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Journal of Power Sources 136 (2004) 171–179
JOURNAL OF POWER SOURCES
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A study of the scattering of valve regulated lead acid batteries in a string

E. Rossinot [a,b], C. Lefrou [a,*], J.P. Cun [b]

[a] Laboratoire d'Electrochimie et de Physico-chimie des Matériaux et des Interfaces, UMR 5631 CNRS-INPG-UJF, ENSEEG, 1130 rue de la piscine, B.P. 75, Domaine Universitaire, 38402 Saint Martin d'Hères Cedex, France
[b] MGE UPS Systems, 140 Avenue Jean Kuntzmann, ZIRST Montbonnot Saint Martin, 38334 Saint Ismier Cedex, France

Received 28 August 2003; received in revised form 27 April 2004; accepted 5 May 2004

Available online 6 July 2004

Abstract

Scattering of the electrical characteristics or performances of VRLA batteries was measured on string with 24 batteries in series, using new batteries from three different manufacturers. Data on open-circuit voltage, and float conditions (currents and voltages) were collected and discussed.

Keywords: VRLA batteries; Standby applications; Float conditions; Scattering

1. Introduction

Standby applications (telephone exchanges, hospital standby supplies, etc.) are peculiar uses of batteries with almost no cycling. In order to provide the user with maximum available capacity at any time, the batteries used in standby installations are generally maintained in an overcharged state by supplying them with a voltage slightly higher than the open-circuit voltage, known as "float voltage". In most of these systems today, valve regulated lead acid (i.e. VRLA) batteries are used to meet requirements. They are efficient in such applications since they can withstand a considerable overcharge without suffering irreversible damage [1].

For most applications requiring high levels of power, this demand is thus satisfied by a large number of batteries assembled in series or in parallel. Float conditions are implemented by applying a float voltage at the terminals of all the batteries. Constant voltage is thus assured at the terminals of each in-parallel branch but there is no control over the distribution of this voltage among the individual batteries. Scattering between batteries may be relatively marked. For example, Berndt in 1985 measured the individual float voltages of 203 cells placed at random in two parallel strings of 180 in-series cells [2]. For a mean float voltage of 2.38 V per cell, he identified a normal distribution curve with a standard deviation of ±33 mV and a difference between the maximum and minimum values of 170 mV.

This scattering is the cause of accelerated aging of the overall system since the "weakest link" of the string ages more rapidly than if its voltage was individually imposed. For normal use (that is to say no air intake because of a defected valve, or abnormal heat effect . . .) of an individual battery in adequate floating conditions, the major mechanism of end of life is the corrosion of the grid at the positive electrode. This irreversible phenomenon is always present during floating, even if it corresponds to a small part of the floating current. However as soon as several batteries are used in series the end of life of the whole system is not always due to the positive grid corrosion of the weakest battery. The weakest battery is often a battery which is at a small overvoltage compared to the other, because of the series disposition. The VRLA batteries are very sensitive to a small overvoltage because the consequence is an undercharge of the negative electrode. This phenomenon is not irreversible, that is to say the battery could recover a normal capacity if it was individually floated. However the whole installation exhibits a capacity decrease, which means the end of life for the industrial system (capacity become less than 80% of the initial value). An exhausted study of aging effect on the evolution of scattering parameters of batteries used in series is over the scope of this work. Thus, the industrial purpose of this study is based on the fact that reducing the scattering of batteries

* Corresponding author. Tel.: +33 4 76 82 6593; fax: +33 4 76 82 6777.
E-mail address: christine.lefrou@inpg.fr (C. Lefrou).

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doi:10.1016/j.jpowsour.2004.05.005

before use in industrial systems will allow a lengthening of life.

Two types of causes of such scattering may be observed in industrial installations [3]:

- Despite rigorous manufacturing process control, the characteristics of different batteries cannot be exactly the same on the completion of manufacturing. Thus, batteries assembled in series in UPS-type applications will be different even if precautions are taken (and this is generally the case) to ensure they come from the same supplier and from the same production batch.
- In industrial conditions, it is not possible to keep a strict check on the length of time batteries are stored before use. Similarly, it is not economically possible to recharge each battery just before it is installed and connected in series or in parallel for the application. Thus, in the industrial setting, in addition to scattering related to the manufacturing process there is also scattering in the state of charge characteristics of the different batteries connected in series due to slightly different self-discharge characteristics.

In a previous work [4], an analysis of the first type of scattering was performed on few individual new and fully charged batteries of three different manufacturers. The low number of batteries tested per batch precludes any real statistical study, but represents a compromise between the total time allotted for experiments and the study objectives (i.e. the analysis of scattering characteristics). This previous study allowed identifying the link between scattering inherent in the manufacturing process and its effects on the electrical performance characteristics of the finished product:

- Open-circuit voltage and capacity are electrical characteristics where scattering is related essentially to dispersion of acid density values inside the battery; and
- Float voltages and current are electrical characteristics where scattering is related essentially to dispersion of the saturation characteristics of the separator of each battery cell.

The present work is a complementary study on a greater number of batteries placed in series string.

