% which usually can be assumed at a not to high cell voltage. Then, hydrogen evolution is small compared to that in flooded cells, and close to the value of self-discharge.

Compared to flooded cells, water loss is no longer related to the overcharging current, which mainly is consumed by the internal-oxygen cycle.

The internal-oxygen cycle effects, that overcharging no longer does occur independently at positive and negative electrodes, since oxygen evolution and oxygen reduction are linked to each other. As a consequence, increased charging voltage mainly increases the internal-oxygen, and nearly no current would be left to level out a charging deficit of the negative electrode that might exist, except the small deficit of oxygen evolution caused by increased corrosion at increased cell voltage.

This charging behavior constitutes a drawback of VRLA batteries, since lost capacity of the negative electrode cannot be regained by normal recharge. Complete recharge of the negative electrode would be possible only at a markedly increased cell voltage, since then the maximum rate of the internal-oxygen cycle is exceeded and the cell partly operates like a vented one. Increased water loss and corrosion must then be accepted, if in practice such an increased voltage cannot be avoided.

5.2.1. Float charging in standby applications

Stationary VRLA batteries are often used as standby batteries for uninterrupted power supply in case of an emergency. In such an application, the battery usually is directly connected to the dc supply of the concerned installation, and is continuously overcharged at a voltage slightly above its equilibrium voltage. Charging reactions no longer occur and the overcharging current must only compensate for the secondary reactions that otherwise would cause gradual self-discharge of the electrodes.

Under such circumstances, current flow that has to be equal through both electrodes, is simplified to:

Reaction rates, i.e. their current equivalents	
at the negative electrode	at the positive electrode
oxygen reduction	oxygen evolution,
+ hydrogen evolution	+ corrosion

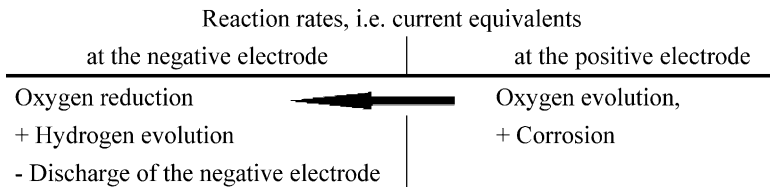
This scheme indicates the important feature of VRLA batteries that at a high efficiency of the internal-oxygen cycle oxygen evolution and oxygen reduction balance each other, and in practice, such a high efficiency is always closely approached.

Oxygen reduction would depolarize the negative electrode to a value more positive than that of the negative electrode. However, even at 100% efficiency of the internal-oxygen cycle, a deficit of oxygen evolution is caused by corrosion that occurs in parallel. This deficit must be compensated for by a corresponding hydrogen evolution at the negative electrode, which means

a certain negative polarization. Thus, polarization of the electrodes is now determined by the balance between the rates of hydrogen evolution and corrosion. Both reactions have to be in a certain range to balance each other at a sufficient polarization of positive and negative electrodes to keep the battery properly charged.

5.2.2. Unbalanced cells

The required balance between hydrogen evolutions cannot always be achieved, and repeatedly batteries have been observed that gradually lose capacity although they were floated at the specified cell voltage [5]. Such a situation is observed when hydrogen evolution exceeds corrosion, even when the negative electrode is no longer polarized or even slightly polarized to values above its equilibrium potential. In other words, hydrogen evolution at zero polarization of the negative electrode exceeds the equivalent of corrosion at the polarized positive electrode, even when polarization of the positive electrode corresponds to the total deviation of the cell voltage compared to its equilibrium value. Then, the above described balance between hydrogen evolution and corrosion is disturbed, and polarization of the negative electrode reaches zero or even slightly positive values. The too high hydrogen evolution is then automatically compensated by an anodic current that causes gradual discharge of the negative electrode according to the following scheme:



Oxygen reduction, hydrogen evolution, and gradual discharge form now the overcharging current at the negative electrode that balances oxygen evolution and corrosion at the positive electrode.

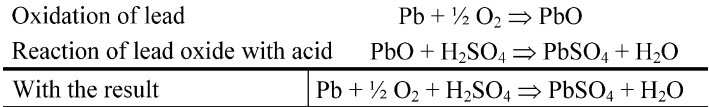
The discharging current can be interpreted as a current that automatically appears to fulfill the general rule that equal current has to flow through positive and negative electrodes. A too high share of reducing current is lost by hydrogen evolution and this

missing share is then compensated by an anodic current, that does not come from the outside, but is taken as discharging current from the negative electrode itself.



