

Characterisation of photovoltaic batteries using radio element detection: the influence and consequences of the electrolyte stratification

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Abstract

In photovoltaic (PV) applications, electrolyte stratification is a common phenomenon, which favours the formation of irreversible lead sulphate especially at the bottom of the electrodes. This degradation leads to premature capacity losses. In this paper, the influence and the consequences (in terms of electrodes degradation) of electrolyte stratification have been studied using experimental cells.

Firstly, in order to measure local current and voltage, an experimental cell has been realised, consisting of two identical systems with three electrodes (two negative electrodes and one positive electrode) connected in parallel and located one above the other in the same battery container. A cycling procedure which favours acid stratification has been performed on this experimental cell. After eight cycles, contrasting changes have been observed in the two systems. The stratification phenomenon induces a vertical potential gradient which is at the origin of the unbalanced behaviour between the two systems: the lower system is deeply discharged and partially recharged and the opposite behaviour is observed in the upper system. Consequently, the lower part of the system tends to show considerable sulphation due to the cycling in a low state of charge.

This degradation has been characterised using radioelement detection. After incorporation of $\text{H}_2^{35}\text{SO}_4$ into the electrolyte, the distribution of radioactive lead sulphate ($\text{Pb}^{35}\text{SO}_4$) on the electrodes was followed by laser reading of photostimulable screens. This allowed recreating the kinetics by which irreversible sulphate appears, and to show its link with the phenomenon of electrolyte stratification.

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1. Introduction

In a context of fast expansion, due to the strong development of individual photovoltaic installations, it is increasingly important for these systems to be reliable and cost-effective. In this application, the lead–acid battery is the more commonly used technology due to its low cost and its great availability. However, the analysis of these systems when running shows that the weakest element is the battery, given the extremely variable length of service life that can be observed: lifetime of batteries in PV systems are shorter than they should be.

In previous studies, numerous post-mortem analyses have been performed on batteries, which have been operating in PV installations [1]. As a major ageing effect, irreversible sulphation was identified in many investigations. Moreover, in most cases, the lead sulphate distribution follows a vertical gradient: the concentration of these discharged

species is higher in the lower part of the electrodes than in the upper part. The positive electrodes were particularly affected by this irreversible lead sulphate distribution. Thus, these analyses show a strong link between this degradation and electrolyte stratification.

Electrolyte stratification is widely spread not only in photovoltaic applications, and better understanding of this phenomenon may be the solution to many practical problems. What is the influence of stratification on battery working?

Some authors have performed chemical titration [2,3] to evaluate lead dioxide consumption and production in different vertical parts of the electrode during discharge in stratification conditions. At the beginning of the charge, they have observed that the higher part of the battery is more active than the lower part. Thus, a lot of sulphuric acid molecules are produced during this period and fall to the bottom of the battery. If the charge continues until high state of charge reaching gassing, the stratification decreases. Nevertheless, some authors [2] limit this influence: the electrolyte is more homogenised in the lower part than in the upper part of the battery.

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During the discharge and using the same characterisation experiment (namely chemical titration) Chao et al. [4] have shown that the discharge is more important in the lower part.

If these experiments show some consequences of electrolyte stratification, they don't give any explanation on the related degradation mechanisms.

Sauer [5] has simulated the influence of stratification on the current–voltage relation. In this work, an electrical circuit model has been used and the electrodes are divided into three parallel circuits in order to take into account the effects of acid stratification. In this study, Sauer has calculated the current distribution in each part of the electrical circuit. However, no experimental measurements were performed to check the prediction of the model.

The objective of the present work is the experimental observation of the influence of electrolyte stratification on the electrodes behaviour. Firstly, an experimental set-up was built to measure the vertical current distribution in the case of electrolyte stratification. In the second part, our objective was the observation of the degradations on positive electrodes: a non-destructive technique has been used to follow the distribution of radioactive lead sulphate ($\text{Pb}^{35}\text{SO}_4$) by laser reading of photostimulable screens.

In the past, some radioelement detection has already been used to characterise lead–acid batteries. Bode and Euler [6] introduced $\text{H}_2^{35}\text{SO}_4$ into the electrolyte of lead–acid batteries and characterised the discharged electrodes with a view to determine the most reactive parts of the active mass. In our study, the tracer detection was realised with high-resolution radiographic screens and the electrodes were characterised after recharge.

