

# Study of the “coup de fouet” of lead-acid cells as a function of their state-of-charge and state-of-health

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## Abstract

This paper shows some new results concerning the influence of operating conditions on the phenomenon known as “coup de fouet”, a voltage drop which occurs at the beginning of the discharge of lead-acid batteries (LABs) previously fully charged. Even if this phenomenon is often suggested for diagnosing the state-of-charge (SOC) and the state-of-health (SOH) of LABs, it remains badly understood. Furthermore, this study deals with other transient voltage responses of LABs to galvanostatic polarisations that depend on their SOC, either on discharge or on charge. A special attention is paid to a phenomenon occurring at the beginning of the charge of these batteries after a full discharge, and which can be compared to the “coup de fouet” on many aspects. Without giving a final answer concerning the origin of these two phenomena, our results present some contradictions with the explanation generally accepted today. It is, also, shown that the study of these phenomena constitutes an original means to investigate the full-charge and full-discharge conditions, together with other characterization methods like impedance spectroscopy. On the other hand, results presented show that it is not possible to connect the “coup de fouet” parameters to the battery capacity without taking care of the high-SOC level, the rest time preceding the discharge, and the depth of the latter discharge, which compromises the reliability of this method suggested in several papers and patents, in particular in applications with irregular cyclings.

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**Keywords:** Lead-acid battery; “Coup de fouet”; Transient voltage response; State-of-charge; State-of-health; Internal resistance

## 1. Introduction

The “coup de fouet” is a phenomenon particular to lead-acid batteries (LABs), which occurs at the beginning of the discharge of a battery (or a cell) previously fully charged. It corresponds to a short voltage drop (Fig. 1a) of about 10–30 mV by cell, lasting a few minutes or less depending on the operating conditions [1]. Then, the cell voltage recovers to reach a plateau value that indicates the end of the “coup de fouet”, after a few minutes to 1 h depending on the operating conditions too.

Since the early work of Berndt and Voss in 1964 [2], very few studies have been performed to determine the mechanism responsible for this voltage drop. According to these authors, the “coup de fouet” can be ascribed to a crystallization overvoltage, which is the energy gap that is necessary to the formation of PbSO<sub>4</sub> nuclei on the plates from the Pb<sup>2+</sup> supersaturated

electrolyte during the first instants of the discharge. This idea is largely accepted today in the literature. As far as we know, only Pavlov et al. [3,4] and de Oliveira and Lopes [5] have suggested another explanation for this “voltage dip” later. The first authors consider that the phenomenon could be the consequence of the gel-crystal nature of the PbO<sub>2</sub>: amorphous PbO<sub>2</sub> due to the oxygen sorption by the PbO<sub>2</sub> particles during the preceding overcharge would be transformed into crystallized PbO<sub>2</sub> during the first instants of the discharge. The latter authors consider that the phenomenon could be due to a PbO<sub>2</sub> dielectric layer at the Pb/PbO<sub>2</sub> interface formed by the oxygen evolution during the overcharge.

In the last 5 years, several authors published interesting results about this phenomenon, however, without investigating its mechanism. They demonstrated its possible use in the diagnosis of the state-of-charge (SOC) [6,7] and the state-of-health (SOH) [1,8–10] of LABs. A linear relationship was presented between either the peak voltage or the plateau voltage of the “coup de fouet” (Fig. 1a) and the battery capacity, i.e. the SOH of the battery. This method is the subject of several patents [11,12].

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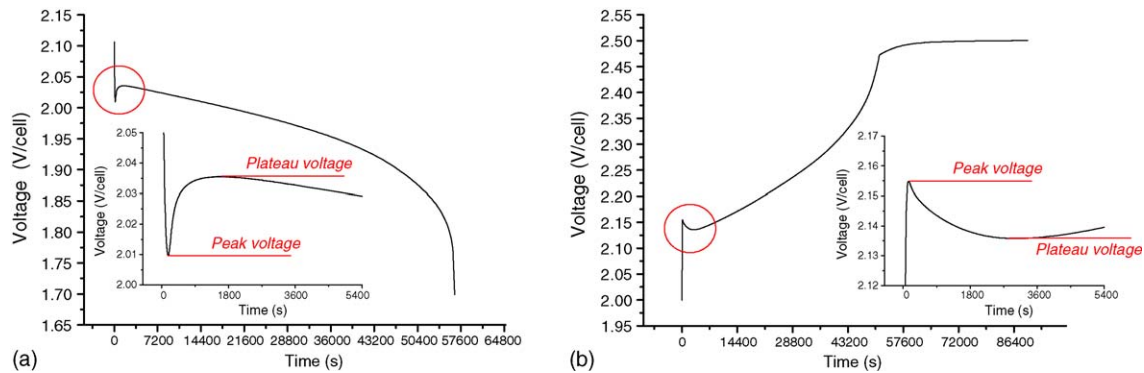