Due to the high rate of the discharge reaction, a few millivolts of polarization are sufficient to compensate for the too high hydrogen evolution.

The described situation can also be interpreted as “chemical discharge” by oxygen, left unrecombined in the cell, according to



Such an oxidation is possible since the negative electrode is polarized slightly above its equilibrium potential.

Both ways of looking at the situation lead to the same the self-discharge current that indeed is fairly small, but it runs continuously under such float conditions, and thus it is only a question of time to reach a noticeable capacity loss.

Fig. 4 illustrates the situation. It indicates that the situation would be improved by an increase of corrosion that could be achieved by increased cell voltage. Increase of the cell voltage would not increase hydrogen evolution as long as the corrosion rate would not exceed hydrogen evolution. Only when this is reached, hydrogen evolution must be increased by a corresponding polarization. Then, the situation of the negative electrode would be stabilized, however, at a much higher rate of the internal-oxygen cycle, which is synonymous to a correspondingly increased float current.

5.2.3. Internal catalyst

A measure to avoid gradual self-discharge of such a missing balance between hydrogen evolution and corrosion is an internal catalyst that directly recombines hydrogen and oxygen into water. The aim of such an internal catalyst is a sufficient (slight) reduction of the internal-oxygen cycle. The direct recombination of the always abundant hydrogen consumes oxygen that otherwise would be recombined at the negative electrode or left within the cell and cause “chemical discharge”. Stabilization

of the float situation is reached, when the directly recombined current equivalent not only compensates for the too high hydrogen evolution, but also requires a further slight increase of hydrogen evolution, which automatically means an adequate increase of negative polarization, and thus prevents further discharge. Water loss of the cell corresponds then to corrosion rate. Since only the missing balance between corrosion and hydro-

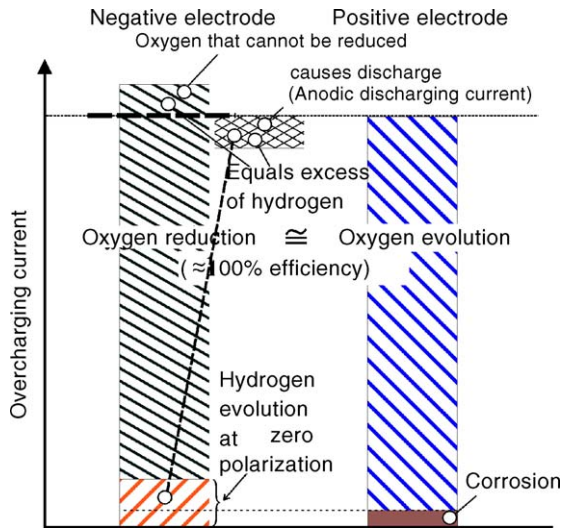


Fig. 4. Float charging of an "unbalanced cell".

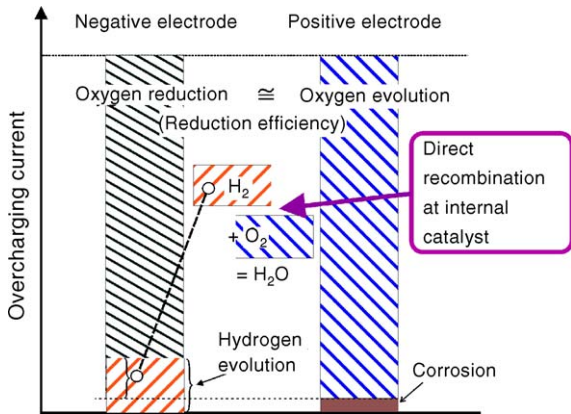


Fig. 5. Effect of an inserted catalyst.

gen evolution has to be compensated for the catalyst can be very small.

Fig. 5 shows the principle of such an arrangement.

Fig. 6 shows the design of such a catalyst, and how it can be inserted. In this figure, a poison filter is shown that is required,

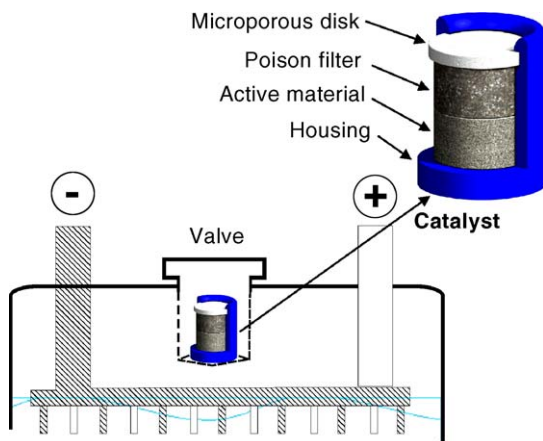


Fig. 6. Internal catalyst and its possible position within a VRLA battery (ref. [1], Fig. 7.20, p. 293, see also Philadelphia Scientific (cf. [6])).

