

A study of the scattering of valve-regulated lead acid battery characteristics

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Abstract

Scattering of the electrical characteristics or performances of valve-regulated lead acid (VRLA) batteries was measured under controlled conditions, using batteries from three different manufacturers. Data on open-circuit voltage, capacity, and float conditions (currents and voltages) were collected for new, fully charged batteries. The physical reasons for the observed scattering were then closely examined in terms of the parameters relating to the manufacturing process, bearing in mind the following question: Which step(s) in the manufacturing process are primarily responsible for the scattering of a particular electrical parameter?

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1. Introduction

Standby battery applications are often encountered in high power installations (telephone exchanges, hospital standby supplies, etc.). In most of these systems today, valve-regulated lead acid (VRLA) batteries are used to meet the requirements. The demand for high power levels is thus satisfied by a large number of batteries assembled in series or in parallel.

In order to provide the user with maximum available capacity at any time, the batteries used in standby installations are generally maintained in an over-charged state by supplying them with a voltage slightly higher than the open-circuit voltage, known as float voltage. VRLA batteries are efficient in such applications since they can withstand a considerable over-charge without suffering irreversible damage [1]. For example, over 10 years, in a standby application (on float for more than 99% of the time), the order of magnitude of the over-charge is 10 times the rated capacity of the battery [2].

For most applications requiring high levels of power, 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 in series. Scattering between batteries may be relatively marked. For example, Berndt measured the individual float voltages of 203 cells placed at random in two parallel branches of 180 in-series cells [3]. 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 branch ages more rapidly than if its voltage was individually imposed. Although aging is not the subject of this study, this brief presentation provides an insight into the industrial implications of studying the scattering of the electrical characteristics of VRLA batteries and its origins.

Two causes of such scattering may be observed in industrial installations [4].

1. 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

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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 conditions and characteristics.

In the present study, the experimental conditions were chosen so as to eliminate the second type of scattering: measurements were always performed on fully charged batteries, as described in the experimental protocol.

After presenting and analyzing different stages in the manufacturing process of VRLA batteries, from where most of the scattering in electrical characteristics originates, this study identifies the link between the scattering inherent in the manufacturing process and its effects on the electrical performance characteristics of the finished product. For example, the previously noticed fact that there is no link between the capacity and the float voltage of a batch of batteries [4–6], will be accounted for in terms of their scattering origins.

2. Experimental

2.1. Batteries

The different experiments were conducted on new VRLA 12 V/5 Ah batteries from three different manufacturers. 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 does not affect the understanding or scientific discussion of the results obtained. With regard to manufacturer A, the study involved two different batches, produced at two different times, about 1 year apart. Table 1 summarizes, for each batch, the number of batteries selected for study. Two batteries were eliminated from the study since they exhibited capacity values which

were clearly non-standard (abnormally low) during the first test. 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 (that is, the analysis of scattering characteristics).

2.2. Measuring apparatus

Voltage measurements were conducted using Keithley 2000 multimeters. Float data (voltages and currents) were obtained by means of a Solartron 1287 potentiostat. For these latter measurements, four connecting wires were used: two wires to transmit the current, and two wires, in which the current was very weak, to measure the voltage. Very precise voltage measurements can be obtained with this type of set-up by avoiding the ohmic drop in the connection cables.

2.3. Experimental protocol

The experimental protocol is represented in Fig. 1 and described below. 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 13.62 V. The batteries were then maintained at a float voltage of 13.62 V (or 2.27 V per cell) for 7 days to ensure that they were fully recharged. The batteries were then discharged at a constant current ($C_{10}/10$ regime, or 0.5 A) down to a voltage of 10.80 V (or 1.8 V per cell). On the basis of the duration of this discharge, it was possible to determine for each battery the capacity available for the $C_{10}/10$ regime, referred to as Q . Each battery was then recharged using the same protocol as before and 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 [7]. These operations were conducted at ambient temperature.

For the second part of the experimental protocol, the batteries were placed in a thermostatically controlled bath at 20.0 ± 0.1 °C. Eight different constant voltage ranges between 13.26 and 14.40 V (or 13.62 and 15.5 V for the manufacturer C) were applied to each battery. These different values were deliberately applied to the same battery in random order (neither increasing or decreasing) so as to avoid any systematic drift in results due to the experimental protocol. The current was measured after 2 weeks in float conditions, a period which seemed a reasonable compromise between the total time required for the experiments and the need to obtain values as close as possible to a steady state. The change in the current measured after 1 week was still too great for the measurement to be considered as indicative of the steady state. For this reason, the measurement was made after 2 weeks, when the conditions were closer to the steady state. With this protocol, uncertainty about the current was fairly considerable (change in battery characteristics over time and real non-steady state of the measurement) and much greater than the uncertainty of the measuring technique