Fig. 1. “Coup de fouet” at the beginning of: (a) the discharge and (b) the charge of a LAB (Fulmen Solar Bloc, 12 V, 50 Ah at C/10).

The “coup de fouet” has also been proposed as a full-charge indicator and could be used for battery management, as shown in a multi-battery management system patent [13].

A “similar” phenomenon occurs at the beginning of the charge of a battery previously “fully” discharged. In that case, the cell voltage shows a maximum (Fig. 1b). This voltage jump of about 10–80 mV by cell has also been studied by Berndt and Voss in 1964, who concluded that this phenomenon could be the consequence of the insulating  $\text{PbSO}_4$  layer covering the surface of the discharged active mass. As in Berndt and Voss’ publication, the two phenomena are studied jointly in this paper.

The first motivation of this paper is to present an original way to determine the states of “full” charge and “full” discharge of LABs, with the goal of defining relevant threshold criteria of the end-of-charge and the end-of-discharge, respectively. These thresholds are indeed major parameters for any charge controller or battery management system and, however, so obscure yet, in particular in irregular conditions of charge and discharge as in photovoltaic (PV) or electric vehicle applications. The adjective “full” is used with quotation marks because a full SOC is of course a very relative concept: it is possible to maintain the charge of a battery during a more or less long time, the end of the charge being a compromise between the capacity benefit on one side, and the electrolyte losses by gassing and corrosion on the other side. This is even more obvious at the end of the discharge since a too deep discharge can lead to a premature ageing of the battery.

The second motivation of this work is to improve our understanding of the mechanism responsible for these two phenomena, named here “discharge coup de fouet” and “charge coup de fouet”. We have, also, adopted a common nomenclature for both phenomena:  $U_{\text{peak}}$  is the peak voltage,  $U_{\text{plateau}}$  the plateau voltage,  $t_{\text{peak}}$  the peak time,  $t_{\text{plateau}}$  the plateau time,  $\Delta U$  the amplitude or absolute difference between  $U_{\text{peak}}$  and  $U_{\text{plateau}}$ , and finally  $\Delta t$  is the difference between  $t_{\text{plateau}}$  and  $t_{\text{peak}}$  (Fig. 1). This choice has been made in order to simplify the joint study of the two phenomena without implying a similar behaviour or a same origin for these two phenomena.

While the theories accepted today explain these phenomena for “fully” charged or “fully” discharged batteries, some points remain unclear, as also recognized in Ref. [5] concerning the “discharge coup de fouet”. For instance:

- The “discharge coup de fouet” is still observed on sulphated batteries, presenting therefore some sites favourable to the growth of  $\text{PbSO}_4$  crystals. Furthermore, a “fully” charged LAB is not free of lead sulphate crystals or nuclei, as shown in Fig. 2a.
- De Oliveira and Lopes [5] studied the electrolyte concentration effect on the “discharge coup de fouet”. Their results tend to show that the phenomenon is not related to the  $\text{PbSO}_4$  solubility, but rather to the  $\text{H}_2\text{SO}_4$  conductivity.
- Finally, the same authors have shown that this phenomenon does not occur when  $\text{PbO}_2$  electrodeposited on carbon is discharged, which tends to discredit the nucleation assumption.

Moreover, if considering that nucleation theory has no meaning with regard to the phenomenon observed at the beginning of a charge, it is necessary to seek another explanation for it, in spite of its common points with the “coup de fouet” at the beginning of a discharge. One of the potential explanations is the  $\text{PbSO}_4$  resistance, but it can, also, be criticized:

- The end-of-discharge does not correspond to a total covering of the electrode surface by an insulating layer, but corresponds to a sparse distribution of crystals on the surface and in the bulk of the active mass, as shown in Fig. 2b. Then, crackings of the insulating lead sulphate layer at the beginning of the charge do not seem to be the exact cause of the second phase (voltage decrease) of the “charge coup de fouet”.
- Furthermore, this assumption cannot explain the first phase of the phenomenon, i.e. the voltage progressive increase until the peak voltage that can last up to 30 min under certain conditions (Fig. 8). Indeed, an ohmic resistance should involve an immediate high voltage value.
- Finally, this phenomenon is too reproducible to be allotted to a cracking phenomenon, which should show a strongly random behaviour.