2. Experimental

2.1. Local current measurements

This first study has been realised in order to measure the vertical current distribution in flooded lead–acid batteries in correlation with acid stratification: the electrodes in two different regions of the battery are connected individually to allow the current flow in the two different vertical

positions to be measured. The experimental cell is composed of two identical systems (an upper and a lower part), which consist of two flat negative plates and one positive flat plate (Fig. 1). The positive and negative currents of each part are measured individually as well as the voltage in the upper and the lower part. Capillary tubes have been introduced in the electrolyte between the electrodes in order to measure electrolyte specific gravity at different vertical positions (Fig. 1).

Different stratification measurements are performed in the experimental cell (Fig. 1):

- the total stratification,
- the upper and lower system stratification.

The last two stratification measurements are called “local stratification” measurements.

During this test, intensiostatic charge–discharge cycles ($0.1I_{10}$ current rate) were conducted. While the total current is constant, its repartition is driven by the electrochemistry of the two systems. In this protocol, overcharges are avoided to reduce gas production which may homogenise HSO_4^- distribution: the recharge is stopped when reaching hydrogen and oxygen overvoltages. This limit has been determined during preliminary cycles: the steep potential increase is observed at 70% state-of-charge (SOC). Therefore, the experimental cell has been tested between 20% SOC and 70% SOC. This deep cycle procedure enhances electrolyte stratification [1].

2.2. Irreversible lead sulphate distribution using ^{35}S

For this experiment, other experimental cells were prepared. These cells were composed of three flat plates (one positive and two negative, Fig. 2) and only one system has been prepared and studied.

The tracer incorporated in the electrolyte (^{35}S) is available from Amersham Pharmacia Biotech in the form of freeze-dried sulphuric acid. ^{35}S is a β -emitter. A tracer corresponding to an activity of $2.5 \mu\text{Ci}\cdot\text{L}^{-1}$ was used in each experimental cell. After being dissolved in deionised water, the radioactive acid was added to the electrolyte 3 days before the beginning of the cycling, in order to obtain

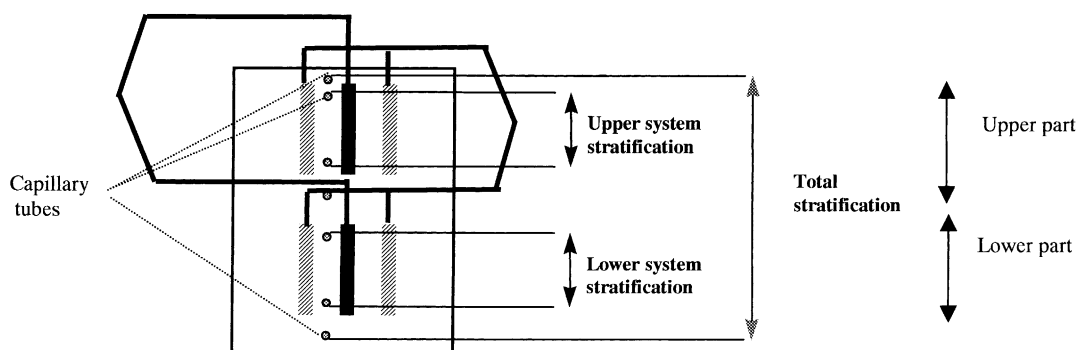


Fig. 1. Experimental cell elaborated with two identical systems for local current measurements.

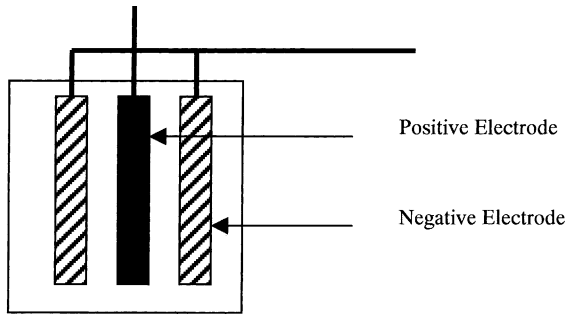


Fig. 2. Experimental cell elaborated for radioelement detection.

good homogeneity between the initial species (HSO_4^-) and the tracers ($\text{H}^{35}\text{SO}_4^-$).