Table 1
Number of batteries selected for the study of each batch of new batteries (see Section 2.1 for a precise definition of the different batches)

Batch	No. of batteries studied
A1	11
A2	7
B	14
C	13

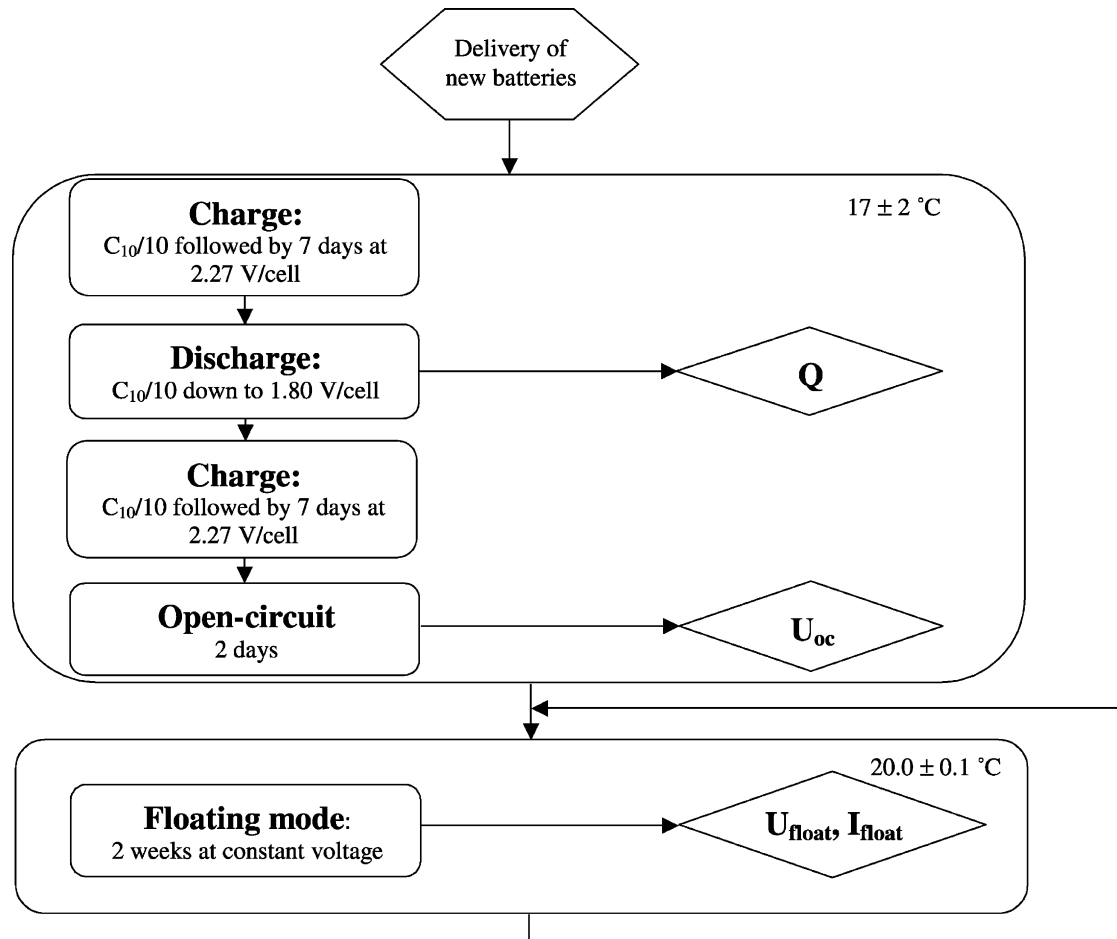


Fig. 1. Experimental protocol.

as such. The precision of the current values shown is therefore limited, but this should not prevent discussion of the results. Thus, for each of these 2-week periods, two values were obtained for each battery (U_{float} , I_{float}).

3. Main sources of scattering in the manufacturing process

3.1. Stages in the manufacturing process

Because of the tolerances inherent in each stage of the manufacturing process, the manufacture of VRLA batteries is the source of certain disparities, even when considering batteries from the same batch and same supplier. Among all the manufacturing parameters, it has already been shown [4,6,8,9] that the characteristics of the electrolyte have an important impact on the electrical performance of the finished battery.

In a VRLA battery, the electrolyte is made up of a separator (made of glass fiber for the batteries examined in this study) impregnated with an aqueous solution of concentrated sulfuric acid. There are essentially three stages

in the manufacturing process that can influence the final characteristics of the electrolyte [10]:

- (i) preparation of paste (mixing of oxides and acid);
- (ii) cell, battery assembly and acid fill;
- (iii) formation (charge of the battery, once the valves have been put into service).

The physical characteristics of the composite phase containing the electrolyte, which are an important factor in the analysis of the results, particularly with respect to scattering, are as follows:

- density of acid (or its concentration);
- quantity of acid, or the product of the concentration by the volume;
- saturation of separator, that is, the ratio of the volume of the separator pores filled with acidic solution to the total volume of the separator pores;
- compression of the separator, which is notably linked to its saturation and the quantity of acid.