## 2. Experimental

Four lead-acid cells (2 V nominal) were assembled from CEAC flat-plates with low-grade antimony (negative plates UXR CS 2308705 and positive plates UXR CS 2300180), immersed in sulphuric acid of density 1.28. Two cells of

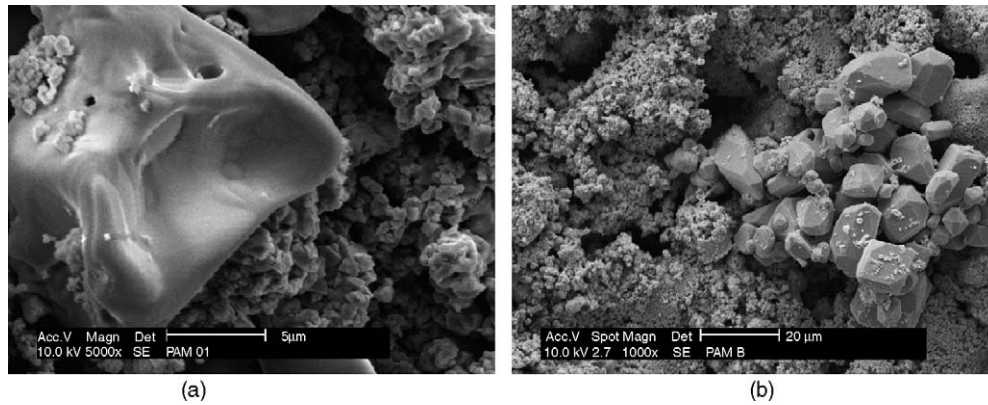


Fig. 2. Residual  $\text{PbSO}_4$  crystals on the positive electrode at the end of a “full” charge (a) and  $\text{PbSO}_4$  agglomerates at the end of a “full” discharge (b).

approximately 20 Ah at  $C/20$ , one positive-limited and the other negative-limited, were assembled in order to study the effect of the cell configuration on the “coup de fouet” phenomena. Two other cells of approximately 6 Ah at  $C/6$ , both positive-limited, were prepared in order to study the influence of several operating conditions (see Sections 3.2–3.4), on the “discharge coup de fouet” for the first-one, and on the “charge coup de fouet” for the second-one. Finally, four tubular-plates flooded batteries (12 V Fulmen Solar Block,  $C = 50$  Ah at  $C/10$ ) were, also, studied for comparison with the observations made on cells. All cells and batteries have been placed in thermo-regulated baths at  $20^\circ\text{C}$ .

The cells were cycled with a multi-potentiostat–galvanostat Solartron 1470 controlled by the Corrware software. The batteries were cycled on cycling benches developed in the laboratory and consisting in four loads Chroma 63103 and four supplies Xantrex XKW 20–50, controlled by a PC with the Agilent VEE software.

### 3. Results and discussion

#### 3.1. Transient voltage phenomena and contribution of each electrode

First, the terminal cell voltage and the potential of the positive and negative electrodes, have been measured against a  $\text{K}_2\text{SO}_4$ -

saturated mercury/mercurous sulphate reference electrode (SSE;  $E_{\text{SSE}} \approx 655$  mV versus a standard hydrogen electrode) in order to determine the contribution of each electrode to the “coup de fouet”, which is the subject of conflicting opinions in the literature. Indeed, if Berndt and Voss already mentioned different opinions in their article [2] and finally ascribed the “discharge coup de fouet” to the positive electrode, Pascoe and Anbuky have again suggested a contribution of the negative electrode in a recent paper [1]. Fig. 3 shows a “discharge coup de fouet” on both electrodes but the comparison of the characteristic times  $t_{\text{peak}}$  and  $t_{\text{plateau}}$  clearly demonstrates that the “discharge coup de fouet” on the cell voltage was due to the positive electrode only. The time constant of the “discharge coup de fouet” observed on the negative electrode makes this phenomenon unnoticeable on the terminal cell voltage. Hence, if the phenomena observed on each electrode derive from the same mechanism, the explanations proposed in Refs. [3] and [5] to explain the “discharge coup de fouet”—namely the amorphous-to-crystal transformation and the  $\text{PbO}_2$  dielectric layer—must be put into question since they concern the positive electrode only. It must be noted that a completely identical behaviour during the “discharge coup de fouet” is observed for a positive or a negative-limited cell, which is logical since the major difference between these two configurations appears at the end of the cell discharge.