The principle of the tracers characterisation system is based on exposing a photostimulable screen to contact with the surface to be analysed [7]. Before each exposure, the electrodes have been rinsed and dried for electrolyte elimination. The photostimulable screens used in our study comprise BaFBrEu^{2+} crystals in an organic matrix. During the print, the β -particle rays energise an electron of the Eu^{2+} ion in the conduction band. This electron is then captured by the F centre of the BaFBr complex. During this reaction, the Eu^{2+} is oxidised Eu^{3+} and the complex is reduced into BaFBr . The energised complex has an absorption bandwidth centred around 600 nm. The device used to analyse these films includes a helium:neon laser. When the complex is exposed to the laser beam, the electrons become Eu^{2+} again. At this stage, a photon is emitted at a wavelength of 300 nm. The luminescence thus created is detected by fibre optics. This data is then filtered and amplified, and the intensity of the relative luminescence at a point of the screen measured and recorded. The data is acquired in digital form.

The result obtained by reading the photostimulable screen is a quantitative representation of the image formed on the

film by the radiation produced by the sample. The various emission levels of the radiation received by the phosphorous screens can be relatively quantified by means of data processing software. The resolution of this system is 200 μm . The screens can be initialised and reused indefinitely by exposing them to white light.

During this test, the experimental cell has been tested using the same intensiostatic charge–discharge cycles as in the previous study. This new characterisation method has been patented [8].

3. Results and discussion

3.1. Current evolution in each part of the cell

3.1.1. Recharge step

The two identical systems (upper and lower systems) of the experimental cell have been tested using the cycling procedure, which accelerates electrolyte stratification. During the first cycles, no electrolyte stratification has been measured and the same behaviour has been observed for the two systems.

At the eighth cycle, a lot of changes are observed. First of all, both electrolyte stratification and local current variation are measured: an inhomogeneous electrode behaviour appears (Fig. 3). After 3 h of recharge, an inverse current evolution appears in each system (Fig. 3.2): the current of the upper system decreases and at the same time, the current in the lower system increases. Simultaneously, some evolution in stratification measurements has been also noticed (Fig. 3.1):

the upper system stratification increases first and then levels off;
the lower system stratification increases at the end of the recharge.

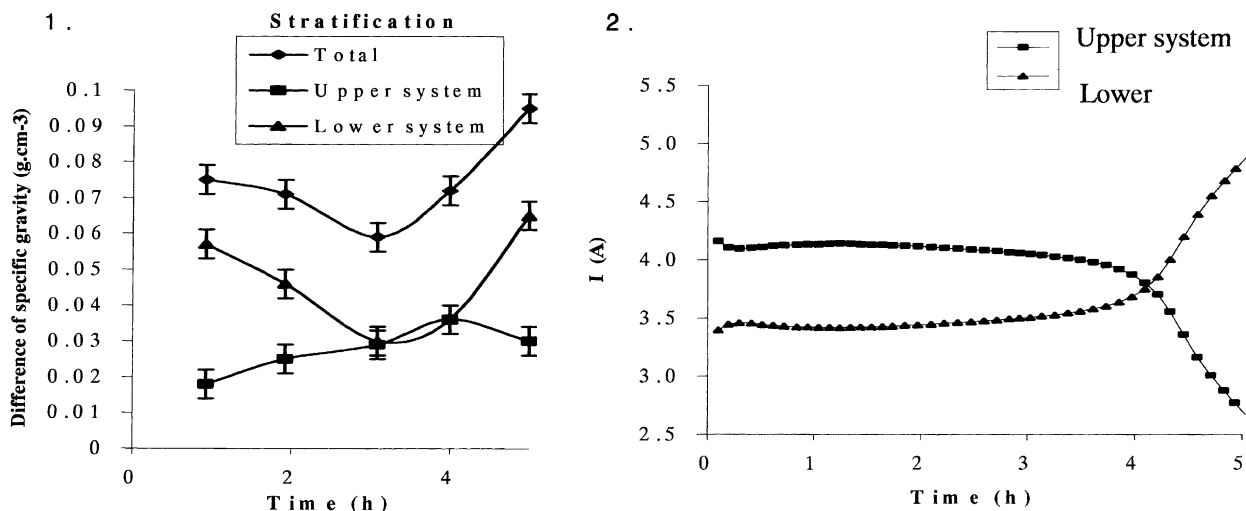


Fig. 3. During the eighth recharge. (1) Total and local stratification; (2) current in each system.