although a VRLA battery represents a very “clean” system, and well known catalytic poisons, like antimony or arsenic that are used as alloying agents in grids of flooded batteries, are banned from use in VRLA batteries. But very small traces of hydrogen sulfide ( $H_2S$ ) are observed in every lead-acid battery, caused by reduction of sulfuric acid at the negative electrode [7]. Such a generation of  $H_2S$  can never be avoided, and small traces are even observed when an electrode of extremely pure lead is polarized in pure sulfuric acid to an extent that is to be expected under float conditions [8]. Within a VRLA battery its concentration is kept very low, since  $PbO_2$  reacts with  $H_2S$  and thus largely removes it. Nevertheless an effective filter is required to maintain the activity of the catalyst during service life of the battery. Since  $H_2S$  is a much more stable gas than  $SbH_3$  or  $AsH_3$  which can be decomposed and filtered by a simple carbon layer (cf., e.g., ref. [1], p. 292), with  $H_2S$  the ‘poison filter’ in Fig. 6 must be an ‘active’ filter that chemically reacts with  $H_2S$ .

Nowadays, such catalyst are used by quite a number of manufacturers, mainly in the US [9].

#### 5.2.4. Cycling in partial state of charge

As already mentioned, VRLA batteries can be cycled in a partial state of charge, since acid stratification does not occur due to the immobilized electrolyte. In such an application, polarization of the electrodes usually remains very low due to the high rate of the charging reactions. This also means that the rate of the secondary reactions is rather slow, and therefore, they can be neglected. Recently, however, the question of a possible use of lead-acid batteries in hybrid cars has attracted growing attention. This application requires cycling at extremely high loads when the battery assists acceleration or recoups braking energy. Under such conditions, polarization of positive and negative electrodes can be considerable because of a limited charge acceptance even in the partly discharged state.

Remarkable polarization during recharge, however, means that also the secondary reactions occur at a considerable rate and can no longer be neglected. In addition, the required huge number of such cycles, especially in an urban cycle with many stops, may sum up their effects and thus cause problems. Gradual discharge of the negative electrode is always observed during such cycling.

An extensive research and development program has been carried out by the Advanced Lead-Acid Battery Consortium (ALABC) with the result of achieving a 10-fold increase in this kind of cycling with VRLA batteries [10].

There are a number of parameters that influence charge acceptance of an electrode, e.g., current penetration into the interior might be too small at such high loads and cause a rather dense layer of discharged material close to the surface. But the previously mentioned interdependence of secondary reactions will also contribute to aggravate the situation as will be shown by the following estimation.

The example is taken from an ALABC report [11] that concerns the influence of various parameters and trace elements on VRLA batteries under high rate partial-state-of-charge conditions. A meticulously carried out cycle test is described in this report, during which cell voltage and single electrode potentials

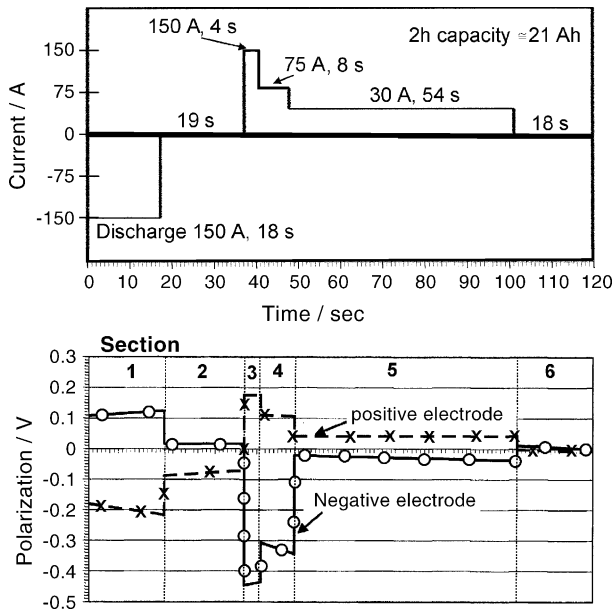


Fig. 7. Current profile and polarization of positive and negative electrodes during a high load cycle of 120 s duration at about 60% state of charge at 40 °C. Potential of the electrodes was measured against an Ag/Ag<sub>2</sub>SO<sub>4</sub> reference electrode. Normal cell, C<sub>2</sub> capacity of about 21 Ah, cycle #5 within a sequence of 10,000 of such cycles. Values taken from Fig. 10 in ref. [11] with kind permission of ALABC.

have continuously been registered. One of the high-load cycles, described in this paper, is here used as an example.