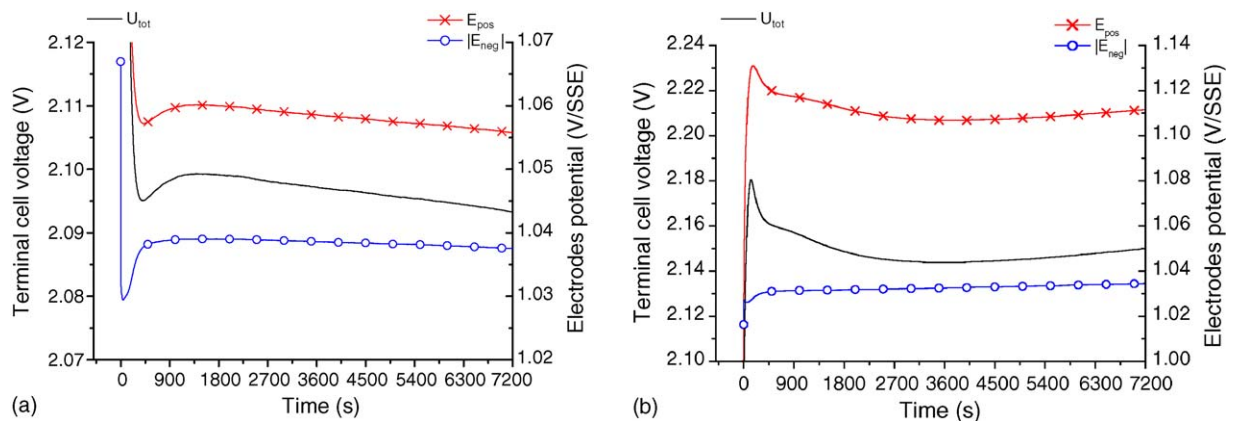


Fig. 3. Contribution of each electrode during: (a) the “discharge coup de fouet” and (b) the “charge coup de fouet” for a positive-limited cell.

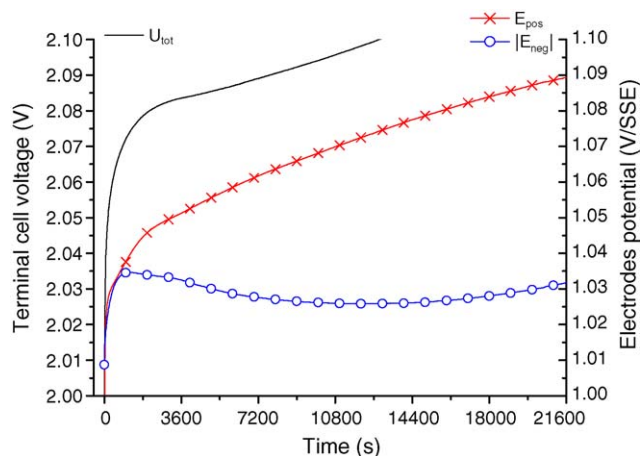


Fig. 4. Contribution of each electrode during the “charge coup de fouet” for a negative-limited cell.

Concerning the “charge coup de fouet” for a positive-limited cell, the contribution of the positive electrode is still preponderant, with a very short transient voltage response on the negative electrode that can be detected in Fig. 3b. Here, the preceding discharge was stopped at 1.75 V. For a negative-limited cell, the “charge coup de fouet” is only present on the negative electrode (Fig. 4), because the positive electrode was not discharged enough, even if the preceding discharge was performed down to 1.60 V. Hence, the “charge coup de fouet” appears on the cell voltage only when it is due to the positive electrode.