However, in the following discussion, this last characteristic will not be detailed, because it plays an important role

only for high regime capacity [8,9]. And no corresponding data are reported in this study.

3.2. Scattering of electrolyte characteristics

The first stage of the manufacturing process, (i), although using acid density which is generally different from those of the second stage (ii), may be considered as having little influence on the final characteristics since it only affects the acid trapped in the structure of the positive and negative plates, after they have been cured. The last two stages, on the other hand, are much more critical for the final electrolyte characteristics.

The electrolyte filling process (ii) varies from one supplier to the next. Thus, scattering of compression, which is inevitable on account of the tolerances in the thickness of the separator plates and the size of the container, will play a different role depending on the process. For supplier B, a controlled volume of acid is poured into each cell, while for supplier A each cell is over-filled and then the excess solution removed (no information for manufacturer C). This difference in the filling procedure obviously has different consequences in terms of scattering of electrolyte characteristics. For supplier B, the quantity of acid introduced is carefully controlled (according to the manufacturer, scattering is of the order of 1%), but the saturation rate of the separator will depend deeply on the compression of each cell. In the case of manufacturer A, the quantity of acid introduced is not as carefully controlled, since it depends largely on the compression rate, but the process ensures that the separator reaches a saturation level of 100% on completion of filling.

The aim of the formation (iii) is to fully charge the battery while at the same time decreasing the saturation rate of the electrolyte. This last operation enables the oxygen produced at the positive electrode to be efficiently transported to the negative electrode where it can be reduced. So, an adequate saturation of the separator allows proper initiation of the oxygen cycle as soon as the battery is used for the first time. This stage produces acid (for normal recharge reactions) and consumes water (when gases are evolved) and therefore tends to increase both the density and quantity of the acid. In addition, it results in a decrease in the saturation rate of the separator, although this parameter is quite difficult to control.

Thus, at the end of the manufacturing process, the following observations may be made.

- Acid density is higher to that of the second manufacturing stage (ii) with slightly more scattering than the level for the acid used for filling (process control around 1%). The final values, as indicated by the manufacturers, are produced in the Table 2.
- Scattering with regard to acid volume is more than 1%, and is less for manufacturer B than for manufacturer A.
- Saturation of the separator is slightly less than 100%, but with considerable scattering. Scattering is less for the

Table 2
Estimated density of acid in finished battery for each manufacturer

Manufacturer	Estimated acid density
A	1.33
B	1.30
C	— ^a

^a This value was not communicated by manufacturer C.

batteries from manufacturer A than for those from manufacturer B.

4. Results and discussion

4.1. Open-circuit voltage for a fully charged battery

Table 3 presents the results obtained for new batteries from the three different manufacturers. For each batch, the mean value of the open-circuit voltage U_{oc} is shown as well as the difference between maximum and minimum values. It was not possible to perform a complete statistical analysis to calculate the distribution curve and standard deviation since there was insufficient data in each population.

It is well known that, on account of the contribution of the electrolyte to the main reactions at the electrodes, the open-circuit voltage value of a VRLA battery depends essentially on the density of the aqueous solution of sulfuric acid [1]. The open-circuit voltage measurement is thus an ideal tool for monitoring the state of charge of a VRLA battery [5]. For example, this measurement is used by manufacturers to control the quality of batteries at the end of the manufacturing process. It enables them to easily identify those batteries with abnormal self-discharging performances. In this study, we were not interested in variations due to the state of charge of the battery, since all the measurements were conducted on fully charged batteries. It was nevertheless interesting to look at the influence of electrolyte density on open-circuit voltage in fully charged batteries, in that the acid density parameter is not generally controlled at a level better than 1 or 2% in the manufacturing process (Section 3.2).

Using thermodynamic data, it is possible to calculate an approximate value for the open-circuit voltage of a fully charged battery and thus to predict the influence of electrolyte density, d , on this value. For relatively high acid density

Table 3
Open-circuit voltage for fully charged battery, U_{oc} (see Section 2.3 for a precise definition of this value): mean value and difference between the maximum and minimum values, ΔU_{oc} , for each batch of new batteries

Batch	Mean U_{oc} (V)	ΔU_{oc} (mV)
A1	13.18	30
A2	13.14	110
B	12.97	60
C	13.17	90

Table 4

Open-circuit voltage for fully charged batteries, U_{oc} (see Section 2.3 for a precise definition of this value): mean value measured and value of thermodynamic voltage, U_{th} , calculated from the acid density estimated for each batch of new batteries

Batch	Estimated acid density	U_{th} (V)	Mean U_{oc} (V)
A1	1.33	13.02	13.18
A2	1.33	13.02	13.14
B	1.30	12.84	12.97
C	–	–	13.17

levels (higher than 1.20), which correspond to those used in the VRLA batteries studied, the thermodynamic value of the voltage, U_{th} , shows a more or less linear distribution [1,11]:

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

that is

$$U_{oc}(\text{V}) \approx U_{th} \approx 6d + 5.04, \quad \text{for a battery containing six cells}$$

Table 4 presents the estimated value (Table 2, Section 3.2) of electrolyte density in new fully charged batteries for each manufacturer, as well as the values deduced from the above relationship for the thermodynamic voltage of a fully charged battery. The last line shows the mean experimental values obtained in this study.