2. Experimental

2.1. Materials

The different experiments were conducted on new VRLA 12V/5Ah batteries from three different manufacturers. The commercial references of the batteries are as follows: Exide SP12V137, Panasonic UP-RWA1232P2 and Yuasa SW200. All three are VRLA batteries with four negative plates, three at the positive electrode and an AGM separator impregnated with acidic solution as electrolyte. In this paper, the different manufacturers are referred to as A, B and C. For reasons of confidentiality, the link between these letters and the manufacturers is not divulged, but this in no way affects the understanding or scientific discussion of the results obtained.

Voltage and current measurements were conducted using Keithley 2000 multimeters.

Although only the voltage of each battery is measured in this study and the six individual cell voltages are unknown, the results are, in the following, often presented in V per cell (which means that this is the mean value of the six individual cells of each battery) in order to facilitate the reading. The study is indeed easily extendable at other types of VRLA batteries (not only 12 V batteries).

2.2. Experimental protocol

The experimental protocol is represented in Fig. 1 and described below. All the experiments were performed at room temperature. The measured temperature exhibits a rather large variation during the few months of tests: $23 \pm 7\,^{\circ}$C. Its influence on results will therefore be discussed.

Each new battery was initially charged at constant current (corresponding to a $C_{10}/10$ regime, or 0.5 A) up to a maximum voltage of 2.27 V per cell (or 13.6 V for a battery). The batteries were then maintained at a mean float voltage of 2.27 V per cell for a few days to ensure that they were fully charged. The batteries are then stored with no use during two months. The open-circuit voltage, referred to as U_{oc}, was measured for each battery. Three strings of 24 batteries in series were built (one for each manufacturer). During the test 1, each 24 batteries string was submitted to a global float voltage of 341 V, which corresponds to a mean value of 2.37 V per cell (or 14.2 V for a battery). During one month, several measurements of the float current (same value for each battery of one string, I_{float}) and of the 24 individual float voltages (U_{float}) were made. The strings are undone and during the test 2 each battery is submitted to a float voltage of 14.2 V (or 2.37 V per cell). The value of the floating current was recorded after two weeks in float conditions for each battery. This delay ensures that the measurements could be considered as steady state results [4]. The test 3 was similar to the test 1. The test 4 was done with the three strings of 24 batteries in series like the previous test. However the global float voltage was put at 327 V, which corresponds to a mean value of 2.27 V per cell (or 13.6 V for a battery). Each battery was then placed in open-circuit. The open-circuit voltage, referred to as U_{oc}, was measured after 48 h so as to allow sufficient time for the value to become reasonably stable [5]. The final test (test 5) was like the test 1.

2.3. Stabilization of measured parameters

Fig. 2a and b show the changes according to the time (during one month) in the room temperature, in the common floating current and in the 24 individual voltages of each battery from manufacturer B during the test 1. These results are qualitatively the same for the other manufacturers or the other tests.

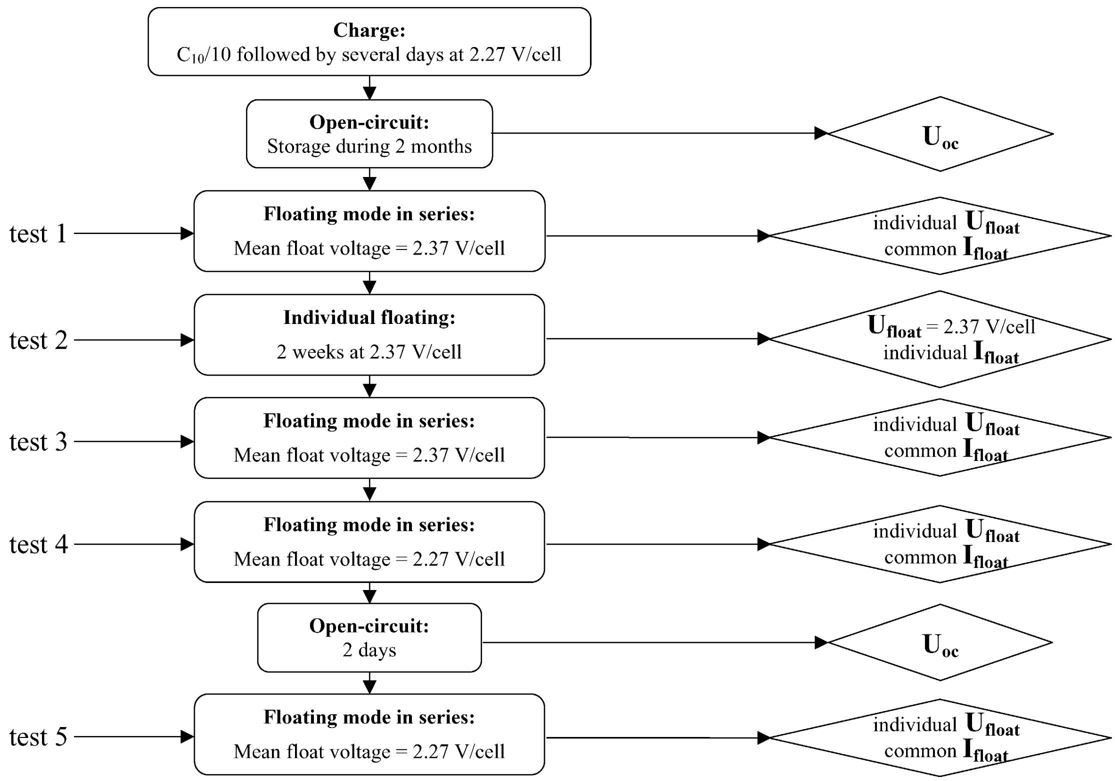

Fig. 1. Experimental protocol.