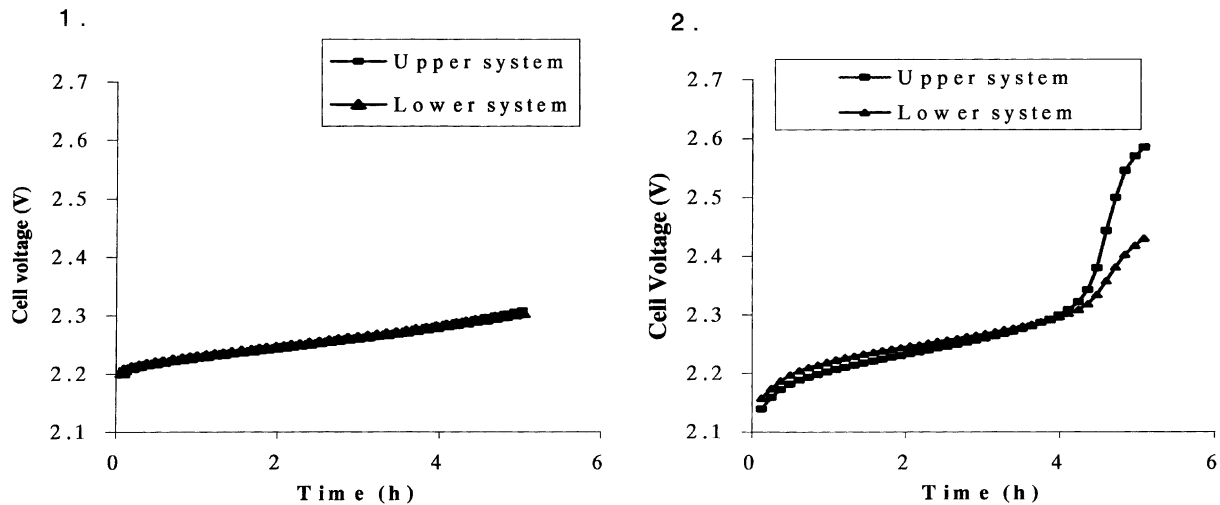


Fig. 4. Voltage–time evolution in each system. (1) During the first recharge; (2) during the eighth recharge.

These results show that the recharge process does not take place at the same time in each system. Thus, the following explanations can be used:

During the first 3 h of recharge, the recharge current is greater in the upper system. Consequently, the recharge is preponderant in this system: HSO_4^- ions are produced and fall to the bottom of the container resulting in an increase of the local stratification. Then, the local stratification levels off as less and less sulphate ions are produced. The recharge is less important in this system and the recharge current begins to decrease.

At the beginning of the recharge, the current is lower in the lower system than in the upper one (the difference between the two current values is about 0.8 A). After 3 h of recharge, the local current increases suddenly: the recharge process is more pronounced. At the same time, more and more sulphate ions are produced increasing the local stratification.

In order to have a better understanding of the sudden change in local current values which occurs after 3 h of recharge, we have measured the local voltage in each system (Fig. 4). During the first cycles, the recharge is stopped before reaching gassing: the end of charge criterion was chosen at 70% SOC to enhance the stratification phenomenon (Fig. 4.1). At the eighth cycle, the recharge curve of the whole system shows a steep increase (Fig. 4.2). This means that hydrogen as well as oxygen are produced at the negative and the positive electrode, respectively. This sudden increase is observed at first in the upper system, indicating that this system achieves its full recharge first.

This unbalanced behaviour is linked to the stratification phenomenon, which induces a vertical potential gradient [5]. The potential of the $\text{Pb}/\text{H}_2\text{SO}_4/\text{PbO}_2$ electrode can be approximated by this law:

$$V_0(V) = 0.84[V] + \rho$$

The upper system is charged first due to the local electrode potential values:

the voltage of the positive electrodes is the lowest. The oxidation of PbSO_4 to PbO_2 is favoured;
the voltage of the negative electrodes is the highest leading to easy reduction of PbSO_4 to Pb .