Given the two approximations mentioned above for the calculation of voltages (U_{oc} is not equal to U_{th} [7]) and the relationship between U_{th} and acid density is not exactly linear [11], a strict numerical comparison was not possible. However, it was interesting to check experimentally that the manufacturer who uses the acid with the lowest density (that is B compared with A) also has the lowest mean open-circuit voltage value for a fully charged battery. Furthermore, the difference of 40 mV in the mean values of U_{oc} measured in batches A1 and A2 from the same manufacturer, corresponds to a 0.5% change in average acid density between the two batches (produced 1 year apart), if the main source of deviation can be attributed to this process parameter. This would thus seem a perfectly reasonable hypothesis.

Finally, still considering the acid density parameter as preponderant over open-circuit voltage for a fully charged battery, the scattering of acid density values was estimated on the basis of the scattering of open-circuit voltage values. This estimation is detailed in Table 5 for each batch of batteries. For manufacturer C, acid density was not known but, given the earlier discussion (when mean values of U_{oc} are very close, acid densities are probably identical), the value for manufacturer A was used for scattering calculations. The relative scattering for acid density values was always less than 1.5%, and thus entirely compatible with the proposed interpretation (Section 3.2).

To conclude this first phase of the analysis, the dominant process parameter for determining the mean, and in

Table 5

Open-circuit voltage for fully charged batteries, U_{oc} (see Section 2.3 for a precise definition of this value): measured difference between the maximum and minimum values, ΔU_{oc} , and relative scattering of acid density calculated ($=\Delta U_{oc}/6d$) for each batch of new batteries

Batch	ΔU_{oc} (V)	Relative scattering of acid density (%)
A1	30	0.4
A2	110	1.4
B	60	0.8
C	90	1.1 ^a

^a An acid density value of 1.33 is used for the calculations for manufacturer C.

particular, the scattering of the open-circuit voltage of a fully charged new battery is the density of the electrolyte.

4.2. Capacity

Table 6 shows the results obtained for new batteries supplied by the three different manufacturers. For each batch, the mean capacity Q is shown as well as the difference between the maximum and minimum values for this parameter.

The first thing to remark about these results is the good reproducibility of the mean capacity value of the two batches from manufacturer A, even though the second batch was produced 1 year after the first. This observation confirms our earlier comments about the links between electrical characteristics and the manufacturing process, while at the same time underlining the quality of manufacturing process control. In addition, the considerable differences (more than 10%) in mean capacity values from one manufacturer to the next suggest that a comparative analysis would be of interest.

It is well known that VRLA batteries are designed to promote the establishment of an efficient oxygen cycle. Thus in a VRLA battery, the quantity of active matter introduced at the negative electrode is excessive compared with that introduced at the positive electrode and the quantity of electrolyte introduced is minimal (“starved” electrolyte) [1]. In these conditions, the capacity of a VRLA battery depends mainly on the electrolyte it contains and not, as is usually the case for other batteries, on the quantity of active matter at the electrodes.

Table 6

Capacity, Q (see Section 2.3 for a precise definition of this value): mean value and difference between the maximum and minimum values, ΔQ , for each batch of new batteries

Batch	Mean Q (Ah)	ΔQ (Ah)
A1	5.56	0.10
A2	5.57	0.19
B	4.48	0.36
C	5.16	0.25

To begin with, a first relationship between the capacity and the electrolyte parameters is provided directly by the results of the discharge reactions, where the sulfuric acid acts as a reagent, so that the quantity of acid available plays a role. However, the relationship is not quite simple since it depends largely on the discharge regime used (that is to say on the value of the current used during the discharge). Thus, for a very high discharge regime (as in UPS applications), the relevant parameters are the concentration of the acid (or the density of the acidic solution) in the charged state and the compression of the cell [9]. The acid concentration profile exhibits a very steep slope so that very low interfacial concentrations are rapidly obtained. Consequently, the discharge ends with a sudden increase in internal resistance, while the bulk of the electrolyte is not yet affected. The compression of the cell has a great influence on the electrolyte thickness and therefore on the internal resistance value, which causes a rapid decrease of the capacity at high regimes. At the other extreme, for a very low discharge regime, the concentration profile is practically flat, but its average level decreases steadily as the battery is discharged and acid is consumed. For this type of regime, the important parameter is thus the quantity of acid initially present in the whole battery. The quantity of acid is of course not independent of the density parameter, but combines the density and volume parameters. For these low regimes the value of the internal resistance has practically no influence on the capacity, as long as it is reasonably low.