The few first days correspond to rather big changes in float voltages and current, compared to the ones measured after these first period of stabilization. Only the stabilized measurements will be discussed afterwards. In the following, only measurements after 7 days of test will then be given on figures and tables and taken into account in mean values.

3. Results and discussion

3.1. *Influence of storage or eventual aging*

Fig. 3 shows the deviation from the mean value of the 24 individual float voltages of each battery from manufacturer B during the test 1. The results are the same as in Fig. 2a. However they are presented for each battery in order to emphasize the individual changes in time. For almost all the batteries there is no significant evolution during the month of test (after stabilization): the biggest evolution is observed in this test for the battery no. 18 and is 33 mV per cell. The average of the 24 individual voltage evolutions is 13 mV per cell. This good precision on the float voltage allows a study of the scattering characteristics in good conditions (the scattering leads to a difference between the extreme values observed for the 24 batteries on the order of 100 mV per cell). These results are qualitatively the same for the other manufacturers or the other tests.

Fig. 4 shows the changes according to the test (for tests 1, 3 and 5) in the deviation from the mean value of the 24 individual float voltages of each battery from manufacturer B. In absence of aging, one would expect that the float voltages of each battery be the same for the three tests: the Fig. 4 would then show all the data aligned on the $y = x$ line (first bisecting line). Except for one battery, the changes between the different tests in individual float voltages are in the same order of magnitude as the precision for one test (±15 mV per cell). This result is an important preamble for this study: no effect of aging is detected during this six months study and the scattering observed in the individual float voltages is significantly higher than the changes in one individual float voltage according to the time.

Another conclusion can be set from these first observations in the comparison between test 1 and test 3. The only difference between both tests holds in the beginning state of the batteries (cf. Section 2.2): in test 3 the batteries are fully charged just before the test whereas they were stored during two months without recharge before the test 1. During this two months storage, the unavoidable self-discharge phenomenon leads to a capacity loss. An estimation of this capacity loss can be drawn from the changes in open-circuit voltage [6], because this voltage is linked to the acid density in the battery [1,7]:

$$U_{oc}\,(\text{in V}) \approx U_{th} \approx d + 0.84 \quad \text{for one cell}$$

The correspondent capacity loss may depend on the battery size. A previous study on the same type of batteries allows an estimation of this correspondence [4]: a change in open-circuit voltage of 20 mV per cell corresponds to a