As soon as the gassing process occurs in the upper part, the internal resistance increases in this part of the cell involving a better recharge of the lower system, which is well recharged only at the end of the recharge period.

3.1.2. Discharge step

The same measurements have been performed during discharge of the experimental cell. As in our previous observation, the same behaviour have been observed in each system during the first eight cycles. After electrolyte stratification establishment, an inhomogeneous behaviour is observed during the discharge period (Fig. 5).

During the first part of the discharge period, the total stratification value is reduced (Fig. 5.1): large amounts of sulphate ions are used to form lead sulphate on both electrodes. This phenomenon seems to be more important in the lower part of the electrodes: the lower system is discharged with higher currents than the upper one (Fig. 5.2). As has been explained previously for the recharge process, the vertical potential gradient linked to the electrolyte stratification leads to the favoured discharge of the lower system:

highest positive voltage in the lower system involving the reduction of PbO_2 to PbSO_4 ;
lowest negative voltage in the lower system leading to easy oxidation of Pb to PbSO_4 .

In the second part of the discharge, the currents in each system have opposite behaviour: the current has higher values in the upper system than in the lower

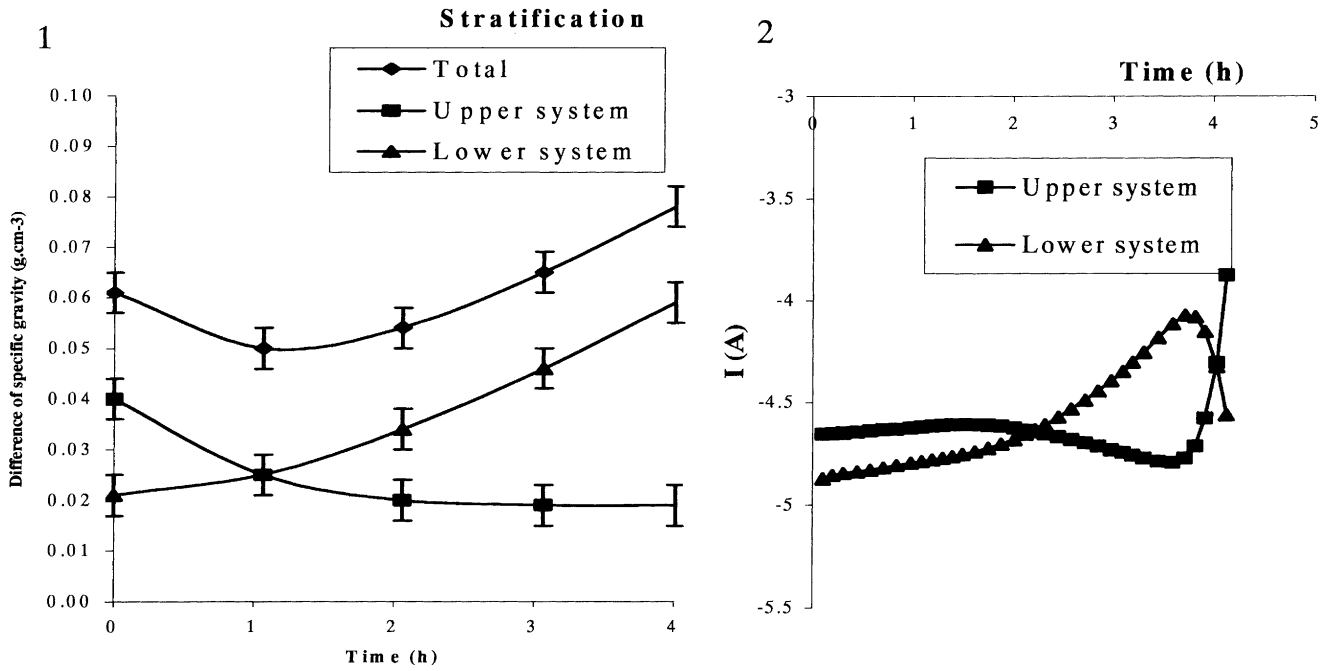


Fig. 5. During the eighth discharge. (1) Total and local stratification; (2) current in each system.

system. The discharge process is more important in the upper part.