The experimental data presented correspond to discharges in a $C_{10}/10$ regime. This is not a very high regime, so that the volume as well as the density of the electrolyte probably influence the observed values. However, we will first examine

Table 7

Correlation between capacity and open-circuit voltage for fully charged batteries: mean values of U_{oc} and Q , ΔU_{oc} and ΔQ values for each batch of new batteries

	Batch			
	A1	A2	B	C
Mean U_{oc} (V)	13.18	13.14	12.97	13.17
Mean Q (Ah)	5.56	5.57	4.48	5.16
ΔU_{oc} (mV)	30	110	60	90
ΔQ (Ah)	0.10	0.19	0.36	0.25

All the experimental data are shown on Fig. 2.

the correlation between measured capacity values and the acid density of the battery. Based on the results presented in the previous section, which showed that acid density was directly related to the open-circuit voltage for a fully charged battery, it is more expedient to examine the correlation between capacity and open-circuit voltage to take into account effective scattering of acid density values.

Table 7 presents mean capacity and open-circuit voltage data as well as their scattering for each of the four batches studied. Fig. 2 shows, for each of the 45 batteries tested, the deviations in capacity in relation to the overall mean value for all four batches as a function of the deviations in open-circuit voltage in relation to the overall mean value. When significant (i.e. not for batch A1), the figure also shows the straight line corresponding to the linear regression of the points for each of the individual batches as well as for the batteries as a whole. The figure thus clearly demonstrates the link between capacity and open-circuit voltage for a fully charged battery, that is between capacity and initial acid density. A more precise analysis of scattering for each batch

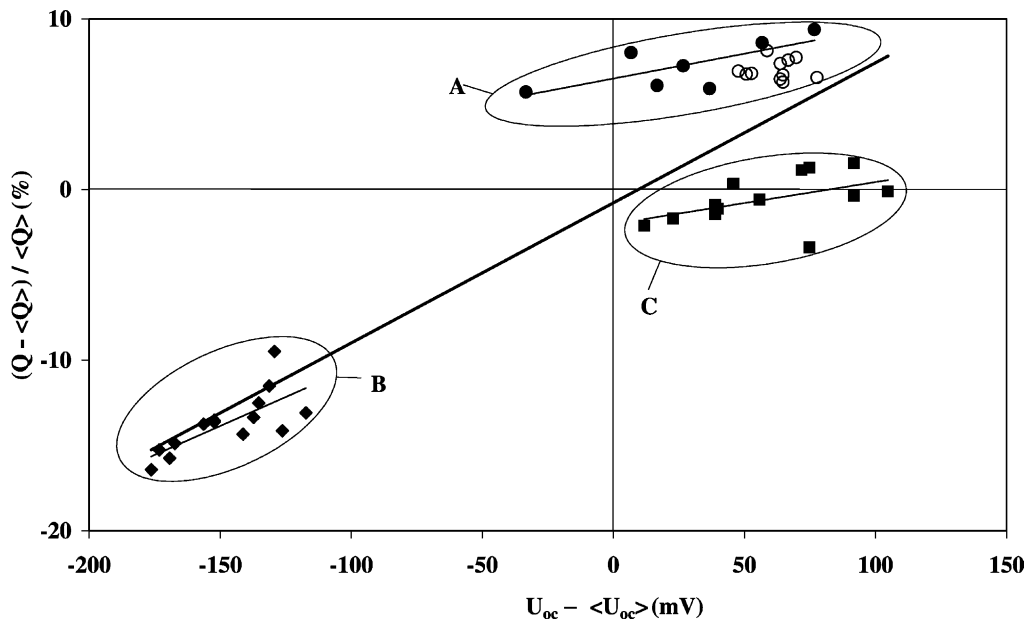


Fig. 2. Correlation between capacity and open-circuit voltage for a fully charged battery: changes in relative difference (%) between the capacity, Q , and the mean capacity of all the tested batteries, $\langle Q \rangle$, according to the difference (mV) between the open-circuit voltage, U_{oc} , and the mean open-circuit voltage, $\langle U_{oc} \rangle$, for all the new batteries. The four batches are marked with different symbols: batch A1 (○); batch A2 (●); batch B (◆); batch C (■).

also shows a correlation even though it is not identical from one batch to the next. The importance of the result is not in the slope values since the experimental data were not sufficiently numerous or precise in each batch to allow a real statistical analysis. What is important is the positive correlation between capacity and open-circuit voltage, and thus initial acid density: capacity tends to increase when acid density increases. This result is in agreement with the interpretation and expectations presented above.

