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Traditional float charges: are they suited to stationary antimony-free lead acid batteries?

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1. Introduction

The self-discharge phenomenon caused by side reactions such as corrosion, water decomposition and recombination is unavoidable in lead acid batteries. Self-discharge rates depend on several factors such as the state of charge, the temperature, grid alloys, etc. These rates are not equal between negative and positive electrodes and are independent of each other. In lead-acid batteries with antimony, the self-discharge rate of the negative electrode is several times stronger than the self-discharge rate of the positive electrode, depending mainly on the battery age and the antimony content in the alloy of the positive grid.

In order to compensate for the self-discharge of lead-acid batteries, a current whose value exceeds the self-discharge of the negative electrode has to be supplied. This is traditionally achieved by applying a constant voltage whose value is slightly higher than the battery open circuit voltage. This is called "float charge". It has to be kept in mind that the float polarization increases gas evolution rates at both electrodes.

In antimony-free lead-acid batteries, e.g. VRLA batteries, the self-discharge rate of the negative electrode is largely reduced and usually becomes lower than the self-discharge rate of the positive electrode. The question is: are traditional float charges really suited to antimony-free lead-acid batteries? Practical situations on field as well as experimental results say no. Standby VRLA batteries maintained under a constant float voltage to compensate self-discharge encounter the problem of short service life, when our results show that traditional float charge currents are far over what is needed to maintain the VRLA battery state of charge.

In order to reduce overcharge, intermittent charges (open-circuit and periodical charges) have been used instead of float charges and have given positive results in reducing thermal runaway and increasing the battery life span. Nevertheless, corrosion of the positive grid is also high during open-circuit periods of intermittent charges. Indeed, it is revealed in the literature that corrosion is minimum when the positive polarization is between 40 and 80 mV.

In this chapter, taking into account this minimum corrosion, a new method of maintaining the charge of antimony-free lead-acid batteries using low currents and periodic charges is

developed and tested. This is called "Low-current" method. This method is derived from the intermittent charge: open-circuit periods are replaced by constant low current periods whose values are about 5 to 10 times smaller than traditional float current values.

Laboratory experiments are focused on studying rates of self-discharge at open circuit and state of charge evolutions of lead-acid batteries in three different cases: float charge, low-current charge and open circuit. The new low-current method, associated to an improved storage architecture system is now used in several electrical substations and hydraulic power plants at Electricité de France (EDF). This association is intended to provide long life span and high reliability to VRLA batteries.

2. Lead acid batteries in stationary applications

Secondary reactions such as corrosion, water decomposition and oxygen recombination are the main cause of self-discharge of stationary lead-acid batteries. Maintaining the charge of standby batteries is necessary to compensate self-discharge. However, if the maintaining-charge current is too high, it can accelerate these side reactions, which can thus become the cause of several failures of standby batteries. An appreciated method of maintaining the charge for stationary lead acid batteries is a trade-off between their state of charge and state of heath.

2.1 Secondary reactions as causes of self-discharge

The self-discharge phenomenon in stationary lead-acid batteries is due to the simultaneous presence of main reactions, i.e. charge and discharge of active materials and unavoidable side reactions such as corrosion, water decomposition and oxygen recombination. At open circuit, the battery voltage does not only correspond to the equilibrium voltage of principal reactions but depends on the mixed voltage of both main and side reactions (Berndt, 1997). Its value is between the equilibrium voltage value of the principal reactions and the one of the secondary reactions. Water electrolysis is one of the principal secondary reactions and its potential difference is 0.7 to 0.75 V lower than the potential difference of the charge-discharge reactions (depending on electrolyte density and temperature). In these conditions, at open circuit, secondary reactions are produced at the expense of principal reactions; the battery is thus discharged or "self-discharged". However, the influence of these secondary reactions is quite weak as the kinetics of oxygen and hydrogen evolutions are very slow. The battery potential difference at open circuit is smaller but very close to the potential difference of principal reactions.

The self-discharge caused by secondary reactions concerns only the positive or the negative electrode. The self-discharge of the negative electrode is mainly related to the evolution of hydrogen and to the reduction of oxygen while the self-discharge of the positive electrode is principally associated to the evolution of oxygen and to the corrosion of positive grids.

2.1.1 Self-discharge reactions at the negative electrode

1. Self-discharge due to hydrogen evolution

H$_2$ evolution: $2H_3O^+ + 2e^- \rightarrow H_2 + 2H_2O$

Discharge of Pb: $Pb \rightarrow Pb^{2+} + 2e^-$

Overall reaction: $Pb + H_2SO_4 \rightarrow H_2 + PbSO_4$ Reaction 1

2. Self-discharge due to oxygen reduction

O_2 reduction: $\dfrac{1}{2}O_2 + 2H_3O^+ + 2e^- \rightarrow 3H_2O$

Discharge of Pb: $Pb \rightarrow Pb^{2+} + 2e^-$

Overall reaction: $Pb + \dfrac{1}{2}O_2 + H_2SO_4 \rightarrow PbSO_4 + H_2O$ Reaction 2

Thus, in the presence of sulfuric acid, Reaction 1 and Reaction 2 cause self-discharge of the negative electrode with lead sulfate $PbSO_4$ as the final product.

2.1.2 Self-discharge reactions at the positive electrode

1. Self-discharge due to oxygen evolution

O_2 evolution: $3H_2O \rightarrow \dfrac{1}{2}O_2 + 2H_3O^+ + 2e^-$

Discharge of PbO$_2$: $PbO_2 + H_2SO_4 + 2H_3O^+ + 2e^- \rightarrow PbSO_4 + 4H_2O$

Overall reaction: $PbO_2 + H_2SO_4 \rightarrow \dfrac{1}{2}O_2 + PbSO_4 + H_2O$ Reaction 3

2. Self-discharge due to corrosion

When the active material (PbO$_2$) supplies the O^{2-} ions to neutralize the Pb^{2+} ions:

Grid corrosion: $Pb \Rightarrow Pb^{2+} + 2e^-$

$\quad\quad\quad\quad\quad Pb + O^{2-} \Rightarrow PbO + 2e^-$ Reaction 4

Discharge of PbO$_2$: $PbO_2 + H_2SO_4 + 2e^- \Rightarrow PbSO_4 + O^{2-} + H_2O$ Reaction 5

Combining Reaction 4 and Reaction 5, we have:

$Pb + PbO_2 + H_2SO_4 \Rightarrow PbO + PbSO_4 + H_2O$ Reaction 6

Once the PbO$_2$ active material loose O^{2-} for corrosion, it will pick up O^{2-} ions of H$_2$O (H$_2$O content of the electrolyte, i.e. 2H$_3$O$^+$ and O^{2-}) to neutralize its charge. Corrosion consumes water.

When the grid is on contact with the electrolyte:

Grid corrosion: $Pb \Rightarrow Pb^{2+} + 2e^-$

$$Pb + H_2SO_4 + 2H_2O \Rightarrow PbSO_4 + 2H_3O^+ + 2e^-$$ Reaction 7
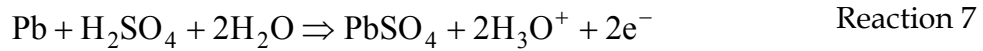
Discharge of PbO_2: $PbO_2 + H_2SO_4 + 2H_3O^+ + 2e^- \Rightarrow PbSO_4 + 4H_2O$ Reaction 8

Combining Reaction 7 and Reaction 8, we have:

$$Pb + PbO_2 + 2H_2SO_4 \Rightarrow 2PbSO_4 + 2H_2O$$ Reaction 9

The formed lead oxide (PbO) in Reaction 6 is converted into lead sulfate according to Reaction 10 as soon as it gets in contact with sulfuric acid:

$$PbO + H_2SO_4 \rightarrow PbSO_4 + H_2O$$

Reaction 10

It is clear that side reactions taking place at negative and positive electrodes are independent of one another and self-discharge rates are not equal between the positive and the negative electrodes.

Self-discharge rates depend on a lot of factors such as temperature, grid alloys and the battery state of charge.

Generally, the approximation holds true that a temperature increase of 10 K (degrees Centigrade) the reaction rate doubles. In electrochemical reactions, this means that equivalent currents are doubled, e.g. a temperature increase of 20 K means a current increase by a factor of 4; a rise in temperature of 30 K corresponds to a factor of 8 (Berndt, 1997).

In lead-acid batteries with antimony grid alloys, the self-discharge rate of the negative electrode is several times stronger than the self-discharge rate of the positive electrode, depending mainly on the antimony content in the alloy of the positive grid and the battery age. Indeed, at charge, the Sb metal, whose equilibrium potential is above that of the negative electrode, dissolves (corrodes) progressively from the positive grid, diffuses through the electrolyte and is precipitated (reduced) at the negative electrode. As this contaminated electrode has a lower hydrogen overvoltage, this results in a greater hydrogen gassing rate (Berndt, 1997). The more aged battery is, the more serious this "antimony affect" is. In antimony-free lead-acid batteries, e.g. VRLA batteries with Pb/Ca grid alloys, the self-discharge of the negative electrode is largely reduced. It should be kept in mind that the electrode with stronger self-discharge rate limits the capacity of the cell.

The self-discharge rate depends also on the battery state of charge as it affects gassing reactions. It is clear that the self-discharge is easier when more active materials are available, or in other words hydrogen H_2 and oxygen O_2 evolution cannot occur at a surface covered by lead sulfate $PbSO_4$.