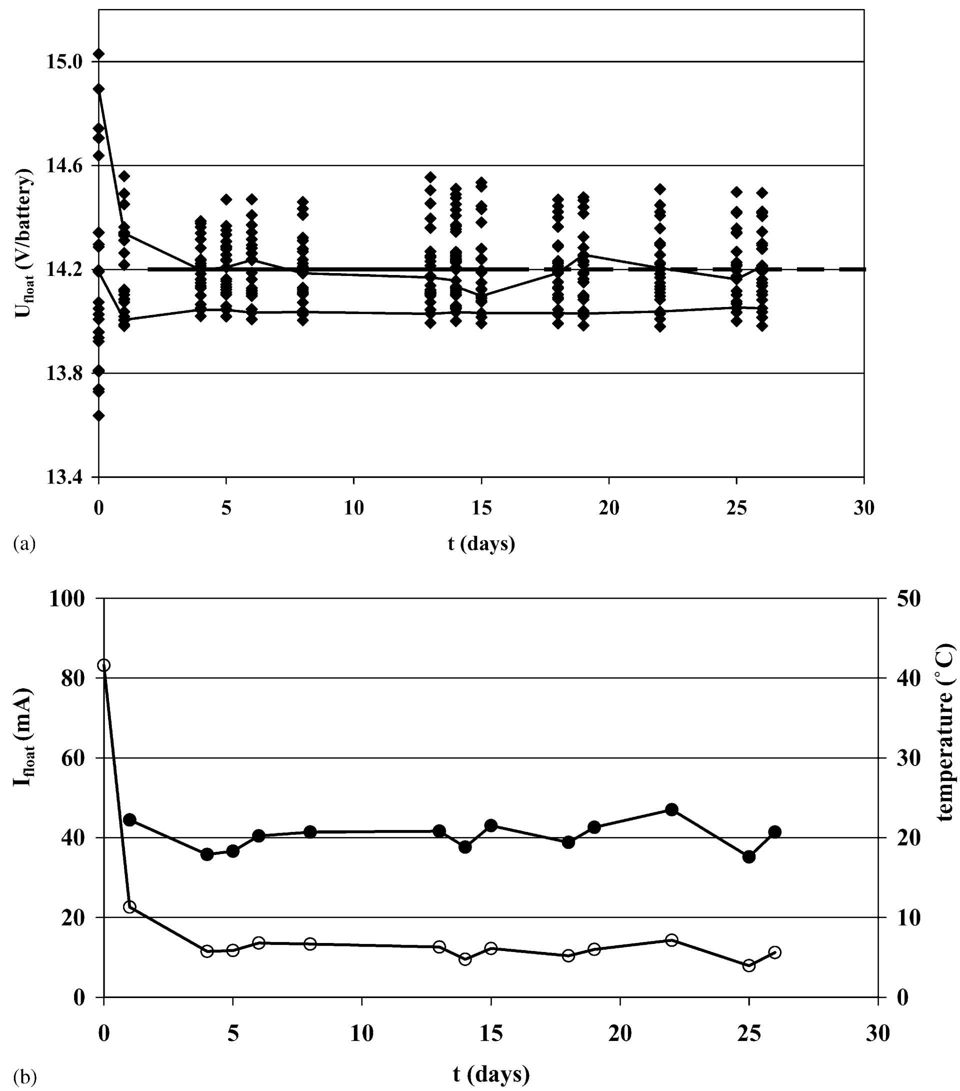

Fig. 2. (a) Changes in the individual float voltage, U_{float}, according to the time, t, of the 24 batteries of the manufacturer B, in the same string during the test 1. For two of the 24 batteries, a continuous line is drawn between the experimental points. The mean value for the float voltage of the batteries in test 1 (i.e. 14.2 V per battery) is shown with a dotted line. (b) Changes according to the time, t, in the room temperature and in the common float current, I_{float}, which goes through the 24 batteries of the manufacturer B, in the same string during the test 1. The different symbols are: (●) for the room temperature (with the right vertical scale), and (○) for the float current (with the left vertical scale).

10% capacity loss. Table 1 presents the measured effect of two months storage on the state of charge of the batteries, through the measured individual open-circuit voltage and the correspondent estimated capacity loss.

In this study, test 1 and test 3 give very similar results. One can therefore consider that there is no influence of two months storage (or about 10% of capacity loss by self discharge) on individual float voltage characteristics, after stabilization. Provided the storage is less than two months, the scattering in floating characteristics due to the self-discharge scattering can be neglected. The scattering measured in floating conditions are essentially caused by the scattering in the manufacturing process [8].

Table 1
Open-circuit voltage data without storage and with two months of storage: mean value and difference between maximum and minimum value (ΔU_{oc}) for the three manufacturers and estimated capacity loss from the open-circuit voltage data

		Manufacturer		
		A	B	C
No storage	Mean U_{oc} (V per cell)	2.18	2.17	2.19
After two months of storage	Mean U_{oc} (V per cell)	2.15	2.15	2.18
	Estimated capacity loss (%)	16	10	3

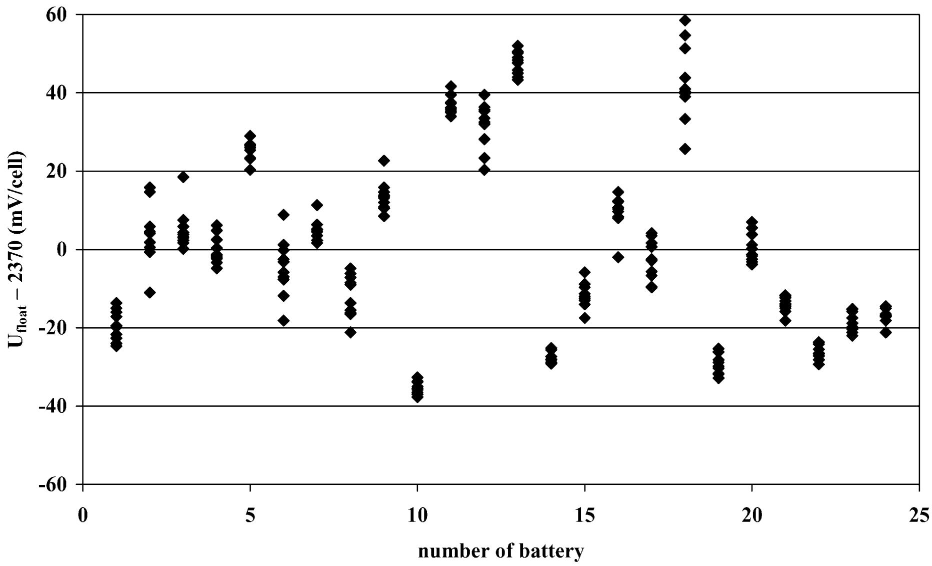

Fig. 3. Deviation from the mean value (2.37 V per cell) of the 24 individual float voltages, U_{float}, of each battery from manufacturer B during the test 1. The results are the same as in Fig. 2a, differently shown.

3.2. Influence of temperature

Fig. 5a and b show the changes, according to the room temperature, in the common floating current and in the difference between the maximum and minimum values of the 24 individual voltages of each battery from manufacturer B during the tests 1, 3 and 5. These results are qualitatively the same for the other manufacturers. There is no evidence of a dependence of float voltage to the room temperature. The following analysis will then consider an independence of float voltages to the temperature in the range 17–27 °C.

On the contrary, there is a strong correlation between the changes in room temperature and the changes in float current. An analysis of this phenomenon is usually done through an Arrhenius behavior:

$$I = \text{constant}\,\mathrm{e}^{-E_{\mathrm{a}}/RT}$$

where the activation energy is strongly related to the kinetics of the oxygen evolution reaction at the positive electrode [9].