A second series of measurements was performed to identify all transient phenomena at the beginning of galvanostatic polarisations on the terminal cell voltage and on the potentials of the positive and negative electrodes. The terminal cell volt-

age profiles in Fig. 5a correspond to the discharge at  $C/20$  of a fully charged cell, which was interrupted after 1 h, restarted after a rest time of 1 h, and then, stopped again after 1 h and so on. The same stop-and-start procedure was, then, applied during the charge of the cell (Fig. 5a'). Thereafter, the same experiment was carried out for monitoring the potential of the positive electrode (Fig. 5b and b') and that of the negative electrode (Fig. 5c and c'). Fig. 5 confirms that the discharge and charge “coup de fouet” are specific of the states of “full” charge and “full” discharge respectively, and, therefore, constitute an original means to detect these extreme values of SOC.

Another transient voltage response can be identified at the beginning of charge for intermediate SOCs (Fig. 5c'). This phenomenon of low amplitude (<5 mV), which appears sometimes on the cell voltage, is clearly due to the negative electrode. It is interesting to note that its amplitude increased with SOC. Nevertheless, it must be clearly distinguished from the “charge coup de fouet” that occurs only at the beginning of the first charge period after a “full” discharge.

### 3.2. Influence of the SOC

The influence of the SOC on the “discharge coup de fouet” has been studied by performing consecutive galvanostatic discharge–charge cycles. The discharges were stopped at a fixed voltage value (1.75 V), and the charges were performed up to a fixed voltage value (2.85 V corresponding, at the current regime used here, to the beginning of the hydrolysis plateau), and, then, during a fixed time that was modified at each cycle (from 30 min to 5 h and, then, from 5 h to 30 min). Performing the test both in increasing and decreasing the SOC allows the impact of the SOH evolution to be minimized. The evo-

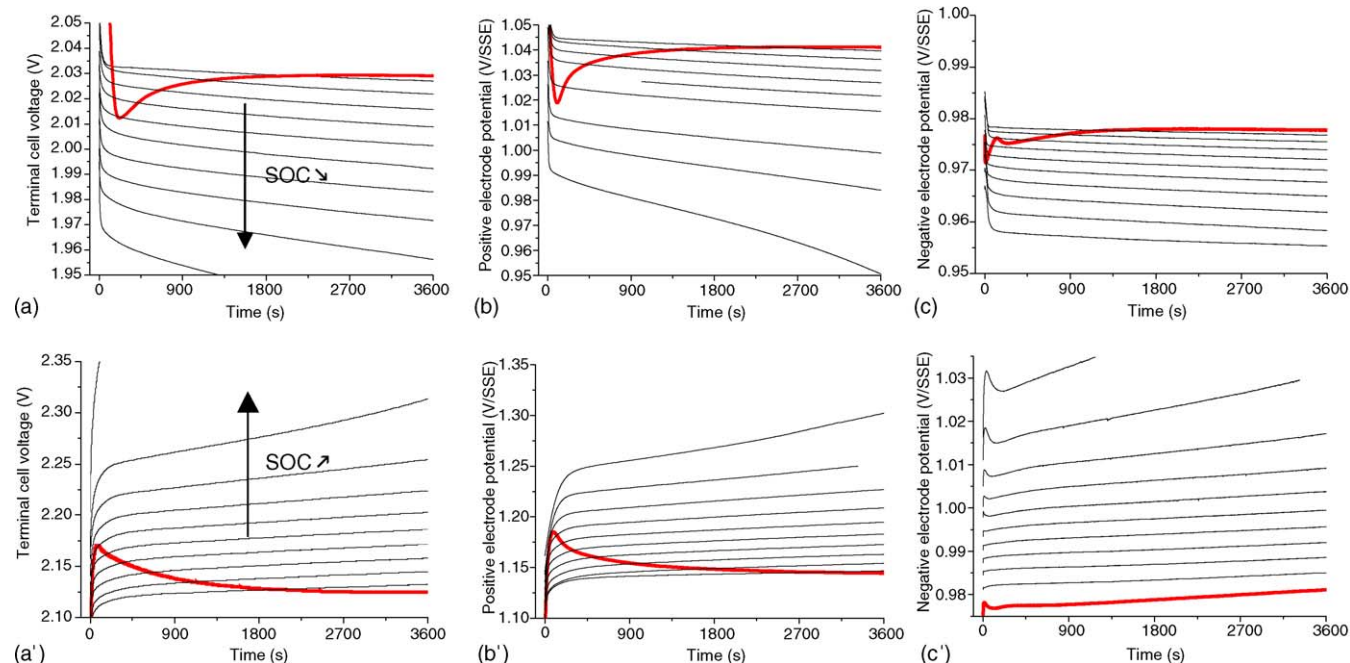


Fig. 5. Evolution of the terminal cell voltage (a and a'), of the positive electrode potential (b and b'), and of the negative electrode potential (c and c'), at different SOC after a rest time of 1 h during a discharge at  $C/20$  (a, b, and c) and a charge at  $C/20$  (a', b', and c'). In bold lines: first galvanostatic polarisations.