2.2 Traditional method of maintaining the charge – float charge: a trade-off between state of charge and state of health

In order to compensate for the self-discharge of lead-acid batteries, a current whose value exceeds the self-discharge of the limit-capacity electrode has to be supplied. Traditionally, a voltage whose value is slightly higher than the battery open circuit voltage is applied to compensate for the difference between mixed potentials and equilibrium potentials of the principal reactions. This is called "float charge".

In reality, equilibrium potentials depend on a lot of factors such as temperature, electrolyte density, grid alloys (Berndt, 1997, Bode, 1977). Moreover, as a constant voltage is applied between two terminals of a cell, the potential distribution is not properly shared between the negative and the positive electrode (Berndt and Teutsch, 1996, Ruetschi, 2003, Brecht, 1998, Martinez and Novak, 1990, Misra et al., 1994), cf. figure 3. In batteries with cells in a series configuration, the phenomenon of voltage scattering on cells is also present (Hawkins et al., 1995, Berndt, 1997, Misra et al., 1994, Rossinot et al., 2003), cf. figure 4. In addition, it should be kept in mind that the float polarization increases gas evolution rates at both electrodes. It is very difficult or even impossible to choose a value of float voltage, which can take into account all of these phenomena without paying the piper. Convenient practical values for float voltage have been empirically determined. To get rid of the risk of under-charge, batteries in float charge are permanently overcharged.

2.2.1 Bimodal float voltage distribution between the negative and positive electrodes – difference between vented batteries and VRLA batteries

The electrode reactions on float charge are described in detail by Berndt and Teutsch (Berndt and Teutsch, 1996). During float charge, hydrogen evolution, oxygen evolution and grid corrosion proceed certainly as presented in figure 1.

In maintaining the voltage above the open-circuit value, the float current serves to compensate for the electrode discharge caused by these side reactions. When this float current is too low, i.e. the positive potential is slightly below its equilibrium value, or the negative electrode potential is slightly above its equilibrium value, the discharge of the electrodes would occur. Otherwise, the battery is completely charged or overcharged. In general, batteries in float charges are permanently overcharged. The float current, i.e. overcharged current, feeds electrons to secondary reactions.

Berndt and Teutsch presented the model used for float charge describing the single cell behaviors at overcharge in (Berndt and Teutsch, 1996). Under normal float conditions as the battery is already completely charged, the charge and discharge reactions of the active materials do not occur. The equal float current flow through both electrodes can be written, cf. figure 2:

At the positive electrode: $I_{float} = I_{O2\,ev.} + I_{corr.}$
At the negative electrode: $I_{float} = I_{H2\,ev.} + I_{O2\,re.}$
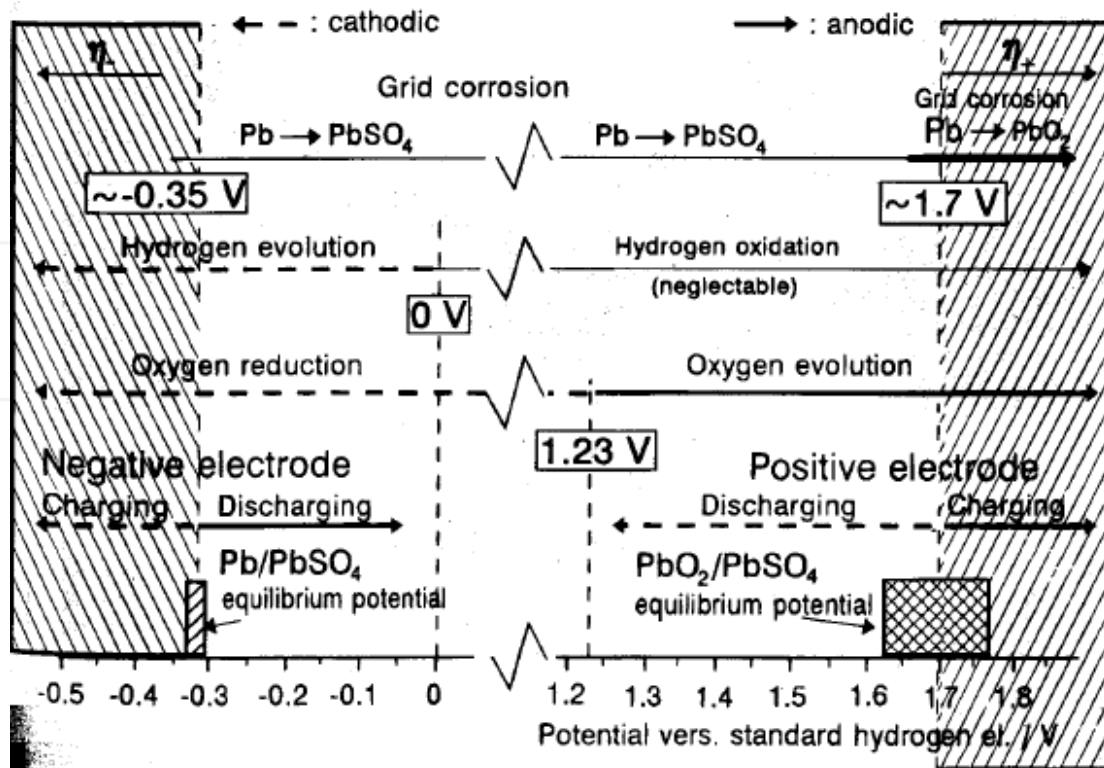The balance reaction: $I_{float} = I_{O2\,ev.} + I_{corr} = I_{H2\,ev.} + I_{O2\,re.}$

Fig. 1. Reactions that occur in lead acid batteries dependent on electrode potential. Equilibrium potentials of charge-discharge reactions (Pb/PbSO$_4$ and PbSO$_4$/PbO$_2$) are presented in columns, because they depend on the acid concentration. (Berndt and Teutsch, 1996)

In general for electrochemical reactions, the current is an exponential function of the electrode potential, cf. Eq.(1). At high overvoltage, current/voltage curve forms a straight line, called "Tafel line".

$$\eta_a = \frac{RT}{\alpha nF} \ln(|i|) - \frac{RT}{\alpha nF} \ln(|i_0|) = a + b\log(|i|) \tag{1}$$

This is applied also for the H$_2$ and O$_2$ gas-evolving reaction in lead acid batteries, since they are polarized by more than 0.3 V already at the battery open-circuit voltage, cf. figure 1. Tafel lines for hydrogen and oxygen evolution have been confirmed in literatures. A slope *b* of about 0.12 V per current decade is nearly always found for hydrogen evolution, while the corresponding slope for oxygen evolution is between 0.07 and 0.14 V per current decade (Berndt, 1997, Bode, 1977). Feder and Carosella revealed that at float charge of a vented lead acid battery, the negative electrode is polarized more than the positive electrode (Feder and Carosella, 1994).
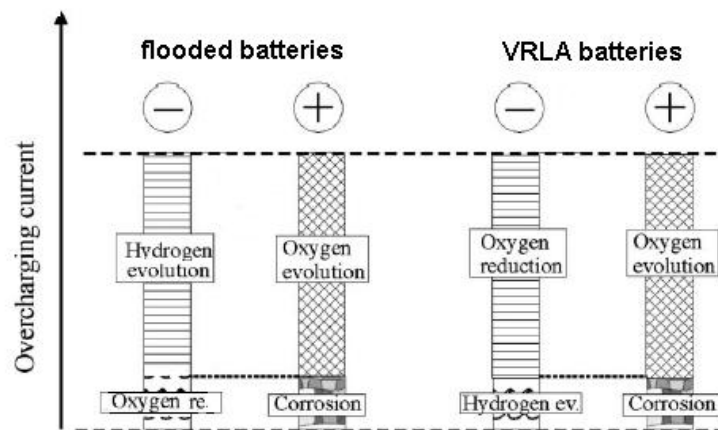
Fig. 2. Description of equal float current flows through both electrodes in the normal conditions at flooded batteries and VRLA batteries (supposing that the recombination efficiency at the VRLA battery is 100%)

In the case of VRLA batteries, the principal reactions at the negative electrode during float charge are hydrogen evolution and oxygen reduction. As the rate of H_2 evolution reaction is low thanks to the utility of antimony free grid alloys, essential float current is for the oxygen recombination. The rate of the oxygen reduction reaction is determined by the rate of oxygen diffusion from the positive electrode to the negative electrode, which does not depend on the electrode potential. If the diffusion of oxygen is sufficiently fast, which is the case in VRLA batteries, the oxygen recombination will occur, as the potential condition - inferior to 1.23V - is already satisfied at the negative electrode. The negative electrode is thus only polarized by the hydrogen evolution reaction. Therefore, in VRLA batteries the positive electrode takes essential polarization and the negative electrode can be depolarized during float charges, cf. figure 3.
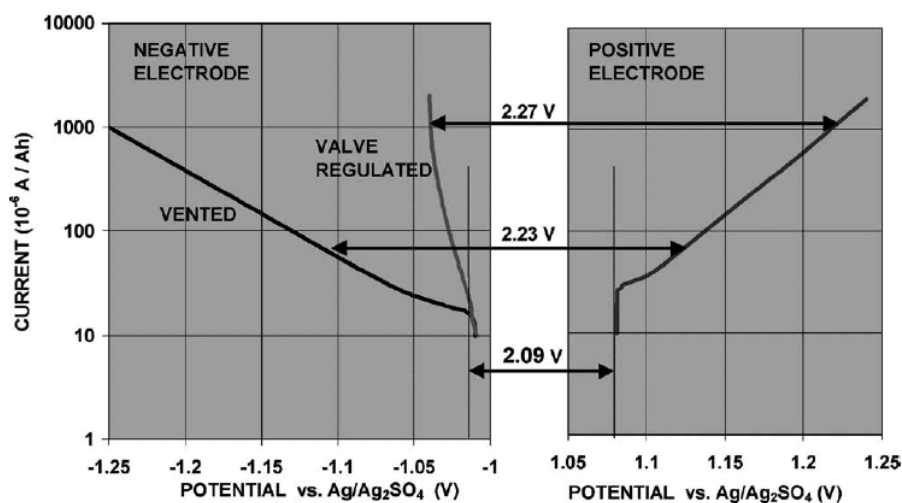