Such an analysis allows a suitable description of the results for the three manufacturers. Table 2 presents the activation energy deduced for each manufacturer. In the

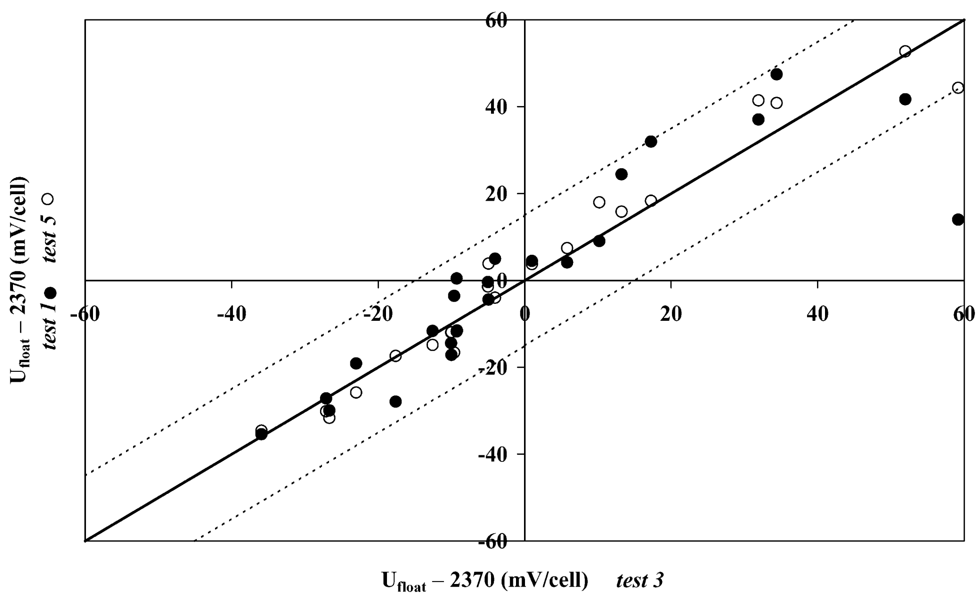

Fig. 4. Changes in the deviation from the mean value (2.37 V per cell) of the 24 individual float voltages, U_{float}, of each battery from manufacturer B in test 1 or 5 (mean value for one test) according to the one in test 3. The different symbols are: (●) for the test 1, and (○) for the test 5. The continuous line represents the $y = x$ straight line. The dotted lines show the ±15 mV per cell precision.