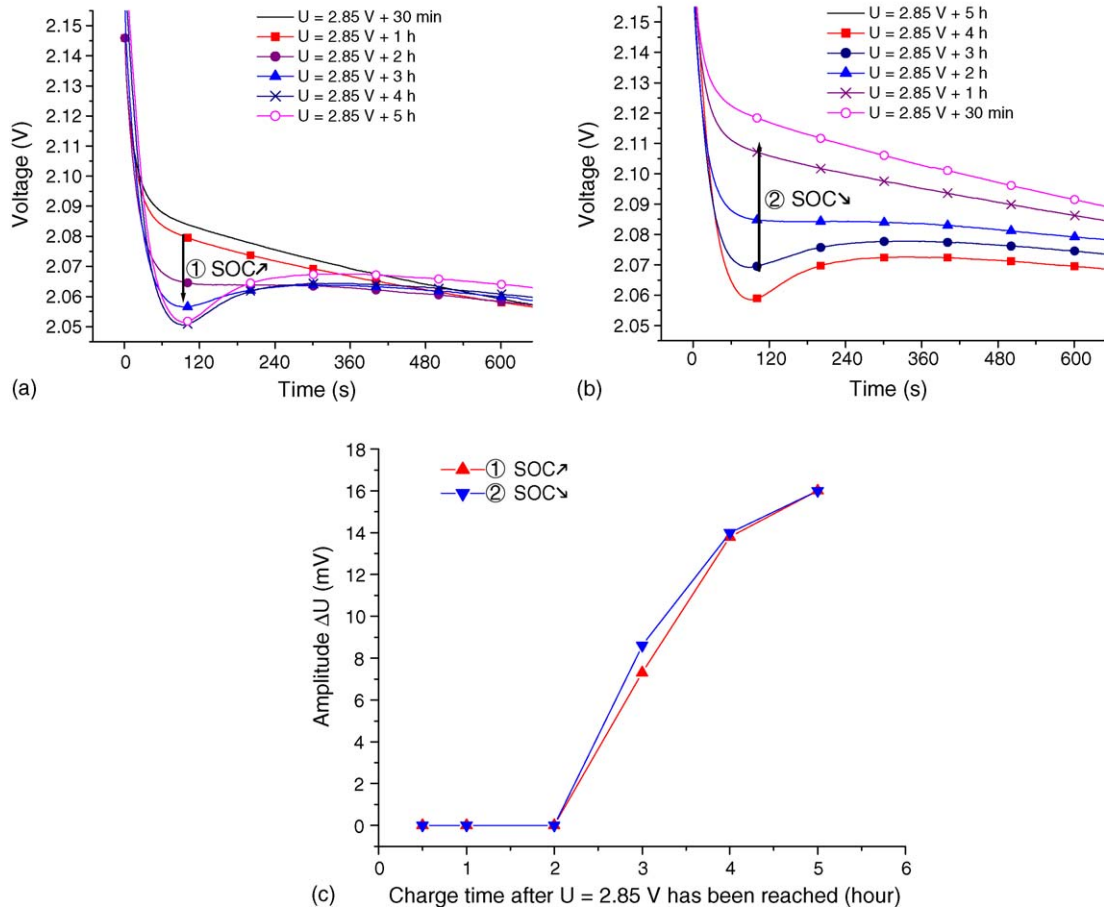


Fig. 6. Evolution of the “discharge coup de fouet” for high SOC increases (a) or decreases (b), and amplitude  $\Delta U$  of the phenomenon (c).

lution of the “discharge coup de fouet” measured after each discharge–charge cycle is presented in Fig. 6. Complete cycles were performed to avoid the influence of the depth-of-discharge (DOD) of the previous discharge (see Section 3.4). On the other hand, a rest time of constant duration (1 h) was observed before each galvanostatic polarisation to eliminate any effect of rest duration (see Section 3.3), and a high current regime (2 A corresponding approximately to  $C/3$ ) was used to limit the experiment time. Preliminary similar results have been found at low currents.