A point which seems worth discussing is the comparison between batches from manufacturers A and C. All these batteries had the same acid density when fully charged (as indicated by the open-circuit voltage values), but the data for the two manufacturers are, however, clearly separated into two zones in Fig. 2. One interpretation in line with the analysis presented above is that the manufacturers made slightly different technological choices. The quantity of acid present in the batteries at the end of the manufacturing process would thus be less for manufacturer C than for manufacturer A. This difference in mean capacity between the two manufacturers should therefore become less marked when a higher discharge regime is used, provided that the internal resistances are the same. In these conditions, the influence of density becomes dominant over that of the quantity of electrolyte.

4.3. Float voltages and currents

Table 8 summarizes, for four batteries from each of the batches A1, B and C, the results of float voltages and currents for two different voltages: the first (13.62 V) corresponds to normal float conditions, and the second to a higher voltage. Because of restrictions in experimentation time, it was not possible to study more individual batteries,

Table 8
Steady-state values (U_{float} , I_{float}) for two different float voltages and four batteries from each of the batches A1, B and C

	Batch		
	A1	B	C
I_{float} (mA) for $U_{float} = 13.62$ V	1.3	1.9	0.2
	1.6	1.8	0.2
	1.3	3.8	0.2
	1.6	1.8	0.2
ΔI_{float} (mA) for $U_{float} = 13.62$ V	0.3	2.1	<0.1
I_{float} (mA) for $U_{float} = 14.20$ V	8.3	9.3	0.5
	13.3	8.0	0.5
	9.8	20.4	0.5
	9.7	9.6	0.6
ΔI_{float} (mA) for $U_{float} = 14.20$ V	5.0	12.4	0.1

The difference between the maximum and minimum values of the float current is indicated for each batch and the two voltages. For batch A1, all the steady-state data are shown on Fig. 3.

and consequently it would not be significant to calculate a mean value. The table therefore shows current values for each of the four batteries for the three batches as well as the differences between the maximum and minimum current values. Complementing this table, Fig. 3 shows all the data for batch A1, that is the eight pairs of values (U_{float} , I_{float}) for each of the four batteries tested.

The first important remark to be made is that the behavior of the batteries from manufacturer C is very different from all the others. For all the experimental data, the average curve of the steady-state current/voltage characteristics of manufacturer C batteries is shifted overall by about

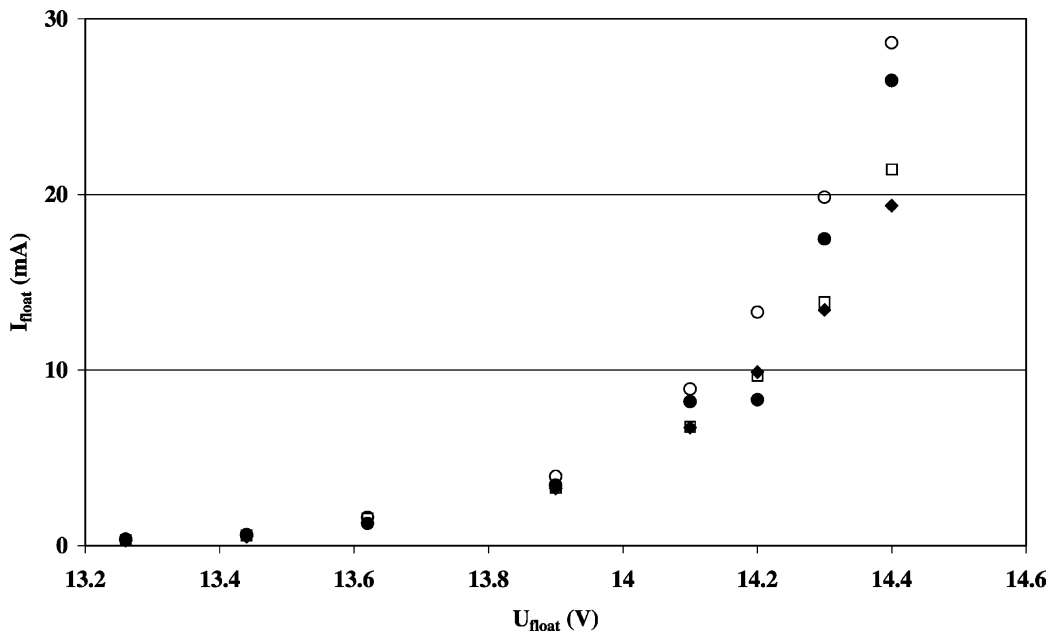


Fig. 3. Changes in the float current, I_{float} , according to the float voltage, U_{float} , of four batteries in batch A1. The four batteries are marked with different symbols: (●), (○), (◆) and (□).