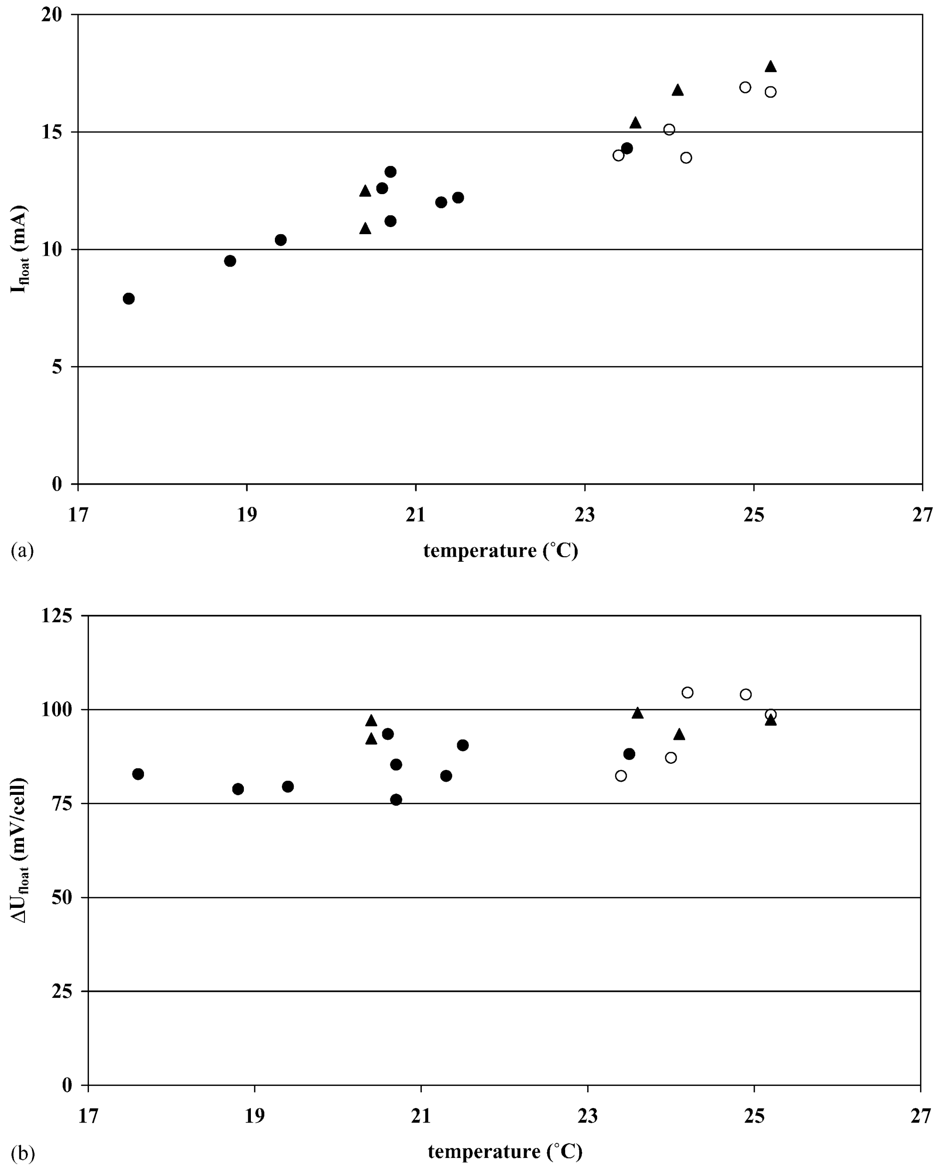

Fig. 5. (a) Changes in the common float current, I_{float}, through the 24 batteries from manufacturer B in series setting in test 1, 3 and 5 according to the room temperature. The different symbols are: (●) for the test 1, (▲) for the test 3, and (○) for the test 5. (b) Changes in the difference between the maximum and minimum values of the 24 individual voltages, ΔU_{float}, from manufacturer B in series setting in tests 1, 3 and 5 according to the room temperature. The different symbols are: (●) for the test 1, (▲) for the test 3, and (○) for the test 5.

following and in order to allow comparisons, the given values of current (in Tables 3 and 4) will be recalculated values at 22 °C (with the previous activation energy values).

Table 2
Activation energy values for each manufacturer deduced through an Arrhenius relationship between the measured float current at different temperatures (see e.g. Fig. 5a)

	Manufacturer		
	A	B	C
Activation energy (kJ mol^{-1})	60	65	75

3.3. Link between the scattering of float voltage and current

Fig. 6 shows the changes, according to the deviation from the mean value of the 24 individual float voltages in a series string setting (mean value for the tests 1, 3 and 5), in the deviation from the mean value of individual (or parallel) float current of each battery from manufacturer B during the test 2 (individual floating setting). These results clearly show a link between the floating behavior in individual setting and in series string setting. The relationship is a monotonous one with negative slopes: the batteries who exhibit great (respectively small) float currents in individual floating setting are the batteries who show minimum (respectively maximum) float voltages in the series string setting.

Table 3
Comparison between floating conditions in a series setting at 2.37 (tests 1, 3 and 5) or 2.27 V per cell (test 4) and an individual or parallel setting at 2.37 V per cell (test 2), for the three manufacturers

			Manufacturer		
			A	B	C
Floating of 24 batteries in series (tests 1, 3, 5)	Mean U_{float} = 2.37 V per cell	I_{float} (mA for all batteries)	18.3	13.0	1.1
		ΔU_{float} (mV per cell)	65	85	80
Floating of 24 individual batteries (test 2)	U_{float} = 2.37 V per cell (14.2 V for each battery)	Mean I_{float} (mA)	18.8	14.0	1.3
		ΔI_{float} (mA)	13.7	20.9	1.6
Floating of 24 batteries in series (test 4)	Mean U_{float} = 2.2 V per cell	I_{float} (mA for all batteries)	1.3	2.0	0.2
		ΔU_{float} (mV per cell)	30	40	75

For the series setting tests, the table collects the common float current, I_{float}, and difference between the maximum and the minimum value of the 24 individual float voltages, ΔU_{float}, in the series setting (mean value for tests 1, 3 and 5). For the parallel setting test, the table collects the mean value of individual float currents and difference between the maximum and the minimum value of the 24 individual float currents, ΔI_{float}.

These results are qualitatively the same for the other manufacturers. Table 3 presents the major characteristics of test 2 compared to tests 1, 3 and 5 for the three manufacturers. This table shows immediately a big difference between manufacturer C and manufacturers A and B on the level of float currents. This is in good agreement with previous study [4]. However the same difference is not observed in the scattering of float voltages around 2.37 V per cell mean value. This will be discussed in more details in the following (cf. Section 3.4). For the three manufacturers a relatively small scattering in float voltages (less than 100 mV per cell) correspond to a rather big scattering in float current in test 2 (on the order of 100% of the mean value).

The observed correlation between the two types of tests (series or individual floating) could be understood looking at the floating behavior. A previous study [4] shows that the float characteristics follow with a good accuracy an usual behavior in electrochemical systems: VRLA batteries exhibits in floating conditions a linear relationship in Tafel representation (i.e. semilogarithmic plot $\log I_{float} = f(U_{float})$). The scattering in electrical floating characteristics could then be reported as scattering in both Tafel parameters (slope and self-discharge current). And one of the major sources of Tafel parameters scattering is the dispersion of the saturation characteristics of the separator of each battery cell, which leads to a dispersion of oxygen recombination rate of each cell [4,8,10–13].