Fig. 6 shows that the “discharge coup de fouet” is not a binary phenomenon, present or not: its amplitude varies as a function of the battery high-SOC level. For example, the higher the SOC level, the larger the amplitude of the phenomenon and the lower the voltage minimum value  $U_{\text{peak}}$ . This result is in contradiction with the linear relationship proposed by some authors [1,8–10] stating that the lower the value of  $U_{\text{peak}}$ , the lower the battery capacity  $C$  and its SOH, since different values of  $U_{\text{peak}}$  were obtained for the same SOH. To be able to use the linear relationship between  $U_{\text{peak}}$  and  $C$  (or  $U_{\text{plateau}}$  and  $C$ ), it is, then, necessary to perform the cell discharge under controlled conditions (current regime and temperature) and, also, to be sure that the same high-SOC level has been reached, which is not obvious in irregular cycling conditions, as in Starting–Lighting–Ignition or PV applications.

The influence of the SOC on the “charge coup de fouet” has been studied too. The galvanostatic charges (at  $C/3$ ) were performed up to a fixed voltage value (2.85 V), then, during a fixed time (3 h), and the galvanostatic discharges (at the same current regime) were stopped at a cut-off voltage limit that was different at each cycle (from 1.90 V to 1.75 V and, then, from 1.75 V to 1.95 V). The evolution of the “charge coup de fouet” measured after each charge–discharge cycle is presented in Fig. 7 that shows that the amplitude  $\Delta U$  of the “charge coup de fouet” increased with increasing DOD, up to a plateau value of about 70 mV obtained when the discharge was interrupted at a cell voltage lower than 1.85 V.

If the completion of the charge and discharge has a significant influence on the discharge and charge “coup de fouet” amplitude  $\Delta U$ , the peak time  $t_{\text{peak}}$  and the plateau time  $t_{\text{plateau}}$  have almost constant values.

Fig. 8 presents the “charge coup de fouet” at the same current regime of 5 A ( $C/10$ ) for discharges completed at the same cut-off voltage value (1.80 V), and performed at different current regimes ( $C/5$ ,  $C/10$ , and  $C/100$ ), which involved different uses of the active mass and, therefore, different DOD. If the cut-off voltage value does not allow this difference to be appreciated, the “charge coup de fouet” varied radically with the discharge current regime. It is, then, clear that the state of the active mass at SOC = 0 has a strong influence on the “charge coup de fouet”. It