Fig. 3. Polarization curves of positive and negative electrodes, when measured against silver–silver sulfate reference electrodes. This figure demonstrates that the positive electrodes of valve-regulated batteries are subjected to much higher potentials than the positive electrodes in vented batteries (Ruetschi, 2003)

2.2.2 Cells in series configuration – scattering problem

In general, in order to obtain a desirable voltage value, one battery is composed of several cells connected in series configuration. A usual phenomenon observed in these assemblies is the voltage scattering between individual cells (Berndt, 1997, Misra et al., 1994, Rossinot et al., 2003, Hawkins et al., 1995). One example given by Berndt (Berndt, 1997) shows that for a mean float voltage of 2.38V per cell, a normal distribution curve with a standard deviation of ± 33mV and a difference between the maximum and the minimum values of 170mV are noticed. There are many reasons producing the voltage scattering. Some of them are found in industrial installations, despite the rigorous manufacturing process control and special industrial conditions (Rossinot et al., 2003).

It is revealed above that the polarization is not properly symmetrical for negative and positive electrodes. The voltage scattering thus reflects the voltage dispersion of negative electrode in flooded batteries (Feder and Carosella, 1994) and of the positive electrode in VRLA batteries (Berndt and Teutsch, 1996, Hawkins et al., 1995).
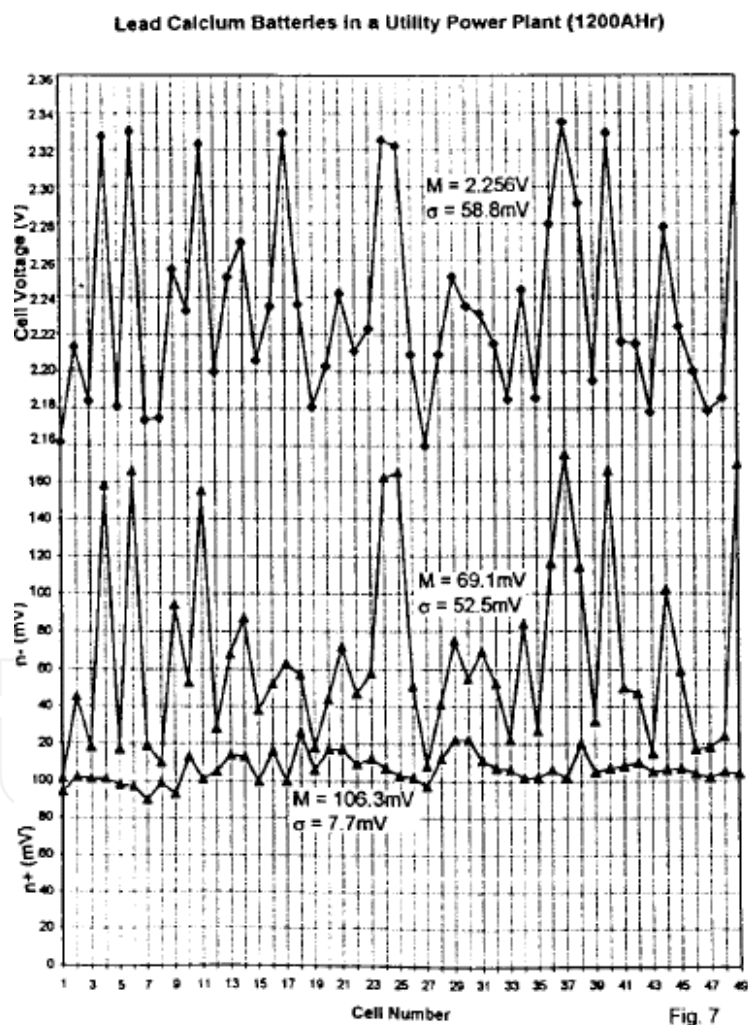

Fig. 4. Distribution of 113 V on 50 vented cells Pb-Ca in series configuration for 9 years of float charge. η⁻ and η⁺ are potentials of the negative and positive electrodes. Voltage dispersion appears obviously at the negative electrodes and its presence is far smaller at the positive electrodes (Feder and Carosella, 1994)

2.3 Secondary reactions as causes of failure modes

At float charges, if both electrodes are well polarized, i.e. float potentials exceed the equilibrium ones; float currents will serve only to produce side reactions. The higher the float current is, the stronger the rates of side reactions are, especially the rates of gas evolution reactions.

Secondary reactions are not only the cause of self-discharge, but also the cause of main failure modes of stationary lead acid batteries under constant float voltages. Flooded and VRLA technologies can be affected by corrosion, including creeping, and degradation of positive electrodes (Berndt, 1997, Ruetschi, 2004, Stevenson, 1996, Wagner, 1995, Feder, 2001, Nakamura et al., 1996, Brissaud et al., 1997, Cooper and Moseley, 2003). VRLA batteries are moreover subjected to electrolyte dry-out and thermal runaway (Nakamura et al., 1996, Wagner, 1995, Berndt, 1997, Elgh, 1994, Cooper and Moseley, 2003).

2.3.1 Corrosion

Corrosion is the cause of different failure modes (Pavlov, 1993, Shiomi et al., 2003, Kosai et al., 1997, Peters, 1996, Ruetschi, 2004, Garche, 1995, Wagner, 1995, Misra and Williamson, 1995, Willihnganz, 1968):

- The oxides, corrosion products, take more volume than the metallic grid. The result is an expansion of the positive grid into three dimensions, in particular into the dimension of each bar of the grid. Under such mechanical stresses, the grid bars get longer and the grid dimension increases, this is called "grid growth" or "grid creeping". This distortion can provoke internal short-circuits when the grown grid comes into contact with the negative top-bar, cf. figure 5.
- The formation of an electric passivation layer (barrier layer) at the interface between a positive grid and its active material prevents electrical contact between them. The passivation layer is sometimes said to be a closely structured $PbSO_4$ layer (high-resistance layer) formed at the grid active-material interface, or lower oxides of lead, such as PbO, that are generated in a high-pH environment.
- When the grid growth becomes excessive, apart from the passivation layer other causes of gradual loss of contact between the active material and the grid are noticed. The first one is the displacement of the active material away from the grid as it is not able to follow the grown grid. The second one is the gradual disappearance of the metallic grid, i.e. the grid is consumed by corrosion and can no longer take the role of electric conductor, cf. figure 6.

VRLA batteries under float charges, along with their grid design and their characteristic of the oxygen recombination, seriously suffer the corrosion consequences. Usually, 4% grid growth over the battery lifetime is the design limit. In most VRLA batteries, the grid sections are smaller; grid growth rates thus should be higher. There is some evidence that designs with absorbed and limited amounts of electrolyte are less tolerant to growth and, therefore, suffer greater capacity losses (Peters, 1996). Moreover, in VRLA batteries, in order to lower the self-discharge rate, Pb-Sb alloys are replaced by Pb-Ca alloys, where the electric passivation of the positive grid alloy, called the "antimony-free effect" usually occurs (Rocca and Steinmetz, 2003, Kosai et al., 1997). In addition, the operation potential of the positive electrode under float charge is higher in VRLA designs, cf. 2.2.1. For instance, the potential of the positive electrode is likely to be 50 to 100 mV higher than in a flooded battery (Peters, 1996). Different publications have demonstrated that there is a zone of positive polarization

where the corrosion is minimum, c.f. 3.2. According to Brecht et al. (Brecht et al., 1989), the corrosion rate is minimum when the positive polarization is between 30 and 70 mV and increases to almost double at 150 mV. Therefore, the increase of the grid growth due to corrosion is further encouraged in VRLA batteries under float charges.