1 V (or 165 mV per cell) towards the high voltages, while the open-circuit voltage is identical. For example, a float voltage of 15.00 V (or 2.50 V per cell) had to be applied to the batteries of manufacturer C to obtain the float current values (around 7 mA) reached between 13.90 and 14.10 V (or 2.34–2.35 V per cell) for the batteries of manufacturers A and B. Another important point is that scattering of the characteristics for the batteries of manufacturer C was much less marked than for the batteries of the other manufacturers. For example, for the highest float current (around 25 mA), the difference between the maximum and minimum current values was 3 mA for the four batteries of manufacturer C, as opposed to 9 mA for those of manufacturer A and 25 mA for those of manufacturer B. Given our limited information on the manufacture of type C batteries, it is difficult to discuss the reasons which might explain this difference in behavior. Like previous authors already pointed out, it may be related to a change (in this case: a decrease for C) of the active surface area of the positive electrode caused by a different process [12].

Another preliminary remark could be made with the example of manufacturer B. Significant scattering of float characteristics cannot be detected and minimized by first operating a selection based on the capacity or open-circuit voltage values of fully charged batteries. This agrees with previous results [4–6], indicating that there is no correlation between capacity and float voltages.

In general, for all manufacturers, an increase in scattering was observed when the current and voltage increased. In addition, the scattering exhibited by the batteries of manufacturer B, for the four batteries studied, was greater than that observed in the batteries of manufacturer A.

An interesting way for analyzing this type of steady-state data is to examine them in a semi-logarithmic plot: $\log(I_{\text{float}}) = f(U_{\text{float}})$. In fact, for steady-state data, and assuming simplified mechanisms, as soon as polarization (that is, the difference between applied and open-circuit voltages) is higher than 100 mV per cell, or 0.6 V for one battery, the Tafel approximation predicts a linear relationship characteristic of the electrode reaction kinetics (anodic at the positive electrode and cathodic at the negative electrode).

Fig. 4 shows a semi-logarithmic plot, for the three batches studied, of the steady-state points for high polarization values, that is for float voltage values greater than 13.8 V. A linear relationship can be observed, with a very good correlation for most of the batteries. The parameters of these lines are shown for each battery in Table 9. This table shows the reciprocal of the slope, b , expressed in millivolts per decade (reduced in the table to a value for one cell to facilitate comparison with the literature) and the value of the ordinate (I_0 , expressed in microAmpere) which would be obtained by extrapolating this line to the open-circuit voltage, also shown in Table 9.

A first remark should be made regarding the values for the batteries of manufacturer C. The atypical behavior noted previously is reflected mainly in the self-discharge current values which are particularly low (about 1 order of magnitude lower than for A and B), while the slopes are of similar magnitude. It would seem therefore that the batteries of manufacturer C exhibit a particularly high oxygen and/or hydrogen evolution over-voltage, although we have so far been unable to identify the origin.

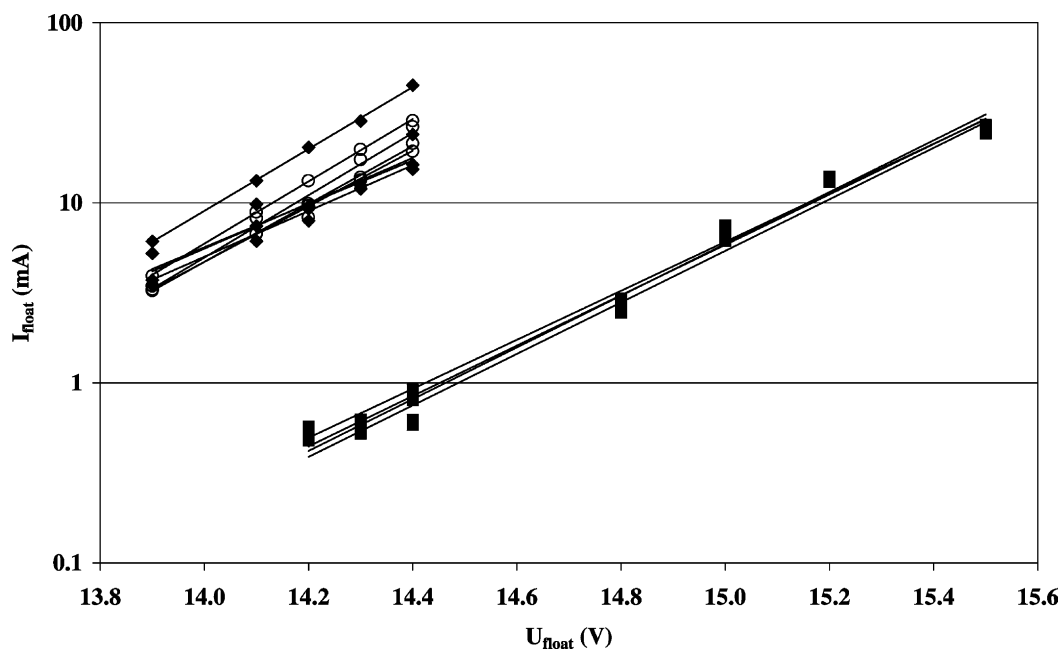


Fig. 4. Changes (shown using a semi-logarithmic plot) in the float current, I_{float} , according to the float voltage, U_{float} , for four batteries in each of batches A1, B and C. Only values with a high polarization (that is with a voltage higher than 13.8 V) are represented. The three batches are marked with different symbols: batch A1 (○); batch B (◆); batch C (■). The straight lines show the linear regression of data for each battery.