Fig. 7 illustrates, in a current versus voltage representation, how the Tafel behavior with scattering could explain the observed correlation between currents and voltages scattering in individual or series setting. The battery which exhibits the "higher" Tafel behavior (continuous line) will show great

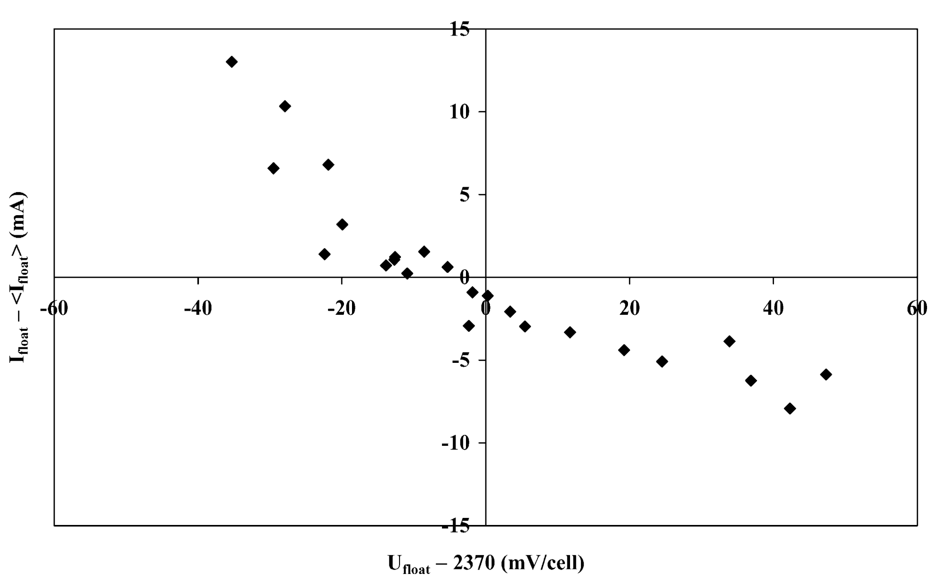

Fig. 6. Changes in the deviation from the mean value of individual float current, I_{float}, of each battery from manufacturer B during the test 2 (individual floating setting), according to the deviation from the mean value (2.37 V per cell) of the 24 individual float voltages, U_{float}, in a series string setting (mean value for all the tests 1, 3 and 5).

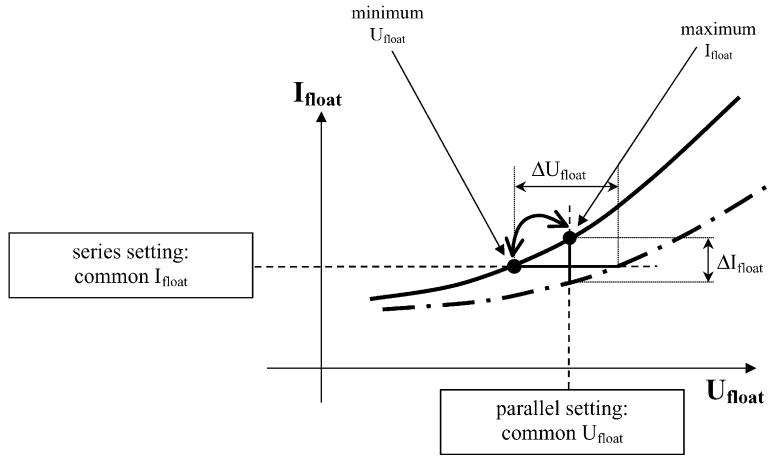

Fig. 7. Scheme which illustrates the influence of the scattering in Tafel parameters on the behavior of several batteries in an individual floating setting (common float voltage) or a series string one (common float current). The floating characteristics (I_{float}, U_{float}) of two extreme batteries are represented. The continuous line correspond to the battery with “higher” Tafel parameters.

float current in individual setting and minimum float voltage in series setting.

3.4. *Influence of the mean value of float voltage*

Fig. 8 shows for the manufacturer C the changes in the deviation from the mean value 2.27 V per cell of the 24 individual float voltages in a series setting (test 4), according to the deviation from the mean value 2.37 V per cell of individual float voltages in a series string setting (mean value for the tests 1, 3 and 5). These results clearly show a link between the two types of data. The relationship is a monotonous one with positive slopes: the batteries who exhibit great (respectively small) float voltages around 2.37 V are the batteries who show great (respectively small) float voltages around 2.27 V.

Table 3 presents the results for the three manufacturers summarized in term of float voltages expanse ($\Delta U_{\mathrm{float}}$). The peculiar behavior of the batteries from manufacturer C is seen again in the float current level and in the almost constant value of the float voltages expanse in all the tests (2.27 and 2.37 V per cell). This particularity could be discussed in term of Tafel behavior, as follows. Neglecting the influence of the scattering in open-circuit voltage, the overvoltages (η) of two cells in the series string can be written:

$$\eta_1 = b_1(\log I - \log I_{01}) \quad \text{and} \quad \eta_2 = b_2(\log I - \log I_{02})$$