(a)   (b)

Fig. 5. Due to corrosion, short-circuit took place and caused explosion accident in a standby tubular battery: (a) positive plate lengths were increased and touched the negative collective bar, (b) positive plates were distorted; the positive terminal obviously became more higher than the negative terminal; battery was destroyed after explosion (Source: EDF)
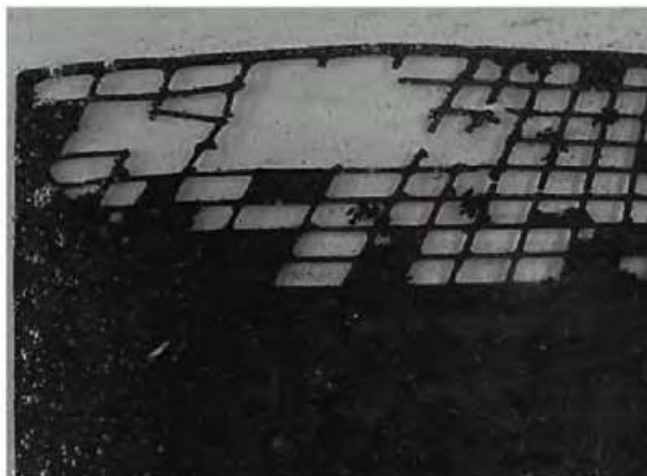

Fig. 6. Corroded positive plate of a starter battery, at the end of 5 years of service life in a passenger car (Ruetschi, 2004)

2.3.2 Water loss

Water electrolysis, i.e. evolutions of hydrogen at the negative electrode and of oxygen at the positive electrode, as well as positive grid corrosion cause water loss of the electrolyte, cf. 2.2.1. In VRLA batteries, despite of the recombination of oxygen at the negative electrode, water loss always occurs. This is due to the evolution of hydrogen, which cannot be re-oxidized to water at the positive electrode, at least not at a significant rate. Other causes of water loss such as container leakages, water evaporation, which are not mentioned in this chapter, aggravate the situation.

Dry-out

Water loss is not a problem as long as the electrolyte level can be refilled like in the case of flooded batteries. However, in the cases where maintenance intervals are not being properly respected or float charge rates are too high, water loss can reduce the capacity of the battery and finally limit the battery lifetime. Water loss induces a higher acid concentration, which results in an increase of the electrode equilibrium potentials. This means that oxygen and hydrogen overvoltages at open-circuit increase which lead to the growth of gas evolutions or of self-discharge rates. This would require an increase of float currents and of charge currents. If this demand is ignored, an insufficient state of charge and sulfation of plates can occur. If the electrolyte level is below the plate edges, the part of the plates above the acid level cannot be charged properly and this part of the plates will then undergo sulfation as well (Ruetschi, 2004). A dangerous case can happen when there is short-circuit in a non-electrolyte area; ignition of hydrogen can take place and provoke an explosion (cf. figure 5).

In the case of VRLA batteries, as water cannot be refilled, water loss can become a serious problem, especially at high temperatures or excessive float voltages. Electrolyte "dry-out" is often observed. Apart of the increase of gas evolutions as mentioned above, the electrolyte decrease leads also to a decrease in the contraction of separator, when the electrolyte content is under 90 % (Nakamura et al., 1996). As separators in actual batteries initially retain about 95% of the electrolyte, separators shrinkage is not appreciable. This shrinkage can bring later to poor contacts between the plates and the separators, increasing the internal resistance. The increase of acid concentration due to water loss can induce also an increase of the oxygen recombination efficiency (Wagner, 1995). This chemical reaction of oxygen reduction is a strong heat source. Oxygen evolution is higher with the increase of acid concentration. Excessive recombination efficiency can increase dramatically the temperature of the battery and can lead to a so-called "thermal runaway".

Thermal runaway

Thermal runaway is a current phenomenon observed at VRLA batteries (Pavlov, 1997, Giess, 1997, Culpin, 2004, Berndt, 1997, Hu et al., 2006). It is defined as an unstable state of operation where heat generation increases faster than heat can dissipate (Berndt, 1997). It is also described as an increase of charge current or float current that occurs as a result of an increase of the cell temperature from an initial applied constant potential. In other words, thermal runaway is usually considered to be the result of positive feedback of current and temperature when a cell is subjected to float charge at constant potential (Culpin, 2004). The initial float current flowing through the cell causes an increase in cell temperature that causes an increase in current that further increases the temperature until both current and temperature reach high values.

Two main source of heat during charging are the reversible heat effect of the cell reactions and the Joule heating caused by the charge current. The internal oxygen cycle represents a special form of Joule heating and is a strong heat source (Berndt, 1997).

The important parameters that mainly influence the internal oxygen cycle are the applied float voltage, the ambient temperature and the separator dry-out or the electrolyte saturation level in the separator pore volume. High float voltages and high temperatures induce more water loss, which in turn reduces the electrolyte saturation in the separator pore volume. The lower is the saturation the more favorable is the condition for the internal oxygen cycle to take place.

According to J. Hu et al. (Hu et al., 2006), when the saturation is low, there is more gas space in the AGM separator for oxygen generated from the positive plates to transport to the negative plates, where the oxygen recombination occurs. Oxygen reduction shifts the potential of the negative electrode to a less negative value. Since the applied voltage was unchanged, the potential of the positive electrode shifts more positively, which in turn leads to the generation of more oxygen on the positive plates. So the float current response becomes increasingly high. The thermal runaway occurs. In fact, the increased current at a constant float voltage is mainly used for oxygen evolution on the positive plates and the oxidation of Pb by O_2 on the negative plates to produce $PbSO_4$ (cf. reaction of self-discharge by O_2 reduction).

According to B. Culpin (Culpin, 2004), at high saturations, oxygen transport by the pressure-assisted route gives good recombination efficiencies of the order of $95 \div 97\%$, but only at low float currents. At low saturations oxygen transport is mainly by pure diffusion and the recombination efficiency is high even at high current. This high recombination current generates much more heat than when gassing overvoltage occurs and thermal runway takes place.

Both authors show that the battery is out of control and thermal runaway occurs at a specific saturation of the separator around $80 \div 85\%$ even at low applied float voltages.

B. Culpin resumed the thermal runaway procedure in three stages:

- Stage 1: recombination efficiency is low; water loss is high, temperature and current rise slowly due to the small and slowly increasing internal resistance and low recombination efficiency.
- Stage 2: the recombination efficiency, even at high currents is high because of the change in oxygen transport mechanism through the separator. Heat generation increases rapidly because of a combination of increased recombination rate and increased internal resistance of the separator.
- Stage 3: the current rapidly decreases to zero as a result of the rapid increase in separator resistance. In fact, the internal resistance increases rapidly when the saturation is below 80 %, e.g. at 40% saturation the separator has a resistance 30 times of that in a fully saturated state.

3. New method of maintaining the charge for improving battery life span – low current method

3.1 Heritage of intermittent charges

In order to limit the overcharge problem, instead of continuous charge, periodic charges (ON phases) are applied and the rest of the time the battery is kept on open circuit or open-circuit voltage (OFF phases) (Reid and Glasa, 1987). This is called intermittent float or intermittent charge. This method is executed based on the principle that a battery on open-circuit for a given time (from some seconds to some weeks) looses a part of its capacity, which can be restored by a charge.

Different researches have shown positive results of intermittent charge vs. float charge concerning reduced average overcharge (Rossinot et al., 2001, Muneret et al., 2000), increased efficiency of charge phases (Rossinot et al., 2001) and reduced thermal runaway in VRLA batteries (Giess, 2001). However, if the intermittent charge parameters (threshold voltages, charge voltage or current, duration of ON phases and OFF phases…) are not

optimized, the risk of under charge, especially under charge of the negative electrode of VRLA batteries is frequent (Muneret et al., 2000). Improving intermittent charge parameters is still an open subject of research.

Characteristic	(Gun et al., 1997)	(Reid and Glasa, 1987)	(Kita et al., 1993)	(Giess, 2001)	(Rossinot et al., 2001)
Phase OFF Duration Fin condition	Open-circuit ≈ 15 s End-voltage	2.17V/cell - -	Open-circuit ≈ 2 months End-voltage 2.125 V/cell	2.15V/cell 108 h -	Open-circuit ≈ 1100 s End-voltage 2.16V/cell
Phase ON Fin condition	Constant current	Constant voltage 2.375 V/cell	12 Ah charged	Constant voltage 2.25V/cell	Constant current 23.8 mA/Ah End-voltage 2.34V/cell
α = duration ON/(ON +OFF)	0.0625	0.5	≈ 0.1 to 0.03	0.357	0.0054

Table 1. Bibliography summary of characteristics of intermittent charges for VRLA batteries (Dillenseger, 2004)

3.2 Benefit of corrosion minimum

Reference	Analysis type	Minimum span (mV)	η^+ min (mV)
(Lander, 1956)	Grid without active material, few hours	30< η^+<200	"flat"
(Ruetschi and Angstadt, 1964)	Grid without active material, few hours	100< η^+<250	180
(Willihnganz, 1968)	Service life (accelerated), some years	50< η^+<100	No defined
(Brecht et al., 1989, Brecht et al., 1990)	Grid growth (accelerated), some years	30< η^+<70	40
(Berndt and Teutsch, 1996)	Review of literature	40< η^+<80	60
(Ruetschi, 2004)	Review of literature	20< η^+<80	60

Table 2. Bibliography summary of positive polarization (η+) associated to a corrosion minimum (Dillenseger, 2004)

Different publications about corrosion phenomenon of the positive electrode have demonstrated that there is a potential zone where corrosion is at a minimum (cf. Table 2). This minimum would be at positive polarizations (η+) between zero (at open-circuit) and polarizations at float charges (η+ ≈ 100 mV). According to Brecht et al. (Brecht et al., 1990) this minimum zone is situated in the range of [30;70] mV. This also shows that neither open-circuit periods of intermittent charges nor overcharge by traditional float charges can place the positive electrode potential in the minimum corrosion zone.