The explanation for this sudden change lies in the SOC difference between the two systems. At the beginning of the discharge, the lower system has a higher discharge current leading to the formation of lead sulphate crystals with two consequences:

- the limitation of ionic diffusion in the active mass;
- a decrease of conductivity in the active mass.

After this “barrier” formation involving an increase of the internal resistance, the local current decreases in the lower system and increases in the upper system. The discharge is limited again in this system by the formation of many lead sulphate crystals: the current decreases. At the end of discharge, the lower system is deeply discharged: the discharge current increases in this system (Fig. 5.2).

During discharge, the current distribution is seen to be irregular. The lower system is deeply discharged. Moreover, our previous results have pointed out that this system is less charged than the upper one. Consequently, the stratification phenomenon involves penalising the cycling conditions for the lower system or, for more general considerations, for the lower part of lead–acid batteries electrodes.

3.1.3. Relaxation current

When the cycling procedure has been stopped, relaxation currents (0.15 A) have been observed in each system (Fig. 6). An additional cycling procedure has been performed to study these electrical processes. This cycling procedure consists in the same intensiostatic charge and discharge cycles between 20 and 70% SOC, as the previous study.

In order to perform relaxation current measurements, we have added rest periods of 12 h after each recharge.

During this rest period and after each charge period, different relaxation currents have been observed in each system. When recharge is stopped, the two systems are unbalanced: local current in each system balances the SOC of the electrodes. The current direction follows the potential law between electrodes of the same polarity, connected together.

For the positive electrodes, the current direction shows that there is a reduction in the lower system and an oxidation in the upper system. This relaxation phenomenon leads to the discharge of the positive lower electrodes for the benefit of the upper electrodes.

For the negative electrodes, the current direction in each system indicates a reduction in the upper system and an oxidation in the lower system. Thus, the relaxation process enhances the recharge of the upper system,

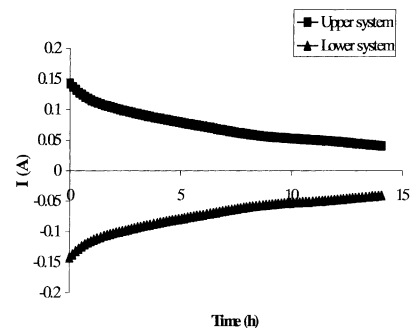


Fig. 6. Relaxation current in each system during rest period.

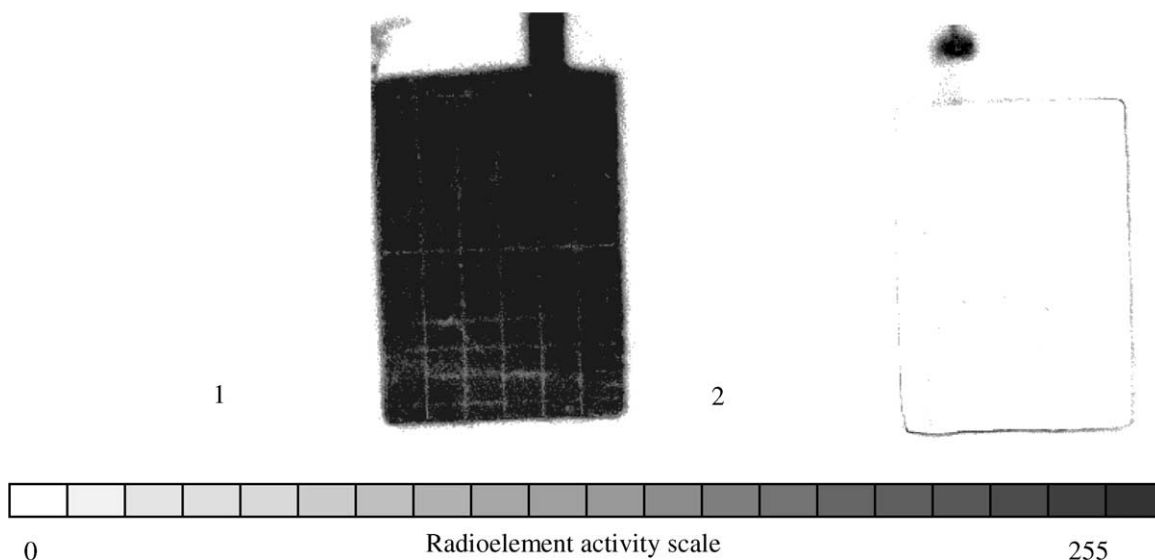


Fig. 7. Image of one side of a recharged positive electrode. (1) After the first discharge; (2) after the first recharge.

although the lower negative electrodes are deeply discharged.