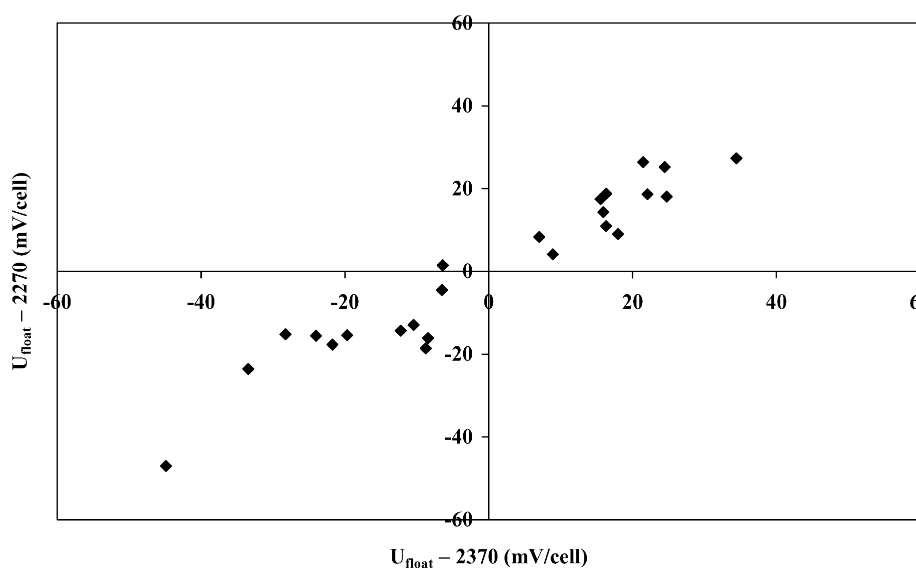

Fig. 8. Changes in the deviation from the mean value (2.27 V per cell) of the 24 individual float voltages, U_{float}, in test 2 according to deviation from the mean value (2.37 V per cell) of the 24 individual float voltages in a series string (mean value for all the tests 1, 3 and 5). The data shown are from manufacturer C.

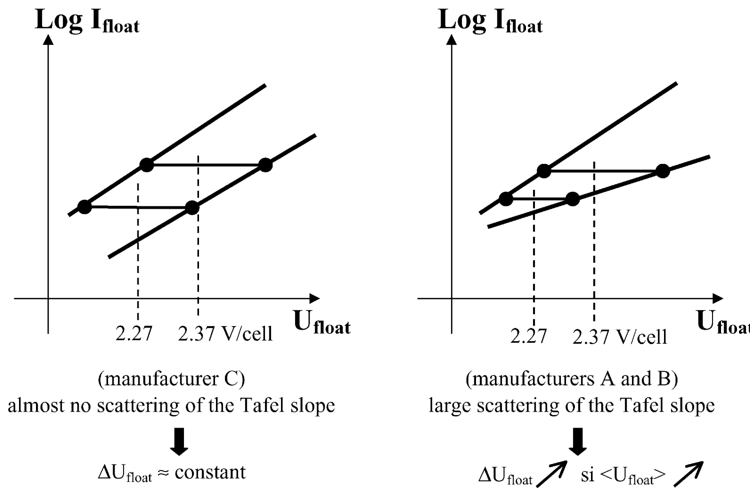

Fig. 9. Schemes which illustrate the scattering in slope on Tafel plot (floating current/floating voltage in a semi-logarithmic plot) and its influence on the behavior of several batteries in a series string at two different level of float voltage.

where I is the common float current, b_1, b_2 are the Tafel slopes and I_{01}, I_{02} are the self-discharge current (second Tafel parameter).

Eliminating the float current, the difference of the float voltage of two cells therefore becomes:

$$\Delta U_{\text{float}} = b_1 \log \frac{I_{01}}{I_{02}} + \eta_2 \frac{b_1 - b_2}{b_2}$$

Assuming the two batteries who present the maximum and minimum float voltage in the tests 1, 3, 4 and 5 are the same, the evolution of the float voltage expanse will simplify as follows:

$$\Delta U_{\text{float}}(2.37) - \Delta U_{\text{float}}(2.27) = \Delta\eta_2 \frac{b_1 - b_2}{b_2} \approx 100 \frac{b_1 - b_2}{b_2} \quad \text{in mV per cell}$$

The float voltage expanse evolution between the tests 1, 3, 5 and the test 4 gives therefore a good idea of the scattering in the Tafel slope parameter.

The Fig. 9 illustrates this influence with two extreme cases: almost no scattering in Tafel slope and big scattering. The previous results (see Table 4) show that the manufacturer C produce batteries with less scattering in Tafel slope than the manufacturers A and B. This important conclusion is in good agreement with a previous study on the same types of batteries [4]. However the present study deals with a larger number of batteries and a more statistical population than the previous.

4. Conclusions

The present study provides data on the open-circuit voltage and steady state characteristics, in float conditions, of the current and voltage of 24 batteries from three different manufacturers, arranged in series string.

The analysis of the scattering characteristics of these data is in good agreement with a previous study on a few individual batteries [4]. This more statistical pool of data confirms that a Tafel description of float characteristics is adequate.

One could emphasize that measurements at more than one level of mean float voltage (in this study two levels are explored) is very useful in order to extract data on the scattering of one particular Tafel parameter (the slope). It is important because previous studies [4,8,10–13] show a strong link between the Tafel slope and the oxygen recombination rate. The study of this scattering give information about the scattering in oxygen recombination and therefore about the scattering, due to manufacture, in the saturation characteristics of the separator of each battery cell.

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