3.3 Principle of the new maintaining charge method

Taking into account this minimum corrosion zone, a new method for maintaining the charge of standby lead acid batteries, called "Low-current" method, has been developed at EDF (Nguyen et al., 2008, Dillenseger, 2004, Alzieu and Dillenseger, 2006). This method is derived from the intermittent charge: open-circuit periods are replaced by constant low current periods. These constant currents, whose values are smaller than traditional float currents, are intended to compensate, at least partially, self-discharge currents, and preferably place the battery in the minimum corrosion zone.
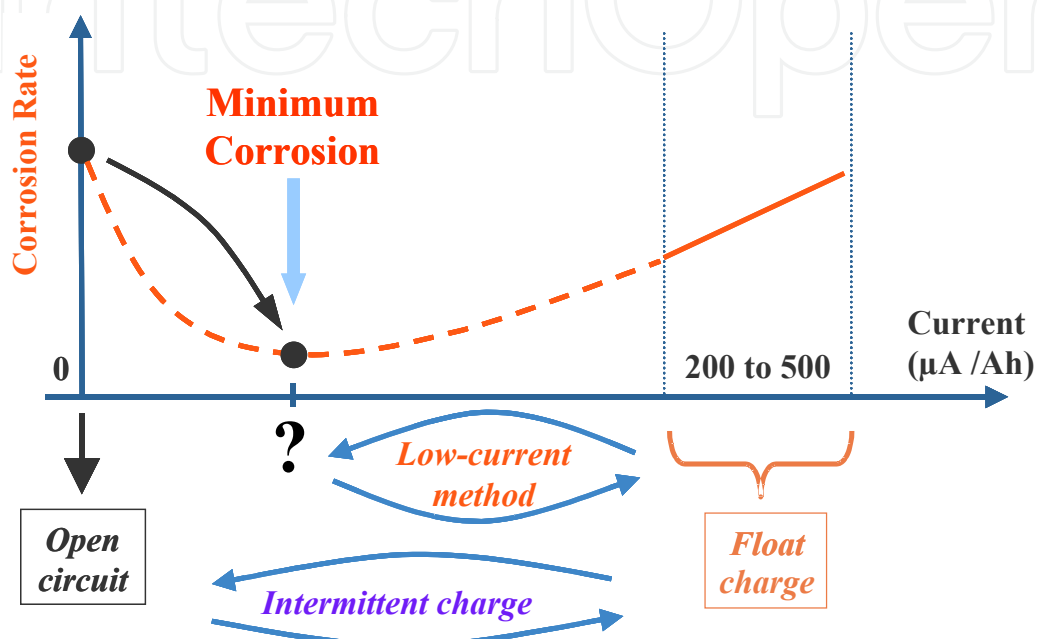
Fig. 7. Low-current method is derived from intermittent charge: open circuit periods are replaced by low currents, whose values are smaller than float current (200 to 500 µA/Ah). Battery should be in the minimum corrosion zone

The choice of piloting the current instead of the voltage to supply low positive polarizations relates to the fact that maintaining a voltage with a value very close to the battery open voltage is difficult and can accidentally discharge the battery (Giess, 2001). Moreover, the scattering phenomenon when a voltage is applied to the battery consisting of cells in series configuration is unavoidable. Monitoring the voltage share for each cell is difficult and expensive while applying a current ensures that every cell receives a given current value.

Although these low currents alone are not supposed to maintain a full state of charge, they can compensate most of the self-discharge. They thus enable the intervals between recharge phases to be considerably extended so that water losses and corrosion associated to these charges are reduced.

Expected results are: (i) a slow down of the corrosion rate of positive grids, (ii) a reduction of the need of periodical charges.
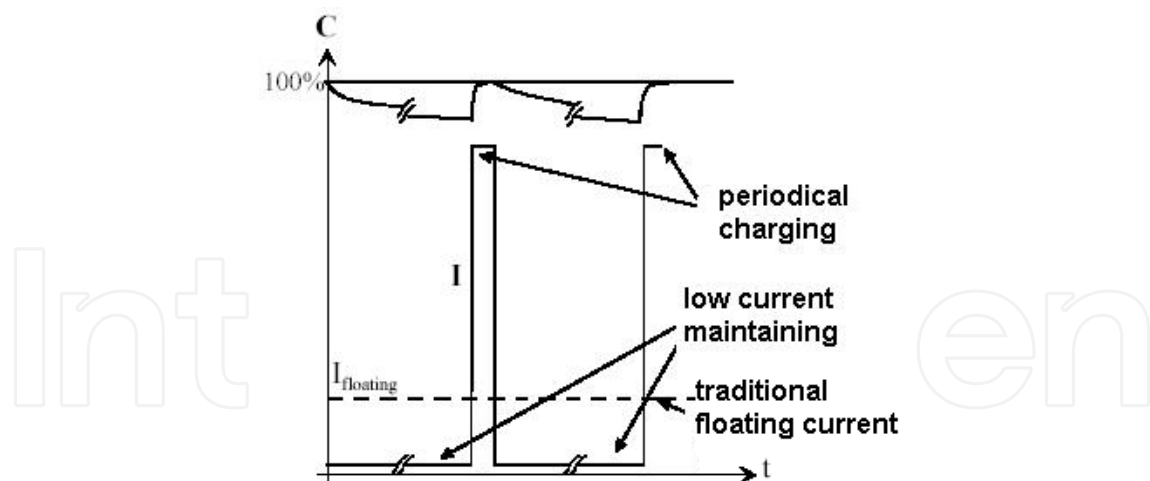
Fig. 8. Principe of new charge strategy using low-current and periodical charges

4. Experimental

Laboratory experiments aim to evaluate the state of charge of batteries subjected (1) to open circuit, (2) to float charges and (3) to polarizations whose values are intermediate between zero and float polarizations, i.e. low current charges. Several current values below float currents have been tested.

Two methods to evaluate the battery state of charge were used:

- Measurement of lead sulfate content in the battery active materials by a chemical titration. This procedure requires the destruction of the battery
- Battery capacity measurement by discharge tests.

We started different experiments with antimony-free vented SLI batteries, Exide 40 Ah/12V L01033C24A. During the experiments, capacity measurement results of these batteries showed a high degree of dispersion, which we attributed to the fact that they are not suitable for repetitive charge-discharge cycles. We then continued these experiments with VRLA AGM batteries, EnerSys 400 Ah/2 V

Low currents were applied using METRIX power supplies AX 502 2.5A – 30 V. As their accuracy does not allow a fine control of currents as low as a few mA, these power supplies were used as voltage regulators and the low currents were set using resistors in series.

Positive polarizations were evaluated using a lead acid battery reference electrode, which was first charged and then stabilized at open circuit. A current path between the tested cell and the reference electrode was provided by a tube filled with immobilized electrolyte.

The discharge-charge cycles were performed with BITRODE Battery Charge and Test System, Module Type LCN 100A – 5V.

Voltages, currents, positive polarizations and temperatures were recorded with Personal Daq 56™ USB Acquisition Systems.

4.1 Lead sulfate content measurement by chemical titration

Batteries used for lead sulfate measurements were antimony-free vented SLI batteries, Exide L01033C24A, 40 Ah-12V. The plates were pulled out of the batteries and rinsed with distilled water for 1 week before picking up active material samples. Lead sulfate contents on the later samples were measured chemically: the successive formation of complexes is

achieved using nitric acid, acetic acid, xylenol orange and titriplex III (EDTA). The last complex is reached using a titrated solution of EDTA. The final stage of this reaction induces a color change: violet to yellow. Sulfate content was calculated from the sample mass and the quantity of EDTA used.

Four batteries were subjected first to open circuit during 231 days, then to low currents of 25, 50, 100 and 200 µA/Ah during 356 days at room temperature (23 ± 4°C) and were finally opened to analyze their lead sulfate content.

4.2 Capacity measurement by discharge test

Before beginning the experiments, we had a preliminary remark that the measurements of self-discharge, even after several months at open circuit, represent only a weak portion of the capacity, e.g. about 10%. The expected results concern differences between reduced rates of self-discharge. These results were supposed to be a few percent of the nominal capacity, which is less than the natural dispersion we generally observe in capacity measurements (e.g. between several batteries taken at random from the same lot of fabrication).

Two methods are *a priori* possible:

- Testing with a big enough number of batteries to obtain precise and meaningful statistical averages. We haven't chosen this method because the number of batteries required is too big for our test facilities.
- Comparing the capacity results of every single battery subjected to n months of self-discharge or float charge or low-current charge to its own capacity measured after a full charge. This is the chosen method.

Battery used for capacity measurements was VRLA AGM EnerSys 400Ah/2V. Four batteries of this technology were taken from the field and replaced by new ones after 6-year service, which corresponds to their mid-life (they are designed to last 12 years or more). In order to stabilize their capacities, these batteries were first subjected to 15 discharge-charge cycles, with discharges at C/10 - 1.8V stop voltage and IUi charges (C/10 until 2.4 V then 2.4 V for 5 hours then C/80 without voltage restriction for 2 hours). The last capacity obtained is the reference capacity. They were then subjected to tests at room temperature (18 ± 3°C): open circuit, low-currents of 29 and 105 µA/Ah and float charge at 2.27V (current response is 414 µA/Ah). After 6 months, these batteries were discharged with the same rate (C/10) to determine their final capacities.