These results show that when the cycling procedure is stopped after a recharge, the upper system is recharged (both positive and negative electrodes) to the detriment of the lower system which is more and more deeply discharged.

3.2. Influence of the stratification phenomenon on battery ageing: irreversible $\text{Pb}^{35}\text{SO}_4$ distribution

In this second experiment, a radioactive acid ($\text{H}_2^{35}\text{SO}_4$) has been incorporated in the experimental cells subjected to the accelerated cycling procedure. The positive electrodes, which were subjected to irreversible lead sulphate distribution, have been characterised using tracer detection.

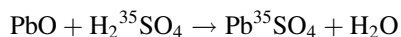
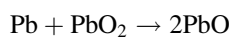
3.2.1. Initial characterisation of the electrodes

In order to validate our experimental protocol, different characterisations have been performed after initial charge and discharge of the experimental cells (Fig. 7).

3.2.1.1. Positive discharged electrodes. During the first discharge reaction, $\text{H}^{35}\text{SO}_4^-$ ions are consumed and lead sulphate is deposited on the electrodes (Fig. 7.1). This initial characterisation demonstrates that the radioelements (^{35}S) fix to the electrodes to form $\text{Pb}^{35}\text{SO}_4$ during the discharge.

3.2.1.2. Positive recharged electrodes. The electrodes have been fully recharged (with a recharge coefficient of 1.2). This recharge oxidises all the lead sulphate into lead dioxide. Only the grid shape is observed and shows the presence of ^{35}S (Fig. 7.2). Indeed, we can assume that lead sulphate is

forming on the grid area due to the process of corrosion in accordance with the following mechanisms [9]:



These initial characterisations have demonstrated that the radioactive emission observed is due to the presence of lead sulphate on the electrode surface.

3.2.2. Characterisation of the positive charged electrodes during the cycling test

After the 10th recharge, the charged electrodes were characterised using the technique described previously (Fig. 8.1). Irreversible sulphates are observed at the surface of the positive electrodes of the tested cells. The irreversible lead sulphate species are located in the lower parts of the electrodes.

The accelerated cycling procedure has been continued on the experimental cells. The same electrodes were characterised again after 20 cycles. In Fig. 8.2, the images obtained after 20 cycles are compared with the former images (obtained after 10 cycles) for the same sides of the positive plates. The main trends observed above are confirmed: the lower part of the plate is more and more sulphated and the transition between sulphated and unsulphated active mass zones has moved to the upper parts of the electrodes.

Moreover, another evolution can be observed in the distribution of the irreversible sulphate: irreversible $\text{Pb}^{35}\text{SO}_4$ is observed near the post of the plate (Fig. 8.2). Indeed, the zone of active mass near the post presents high voltage and current density. Therefore, this part of the electrodes is particularly affected by cycling constraints. The same evolution of irreversible sulphation was observed between the 20th and the 40th cycle.