The considered cycle was registered at the beginning of high rate cycling. The battery had been fully charged (charging factor 1.1), was then placed in a water bath that maintained 40 °C, discharged at 0.5 C<sub>2</sub> to 60% SoC, and then subjected to the high load cycle test. We consider here cycle #5, taken shortly after starting the cycling program.

The upper part of Fig. 7 shows the cycling schedule that consists of a number of constant current pulses. The first charging pulse at 150 A means more than seven times C<sub>2</sub>, a really quite high load. The sequence of the following charging pulses is intended to represent recuperation of braking energy.

In the lower part of Fig. 7, polarization values are shown that were derived from curves of the continuously registered single electrode potential. They are of course, roughly approximated but sufficient to demonstrate the situation.

Charge acceptance governs polarization that in turn determines the rate of the various reactions. In the partial state of charge, the rates of the charging/discharging reactions are by orders of magnitude larger than the rates of the secondary reactions, which can be neglected in regard to their current contribution per cycle. Hydrogen and oxygen evolution, however, reach certain rates, and their effect is additive. Thus, they may have a significant impact when large numbers of these high-load cycles are performed as the figures show that are listed below in Table 1.

In Table 1 values are compiled that are derived from Fig. 3 on the basis of the polarization data in Fig. 7. They are only a rough approximation, since Fig. 3 represents generalized values, which may differ in details from the TAFEL lines of the battery being

Table 1  
Current equivalents of oxygen evolution, corrosion, and hydrogen evolution derived from Fig. 3

Section in Fig. 7	Duration (s)	Positive electrode		Negative electrode	
		Polarisation (mV)	Oxygen evolution (mA/21 Ah, 40 °C)	Polarisation (mV)	Hydrogen evolution (mA/21 Ah, 40 °C)
1	18	-200	0	115	0
2	19	-80	0	16	0
3	4	170	312.8	-440	5468.4
4	8	110	112.9	-320	546.8
5	53	41	99.7	-30	109.1
6	18	1	10.6	0	0
Total			536.0		26357.4



tested. Furthermore, the test temperature of 40 °C was taken into account by a factor of 2.8 according to the general rule that electrochemical reaction rates are doubled per 10 °C, this is another rough approximation. Nevertheless, the following calculation gives an impression of the principle to be demonstrated.

The rate of the secondary reactions increases exponentially with polarization, and thus periods of high polarization contribute tremendously, as can be seen in Table 1, especially for the negative electrode. In total, hydrogen is generated equivalent to 26.4 As per cycle, which is lost as charging current.

The generated oxygen that is left within the cell will reach the negative electrode, cause chemical discharge as described in Section 5.2.1 and thus contribute to the discharge of the negative electrode, which then in total amounts to 26.9 mAs per cycle which means 7.5 mAh per cycle.

The loss of 7.5 mAh means that after 1000 such cycles the negative electrode would have lost 7.5 Ah, provided that the situation is maintained. In practice this will not be the case, since polarization of the electrodes underlies gradual changes, e.g., caused by gradual structural changes of the surface.

In this example, use of an internal catalyst as described in Section 5.2.3 would make no sense, since the amount of generated oxygen is very small, and only an equivalent of 0.5 mAs = 0.13 mAh per cycle would be available within the cell for direct recombination. It would reduce the capacity loss to only 7.2 mAh per high-load cycle.

## 6. Conclusions

VRLA batteries offer quite a number of advances compared to flooded ones, such as acid cannot be spilled, hydrogen evolution is markedly reduced and this again reduces ventilation problems. Most important is the possibility to cycle VRLA batteries in a partly state of charge. This has opened a number of applications that had been out of the limits of flooded lead-acid batteries.

Certain limitations, however, are caused by the always present secondary reactions: hydrogen and oxygen evolution and corrosion. These secondary reactions gain significance in the valve regulated design since the internal oxygen cycle closely links overcharging of positive and negative electrodes which no longer can be overcharged separately. Under float conditions, partly discharge of one of them may be caused by an unbalanced ratio between the rates of hydrogen evolution and corrosion. Increased generation of hydrogen and oxygen, caused by high polarization in the partial state of charge, will discharge the negative electrode. Thus, under certain conditions, the secondary reactions may restrict the use of VRLA batteries.

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