5. Results & Discussion

5.1 Lead sulfate content measurement

Table 3 gives the results of $PbSO_4$ contents at initial state (after 231 days on open-circuit), and $PbSO_4$ final contents (after 356 days more at open-circuit and at constant low currents varying from 25 to 200 µA/Ah). Sulfate content variations during 356 days are the difference between final and initial sulfate contents.

From the obtained % of mass of $PbSO_4$ contents, the % of mol of $PbSO_4$ contents can be calculated as follows.

At the negative electrode we have:

$$PbSO_4(\%mass) = \frac{PbSO_4(\%mol) \times PbSO_4(g)}{PbSO_4(\%mol) \times PbSO_4(g) + [1 - PbSO_4(\%mol)] \times Pb(g)}$$ (2)

so:

$$PbSO_4(\%mol) = \frac{PbSO_4(\%mass) \times Pb(g)}{PbSO_4(g) - PbSO_4(\%mass) \times [PbSO_4(g) + Pb(g)]}$$ (3)

Executed service during 356 days	Applied Current (µA/Ah)	Obtained PbSO$_4$ content (% mass)		Calculated PbSO$_4$ content (% mol)		PbSO$_4$ content variation during service (% mol)	
		NAM	PAM	NAM	PAM	NAM	PAM
Initial state *(231 days at open circuit)*	-	16	30	11.5	24.4	-	-
Self-discharge *(Open-circuit)*	0	21	45	15.4	37.3	3.9	12.9
Low current	25	16.8	24.0	12.1	19.4	0.6	-5
Low current	50	11.5	19.1	8.1	15.4	-3.4	-9
Low current	100	1.9	8.6	1.3	6.8	-10.2	-17.6
Low current	200	1.4	4.8	1	3.8	-10.5	-20.6

Table 3. After 231 days at open circuit, four batteries were subjected to low-currents during 356 days at room temperature 23 ± 4°C. Contents of lead sulfate were measured at the negative active material (NAM) and the positive active material (PAM). Active material samples were taken from the middle of the negative and positive plates.

Calculating the same way at the positive electrode:

$$PbSO_4(\%mol) = \frac{PbSO_4(\%mass) \times PbO_2(g)}{PbSO_4(g) - PbSO_4(\%mass) \times [PbSO_4(g) + PbO_2(g)]}$$ (4)

From the variations of sulfate contents and the duration of the experiments, equivalent currents can be calculated using the first Faraday's law, they are called "Effective current":

$$\text{Effective current: } I_{Effect} = PbSO_4(\%mol) \times \frac{m}{M} \times \frac{nF}{t}$$ (5)

According to the Exide manufacturer, the masses of active materials of L01033C24A, 40 Ah-12V battery are 365g of PbO$_2$ and 300g of Pb.

The Effective current at open circuit (I_{Effect}^0) is the self-discharge current ($I_{selfdischarge}$). It will be presented with a negative value in Table 4, as the battery is discharging.

$$I_{Effect}^0 = I_{selfdischarge}$$ (6)

Applying Eq. (5) to the battery at open circuit, we have self-discharge currents of the

negative electrode (I_{Effect}^{0-}) and of the positive electrode (I_{Effect}^{0+}):

$$I_{Effect}^{0-} = I_{selfdischarge}^{-} = 0.039 \times \frac{300}{207} \times \frac{2 \times 96500}{356 \times 24 \times 3600} = 0.00035 \ \text{A} = 9 \ \mu\text{A} / \text{Ah}$$

$$I_{Effect}^{0+} = I_{selfdischarge}^{+} = 0.129 \times \frac{365}{239} \times \frac{2 \times 96500}{356 \times 24 \times 3600} = 0.0012 \ \text{A} = 30 \ \mu\text{A} / \text{Ah}$$

"Current Balance" is the result theoretically expected when applying a current to the battery. So it is the subtraction of the applied low current and the self-discharge current.

$$\text{Current Balance: } I_{Balance} = I_{Applied} - I_{selfdischarge} \qquad (7)$$

Executed service during 356 days	Applied Current $I_{Applied}$ (μA/Ah)	Effective current I_{Effect} (μA/Ah)		Calculated Current Balance $I_{Balance}$ (μA/Ah)		Calculated rate of side reactions $I_{Side-reac}$ (μA/Ah)	
		NAM	PAM	NAM	PAM	NAM	PAM
Initial state *(231 days at open circuit)*	-	-	-	-	-	-	-
Self-discharge *(Open-circuit)*	0	-9	-30	-9	-30	-9	-30
Low current	25	-1.4	12	16	-5	-26.4	-13
idem	50	8	22	41	20	-42	-28
idem	100	23	42.6	91	70	-77	-57.4
idem	200	24	50	191	170	-176	-150

Table 4. Equivalent currents obtained from the variations of sulfate level and the duration of the experiments, calculated current balances and side reaction rates.

Side reactions are always present inside the lead acid cell at open circuit as well as under low currents. At open circuit, the side reaction rate is the self-discharge current. Under low currents, side reaction rates can be calculated by subtracting the effective currents to the applied current.

$$\text{Side reaction rate under low currents: } I_{Side-reac} = I_{Effective} - I_{Applied} \qquad (8)$$

In figure 9, Effective Currents (EC) are compared to Current Balances (CB) and Side Reaction Rates (SRR) for negative and positive plates.

At open-circuit in figure 9, variations of sulfate content in mole percent are +3.9% for the NAM and +12.9% for the PAM (Nguyen et al., 2008). One can calculate from these sulfate content variations the self-discharge currents during 356 days of the experiment: -9 μA/Ah and -30 μA/Ah for the negative and positive electrodes respectively. The self-discharge rate of the positive electrode is more than three times faster than the self-discharge rate of the negative electrode.

The lowest current we tested, 25 µA/Ah, induces a drastic change in the sulfate content evolution inside the active materials. The sulfate content in the NAM remains almost constant (0.6 % increase) while the sulfate content in the PAM decreases by 5%. So, the positive plate behaves worse than the negative plate at open-circuit but it has a better behavior as soon as the battery receives the lowest applied current.
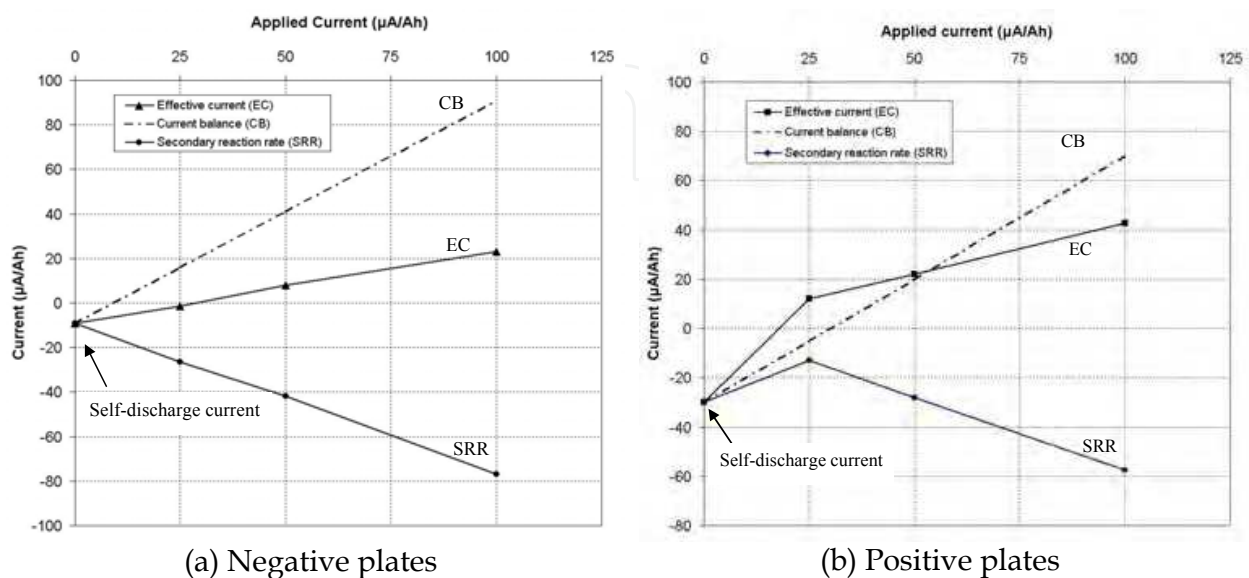

(a) Negative plates   (b) Positive plates

Fig. 9. Equivalent currents calculated from the variations of sulfate levels vs. applied currents: (a) negative plates, (b) positive plates. Current balance (CB) is the subtraction of the applied low currents and the self-discharge currents. Effective current (EC) is the equivalent currents corresponding to the sulfate content variations. Side reaction rate (SRR) is the subtraction of the effective currents and the applied currents

a. Negative plates

Figure 9 (a) shows the calculated current balances and the effective currents for the negative plates.

According to the lead sulfate content variation at 25 µA/Ah, the effective current for NAM is -1.4 µA/Ah. This negative value means that the low current compensates only partially the self-discharge. The current balance at 25 µA/Ah is: 25 - 9 = 16 µA/Ah.