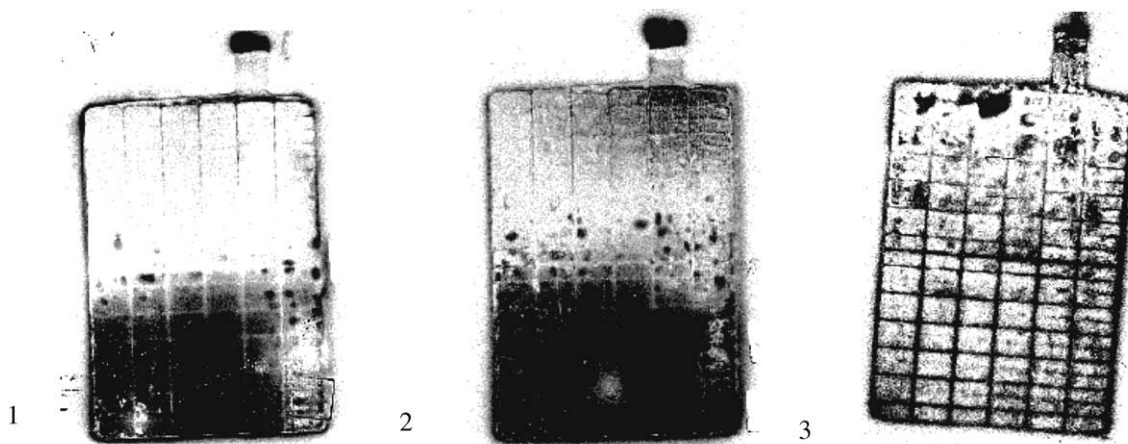


Fig. 8. Image of the same side of a recharged positive electrode. (1) After 10 accelerated cycles; (2) after 20 accelerated cycles; (3) after 40 accelerated cycles.

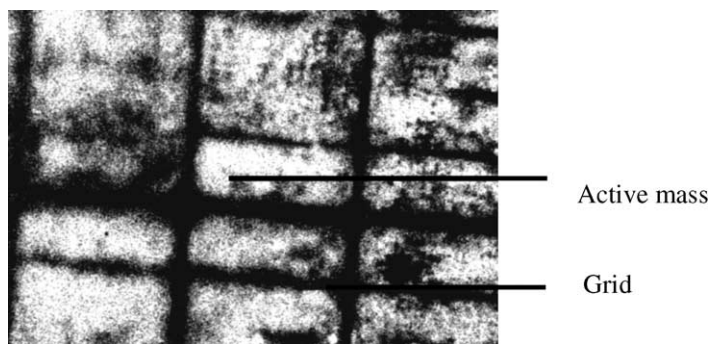


Fig. 9. Detail of a positive electrode after 40 accelerated cycles.

After 40 cycles, a shedding of the positive active mass was observed at the bottom of the experimental cells. This active mass loss was accelerated by the rinsing of the electrodes. The mechanical constraints linked to the presence of large lead sulphate crystals, have caused this active mass shedding. Then, the images obtained after drying (Fig. 8.3) showed that a large amount of $\text{Pb}^{35}\text{SO}_4$ fixed on the active mass in the external layer had been shed and the internal layers presented lower radioelement activity than the previous characterisations (after 10 and 20 cycles). The shedding of the active mass has involved the destruction of the lead sulphate layer.

Indeed, the elimination of the external sulphated layers might have involved experimental cell rehabilitation. Another cycle (charge and discharge) was performed on the experimental cells in order to evaluate the impact of shedding on the discharged capacity and to study the behaviour of positive active mass residual layers. The high capacity loss measured (-80%) showed that the electrodes have been further damaged. This capacity decrease may be related to the forming of a passivating lead sulphate layer at the grid–active mass interface (Fig. 9). This energy gap formed during the cycling limits electronic exchange between the collecting grid and the positive active mass. Consequently, after a $\text{Pb}^{35}\text{SO}_4$ layer has formed at the active

mass surface during the first 10 cycles, our characterisations have demonstrated that an energy barrier has formed near the grid.

4. Conclusions

In this study, a first experimental cell has enabled the observation of local current and potential at different electrode heights and has demonstrated the existence of irregular electrochemical behaviour. Electrolyte stratification appears during recharge and increases during this period. It decreases at the beginning of the discharge and increases as the discharge progresses. The vertical concentration gradient induces irregular working of the electrodes: some parts which are deeply discharged (low part) are not efficiently recharged. The SOC difference between some parts of the electrodes (high and low part) is favoured.

The stratification phenomenon involves irreversible lead sulphate formation in the low part of the electrodes, particularly at the active mass surface near the electrolyte. The incorporation of a radioelement ($\text{H}_2^{35}\text{SO}_4$) has validated the existence of irreversible sulphation of the positive active mass related to electrolyte stratification, from the tenth cycle onwards. It has also enabled various evolution profiles to be

identified, which take place on the plates during the operation of the battery:

1. Firstly, the low part of the active mass is sulphated.
2. As the cycles continue, the sulphated area is extended. The progression takes place from the bottom of the electrodes upwards.
3. This textural ageing of active matter, accentuated by the presence of irreversible lead sulphate, causing mechanical stress, leads to shedding of the active mass.
4. Finally, the battery itself is degraded due to the presence of an energy barrier (a layer of lead sulphate) at the interface between the grid and the active matter.

Acknowledgements

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