Table 9
Steady-state parameters extracted from the semi-logarithmic plot (Fig. 4) of the 12 batteries (from batches A1, B and C)

	Batch		
	A1	B	C
U_{oc}	13.17	13.00	13.19
	13.16	12.94	13.19
	13.18	12.94	13.19
	13.19	12.96	13.13
Tafel slope (mV per decade)	95	130	120
	95	130	115
	110	95	115
	105	140	120
I_0 (μA)	180	270	17
	210	260	15
	260	140	14
	240	320	17

The open-circuit voltages for each battery, the Tafel slopes (mV per decade) and self-discharge (μA) values are indicated. For the Tafel slope, the experimental values are reduced to a value for one cell.

In general, the slope values obtained, between 95 and 140 mV per decade, are of the order of magnitude expected for VRLA batteries. For example, in a study on VRLA batteries by Vaccaro and Landwehrle [13], Tafel slopes range between 80 and 105 mV per decade, whereas they are around 200 mV per decade for flooded batteries [14]. It is generally accepted such slopes give a good indication on oxygen recombination efficiency at the negative plate. Thus, it can be said that, among the batteries studied, the new batteries from manufacturer A had a better recombination rate than those from manufacturer B.

The recombination rate is related, to a large extent, to the properties of the separator. Indeed, the saturation of the separator has to be less than 100% for oxygen transport to take place in good conditions. The optimum level of saturation for the separator is a compromise between the need of electrolyte-free pores to enable rapid transport of oxygen and the need of a high proportion of pores filled with electrolyte to ensure ionic conduction in the system. Furthermore, implementing this optimum level is a delicate part of the manufacturing process, as we have already seen (Section 3.2).

It is not possible to directly compare the values obtained for the Tafel slopes and the known manufacturing parameters, since there is lack of information on the final saturation rates. On the other hand, the scattering of these values can be examined more closely. It is interesting to note the good agreement between the various results: it was easier to control scattering on the saturation rate of the separator with the manufacturing process of manufacturer A than with the process of manufacturer B (Section 3.2), and less scattering was observed in the Tafel slopes for batch A than for B.

For the self-discharge current values, I_0 , a check was first made to ensure that the scattering measured could not be attributed to the combined scattering of open-circuit voltages and slopes. The scattering of acid density thus had a marginal influence on this value. To discuss scattering for this parameter, I_0 , in more detail, it is necessary to examine its physical significance more closely. The Tafel approximation mentioned above is valid for each electrode separately. And there is, of course, no reason for the kinetic parameters to be identical for the positive and negative electrodes. Thus, even in the simplest case (with an E transfer reaction on each electrode), the experimental data obtained for the overall voltage at the battery terminals are combinations of values associated with each of the electrodes. For the slope, the relationship is simple since the measurement, b , is merely the sum of the parameters corresponding to each of the electrodes: $b = b_+ + b_-$. For the current, the relationship (1) is a little more complex since it also combines the values of the slopes:

$$\log I_0 = \frac{b_+}{b_+ + b_-} \log I_{0+} + \frac{b_-}{b_+ + b_-} \log I_{0-} \quad (1)$$

For a VRLA battery, because of the oxygen cycle, the kinetic description at the negative electrode is more complicated. A full rigorous discussion of this question is beyond the scope of this paper [15]. However, what is interesting here is the scattering of the different parameters. If the main source of scattering is that related to saturation of the separator, and thus to oxygen recombination efficiency, scattering of the parameters of the positive electrode is probably negligible compared with that of the parameters of the negative electrode. Furthermore, scattering of the separator saturation values influences not only the slope, as we saw earlier, but also the value of the self-discharge current of the negative electrode. Finally, the scattering observed for the overall apparent self-discharge currents of the batteries can be quite reasonably interpreted as being related essentially to scattering of the saturation values of the separator.

5. Conclusions

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

The values of the scattering of these data and their eventual correlation could be interpreted as follows.

- Open-circuit voltage and capacity are electrical characteristics where scattering is related essentially to dispersion of acid density values inside the battery.
- 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.

This analysis of the causes of the scattering of electrical parameters is a first important step in understanding the possible consequences of scattering when a large number of batteries is used in series in industrial applications.

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