The difference between the current balance and the effective current can be associated to losses of the applied current. Another explanation could be an increase of the secondary reactions involved in the self-discharge process under the polarization resulting from the applied current. These two hypotheses are in fact the same as secondary reactions involved in the self-discharge process and in losses during charging are identical: mainly hydrogen evolution and some oxygen recombination.

b. Positive plates

Figure 9 (b) shows the calculated current balances and the effective resulting currents for the positive plates.

A surprising result is observed at the 25 µA/Ah applied current. The effective current (12 µA/Ah), is higher than the calculated current balance (-5 µA/Ah). Of course, one cannot

have an efficiency that is higher than 100%. The low current effect is then not only a compensation of the self-discharge process, but a modification and/or a rate reduction of the secondary reactions involved in this process. Indeed, one observes a minimum of the side reaction rate at 25 µA/Ah (cf. figure 9).

Secondary reactions at the positive electrode are the oxygen evolution and the positive grid corrosion.

Oxygen evolution takes place at open-circuit, charge and discharge potentials. This reaction is known to increase its rate with positive polarization, so it cannot be the reason of the reduction of the self-discharge process observed in this case.

On the contrary, corrosion can slow down under positive polarizations. This phenomenon is well known in the field of corrosion of metals as anodic protection, or more generally as corrosion passivation.

In the case of lead acid batteries, it is also well known that corrosion reactions are different at open-circuit and during charging. More exactly, corrosion reactions of the positive grid consist of two steps:
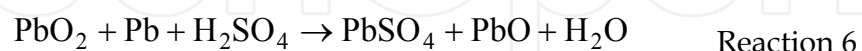
$$Pb + O^{2-} \rightarrow PbO + 2e^-$$ Reaction 11

$$PbO + O^{2-} \rightarrow PbO_2 + 2e^-$$ Reaction 12
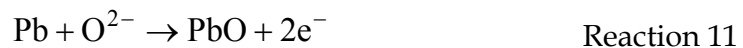
In which, O^{2-} ions are brought by migration from the active material across oxidation layers.

Only the first step, Reaction 11, operates at open-circuit while these both steps occur during charging.

Indeed, at open-circuit, divalent lead (Pb^{2+}) is the stable state for lead. Only the first step of the corrosion reaction occurs but not the second step (Reaction 12, in which Pb^{2+} would oxidize into Pb^{4+}), because Pb^{4+} is not the thermodynamically stable state for lead. As at open-circuit the two electrons of Reaction 11 cannot be evacuated by the external circuit, they are used by reduction of Pb^{4+} into Pb^{2+} in the discharge reaction of the positive active material:

$$PbO_2 + H_2SO_4 + 2H_3O^+ + 2e^- \rightarrow PbSO_4 + 4H_2O$$ Reaction 8
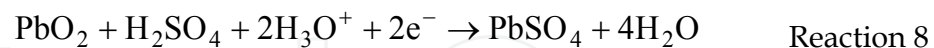
The combination of Reaction 11 and Reaction 8 is then:

$$PbO_2 + Pb + H_2SO_4 \rightarrow PbSO_4 + PbO + H_2O$$ Reaction 6

When PbO is not protected with a dense PbO_2 layer, it reacts chemically with sulfuric acid to form $PbSO_4$ as follows:

$$PbO + H_2SO_4 \rightarrow PbSO_4 + H_2O$$ Reaction 10
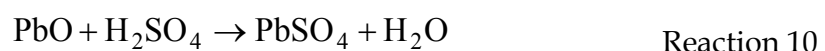
The overall corrosion reaction at open-circuit is then:

$$PbO_2 + Pb + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O \qquad \text{Reaction 9}$$

When this reaction occurs, usually in prolonged open-circuit conditions, positive grids are no more protected. Indeed, the formation of lead sulfate in the corrosion layers leads to mechanical stress, causing the formation of cracks and the destruction of the protective layer.

During charging (under low currents), Reaction 12 takes place. Under positive polarization, Pb^{4+} (in PbO_2) is indeed the stable species of lead. PbO_2 produced in Reaction 12 is formed in the outer part of the corrosion layer. As it is dense, issued from the dense inner layer, and stable in sulfuric acid solution, it takes the role of protecting the PbO inner layer and the positive grid from the electrolyte (Ruetschi, 2004, Berndt, 1997, Garche, 1995).

Under positive polarizations, grid corrosion, which is part of the self-discharge process of the positive electrode, is then slowed down by the formation of a protective layer of dense PbO_2. Therefore, for the positive electrode, this can be the reason why the effective current is sensibly higher than the calculated current balance, as long as corrosion is important part of the positive self-discharge process. Benefit of 25 µA/Ah low current is then triple:

(i) Compensation of the self-discharge:
For intermittent charge, in the prospect of replacing open-circuit periods by low current periods, it is obvious that periodical charges would no longer be necessary or at least would be required less frequently.

(ii) Slowing down of the corrosion rate:
As mentioned previously, several authors indicate a minimum corrosion zone. This minimum is generally situated at positive polarizations in the [30, 80] mV range. Indeed, at 25 µA/Ah, the strong effect observed can be attributed to an important reduction of the corrosion rate. But in this case the positive polarization is in the order of 2 mV much lower than the preceding published values. It must be noticed that our results, obtained from long duration tests (over 19 months) at room temperature, differ from these published results, generally obtained at accelerated conditions.

(iii)Reduction of water consumption:
It concerns water involved in corrosion reactions. In these reactions, the oxygen is taken from the positive active material. In turn, the active material takes oxygen from water of the electrolyte. The oxygen, finally locked in the corrosion product layers, cannot be recombined to reform water. So, the decrease of water consumption due to corrosion is important for the battery life span.

5.2 Capacity measurement

Table 5 gives the capacities of VRLA batteries before (C_{ref}) and after (C_{fin}) 6 months at open-circuit, at low currents of 29 and 105 µA/Ah, and at 2.27V float charge. These experiments were done at room temperature (18 ± 3°C). The battery at open-circuit for 6 months lost (264 - 327)/327 = -19.3 % of its capacity compared to its reference capacity; the capacity of the battery subjected to 105 µA/Ah increased by (329 - 313)/329 = +5.1%.

Figure 10 (a) shows the capacity variations given for each battery in percent of their

reference capacities. These percentages are also the state of charge variations induced by the applied currents during the 6 months of experiments. The capacity variations are converted to the equivalent currents or as named above the effective currents. These effective currents are presented as a function of the applied current in figure 10 (b). The currents balances and the side reaction rates are calculated as the same way in the section 5.1. At open-circuit, the capacity reduction of 63 Ah after 6 months allows calculating the average self-discharge current, which is 36 µA/Ah.

Battery	Reference capacity C_{ref} (Ah)	Applied Current during 6 months at room temperature $18 \pm 3°C$ (µA/Ah)	Final capacity C_{fin} (Ah)	Capacity Variation $(C_{fin} - C_{ref})/ C_{ref}$ (%)
B115	340.0	~ 414 (float charge at 2.27V)	379.0	11.8
B116	313.0	105	329.0	5.1
B117	318.0	29	308.0	-3.1
B118	327.0	0	264.0	-19.3

Table 5. Capacities of the VRLA batteries, which were subjected to open circuit, to 29 and 105 µA/Ah low-currents and to 2.27 V float charge during 6 months at room temperature $(18 \pm 3°C)$ as well as their reference capacities before this service.

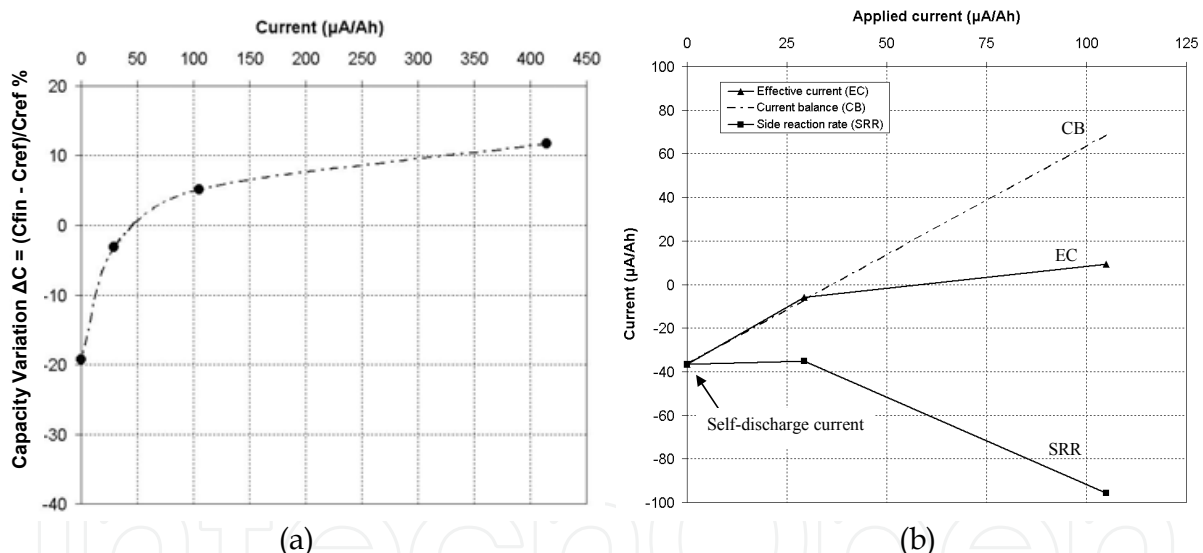(a)   (b)

Fig. 10. VRLA Batteries were tested during 6 months at room temperature $(18 \pm 3°C)$. (a) Relative capacity variations (state of charge variations) vs. applied currents. (b) Equivalent currents calculated from the capacity variations vs. applied currents.

The capacity variation has a strong increase for the lowest applied current (29 µA/Ah). It appears that this low current, whose value is 80 % of the average self-discharge current (36 µA/Ah), compensates 84 % of the self-discharge. Such a high efficiency (superior to 100%) suggests that these VRLA batteries could be positive limited at this mid-life state. Further experiments confirmed that these batteries were indeed positive limited.

Increases of the battery state of charge at the low current of 105 µA/Ah and at float current of 414 µA/Ah indicate that the charge procedure we used does not lead to a real full charge. Charge is then completed slowly at currents beyond 50 µA/Ah. The reference capacity is

supposed to be the maximum capacity the battery is able to discharge after a full charge. But what is a full charge? We all know that absolute full charge of a lead acid battery does not exist. It is an asymptotic state. What we generally call a full charge is in fact the result of a compromise between the search of a high state of charge and the time we can spend on this operation. In practice it is considered that the end of charge is reached, when there is no charging current or voltage evolution during at least 2 hours. Our "full charge" procedure for VRLA batteries was a classical IUi charge. According to the results above, we must consider that our charge procedures were not sufficient to reach states of charge as high as after a few months of float charge or even of low current charge.

According to experiment results, we supposed that when combined with low currents in the order of 25 to 50 µA/Ah, a refresh charge every 6 months or every single year is sufficient to maintain antimony-free batteries in a good state of charge. Higher currents, as traditional float currents (10 times higher), are not necessary and not suited, as they would increase corrosion and water loss. We consider using a refresh charge only when the battery has been subjected to a discharge service.

6. New management system for standby antimony-free battery

Valve regulated lead acid batteries - VRLA batteries - have been developed and used for about 30 years in standby applications. They have shown several advantages compared to flooded lead acid batteries: spill-proof, reduced weight, free from excessive gas evolution or acid spillage, reduced maintenance and reduced cost. However, limitations have been also observed concerning system reliability and battery service life.

Several reliability prediction methods have been used such as complete discharge test (Piller et al., 2001), open-circuit voltage measurement (Bullock et al., 1997), conductance testing (Kniveton, 1995), internal resistance and impedance measurements (Hariprakash et al., 2004, Huet, 1998, Karden et al., 2000, Rodrigues et al., 2000, Shukla et al., 1998, Piller et al., 2001). Among these, the complete discharge test is well known as the most reliable one but it requires service interruption. This has driven EDF R&D to develop the "Stationary Multibat" system, which consists of a new design of the electrochemical storage and an adapted electronic battery management system (Desanti and Schweitz, 2006). This system, combining redundancy and automated periodical capacity measurements, increases reliability and allows a real time monitoring of the battery state of health. Redundancy not only ensures the continuity of service in the case of a cell failure, but also enables complete discharges to be periodically performed without service interruption.

Standby VRLA batteries maintained under a constant float voltage to compensate self-discharge encounter the problem of short service life, e.g. about 3-4 years compared to the so-called 20-year design and to the 20-year lifetime of conventional lead acid batteries in similar conditions (Misra, 2007). Indeed, VRLA batteries under float charges are permanently overcharged and different failure modes have been observed, such as corrosion of positive grid alloys, electrolyte dry-out and thermal runaway (Berndt, 1997, Feder, 2001, Ruetschi, 2004, Wagner, 1995, Dai et al., 2006).

A new management system for standby VRLA batteries has been developed at EDF using the Stationary Multibat system (Desanti and Schweitz, 2006) to ensure system reliability and the Low-current method (Nguyen et al., 2008) to improve the battery life span.

Figure 11 (a) describes a simplified schematic diagram of the Stationary Multibat system.

Three battery-pack strings in parallel instead of one pack are used in order to improve the system reliability. In case of a cell failure such as an open circuit, the system loses only one battery-pack string, i.e. one-third of the total capacity. This configuration also allows each string to be discharged completely across the test resistance to evaluate its real state of health. Each battery string is periodically (e.g. every 6 months) discharged and charged.

Fig. (b) describes how to integrate and to operate Low-current method of maintaining the charge on the Stationary Multibat system:

- A resistance branch is added to reduce the traditional float current with a factor of 5 to 10. In standby state, Programmable Logic Controllers (PLC) K_1 and K_2 are open; the battery is maintained at charge with a low current via the resistance R.
- On backup demand, a voltage drop appears on the DC bus, the battery immediately provides electricity to the DC load via the diode D. Then PLC K_1 closes; the battery directly supplies power to DC load.
- During the periodical discharge test (e.g. every 6 months) to evaluate the battery state of heath, PLC K_2 closes and K_1 stays open. The battery-pack string is discharged across the test resistance. The low current, still provided to the battery pack string, is a parasitic but negligible effect (< 0.1%). Next, the charge is operated via K_1. The charge current is controlled by a Pulse Wave Modulation (PWM). When the charge finishes, K_1 re-opens, the battery is re-maintained the charge with a low current via R.

All those operations are done sequentially and automatically so that no intervention is required from the maintenance.
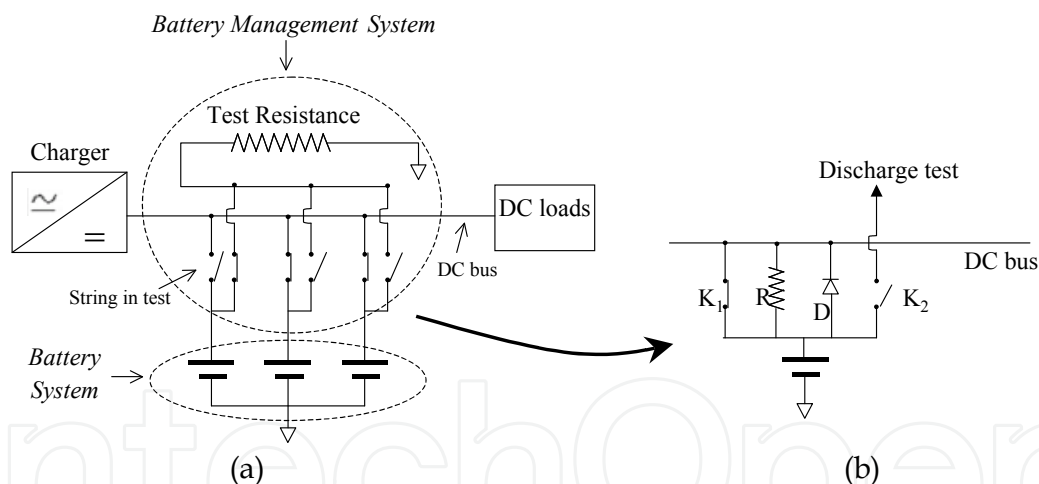

Fig. 11. (a) Simplified schematic diagram of the Stationary Multibat system. (b) Zoom on the power electronic components of one of the three battery-pack strings using Low-current method.

This system is expected to fulfill three targets:

- Increasing the system reliability by a redundancy in the design of the battery system and by an assessment method to control battery state of health.
- Improving battery life spans by the Low-current method, leading to reduced corrosion and water loss.
- Decreasing maintenance costs.

7. Conclusion

Antimony-free lead-acid batteries were tested for several months at open-circuit, float charge and intermediate rates of charge – called "Low-current" in this chapter. The following conclusions can be drawn from this study:

- In antimony-free lead acid batteries, the self-discharge rate of the positive electrode is higher than that of the negative electrode.
- Low-currents beyond 25 µA/Ah appear to be able to maintain the state of charge for both positive and negative plates.
- The effect of 25 µA/Ah low current on the positive active material is much higher than a simple compensation of the self-discharge. This can be explained by a passivation phenomenon of the positive grid corrosion. In other words, it constitutes an anodic protection of the positive grid.
- The use of low-current periods in place of open-circuit periods in the intermittent charging method should increase the life span of VRLA batteries, as it both lowers the water consumption and the corrosion rate of positive grids.

Combining the Low-current method, battery redundancy and automated periodical capacity measurements, VRLA batteries should provide long life spans and high reliability. Several management systems of this kind are being experimentally used at EDF.

Acknowledgment

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Trends in Telecommunications Technologies

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The main focus of the book is the advances in telecommunications modeling, policy, and technology. In particular, several chapters of the book deal with low-level network layers and present issues in optical communication technology and optical networks, including the deployment of optical hardware devices and the design of optical network architecture. Wireless networking is also covered, with a focus on WiFi and WiMAX technologies. The book also contains chapters that deal with transport issues, and namely protocols and policies for efficient and guaranteed transmission characteristics while transferring demanding data applications such as video. Finally, the book includes chapters that focus on the delivery of applications through common telecommunication channels such as the earth atmosphere. This book is useful for researchers working in the telecommunications field, in order to read a compact gathering of some of the latest efforts in related areas. It is also useful for educators that wish to get an up-to-date glimpse of telecommunications research and present it in an easily understandable and concise way. It is finally suitable for the engineers and other interested people that would benefit from an overview of ideas, experiments, algorithms and techniques that are presented throughout the book.