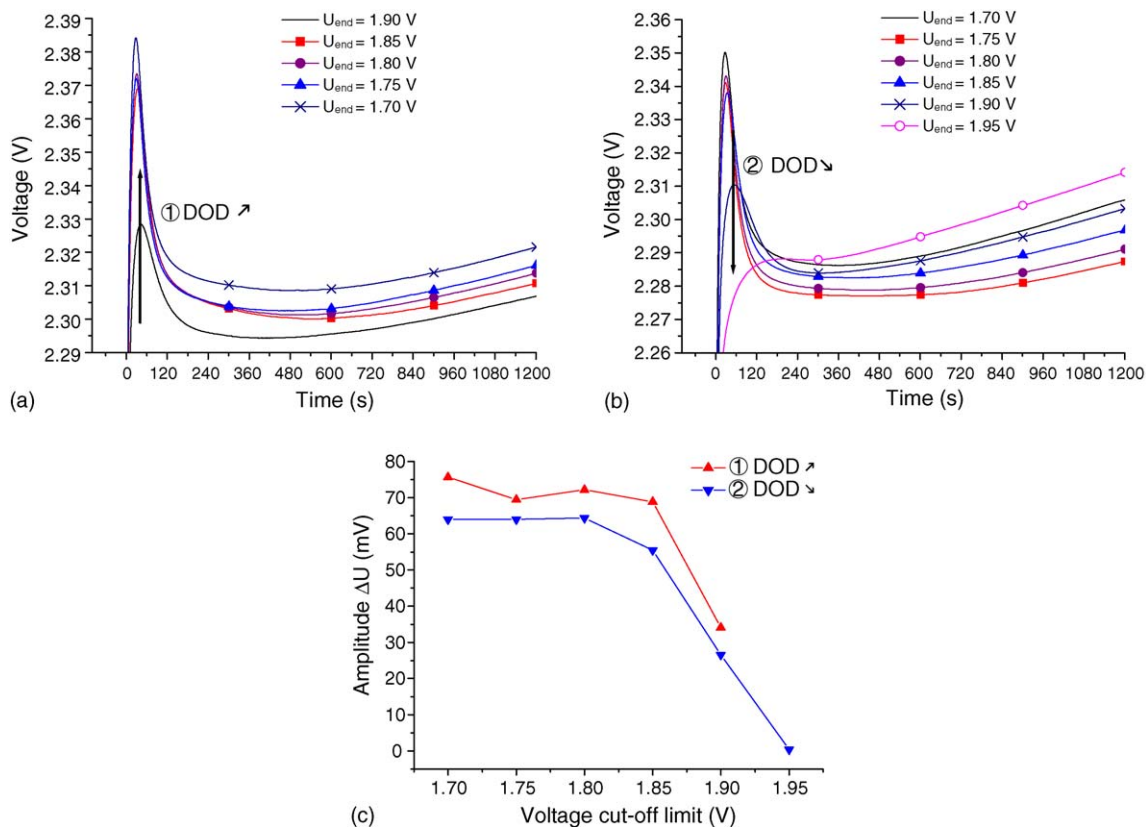


Fig. 7. Evolution of the “charge coup de fouet” for increasing (a) or decreasing DOD (b), and amplitude  $\Delta U$  of the phenomenon (c).

can be noted that the value of  $t_{\text{peak}}$  exceeds 30 min in the charge following the discharge at  $C/100$ , which cannot be attributed to the resistance of the  $\text{PbSO}_4$  layer but rather to mass transport effects, probably due to an increase in the  $\text{HSO}_4^-$  concentration in the pores partly closed by the  $\text{PbSO}_4$  crystals.

In the research of reliable criteria of end-of-charge and end-of-discharge, especially in the case of irregular cycling conditions like in PV applications, the study of the “coup de fouet”

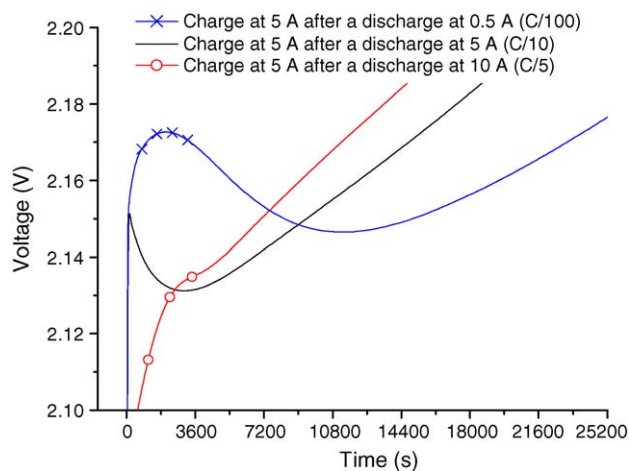


Fig. 8. “Charge coup de fouet” at the same current regime (5 A) after discharges at three different current regimes ( $C/10$ ,  $C/5$ , and  $C/100$ ) and down to the same cut-off voltage value of 1.80 V.

appears, here, as a promising way to define, or at least to validate, new criteria on the state of the active mass.

### 3.3. Influence of the rest time preceding the galvanostatic polarisation

The influence of the rest time between the end of the previous charge (respectively discharge) and the subsequent discharge (respectively charge) has been studied with all other conditions being maintained constant. Concerning the study of the “discharge coup de fouet”, the preceding galvanostatic charges (at  $C/3$ ) were performed up to a fixed voltage value (2.85 V), next during a fixed time (3 h) and, then, by modifying the rest time before the following discharges. Concerning the study of the “charge coup de fouet”, the preceding galvanostatic discharges (at  $C/3$ ) were performed down to 1.75 V and, then, by modifying the rest time before the following charges. In both cases, the rest time was successively increased and decreased to minimize the influence of the cell ageing.

Figs. 9 and 10 show a significant influence of the rest time: the longer the rest time, the higher the amplitude of each “coup de fouet” phenomenon. This result suggests a mechanism based on mass transport limitations and puts into question the commonly accepted explanations by the nucleation theory for the “discharge coup de fouet”, and the  $\text{PbSO}_4$  resistance for the “charge coup de fouet” [2]. In a former publication, Armenta-Deu and Victoria Calvo-Baza [14] have shown that an electrolyte circu-

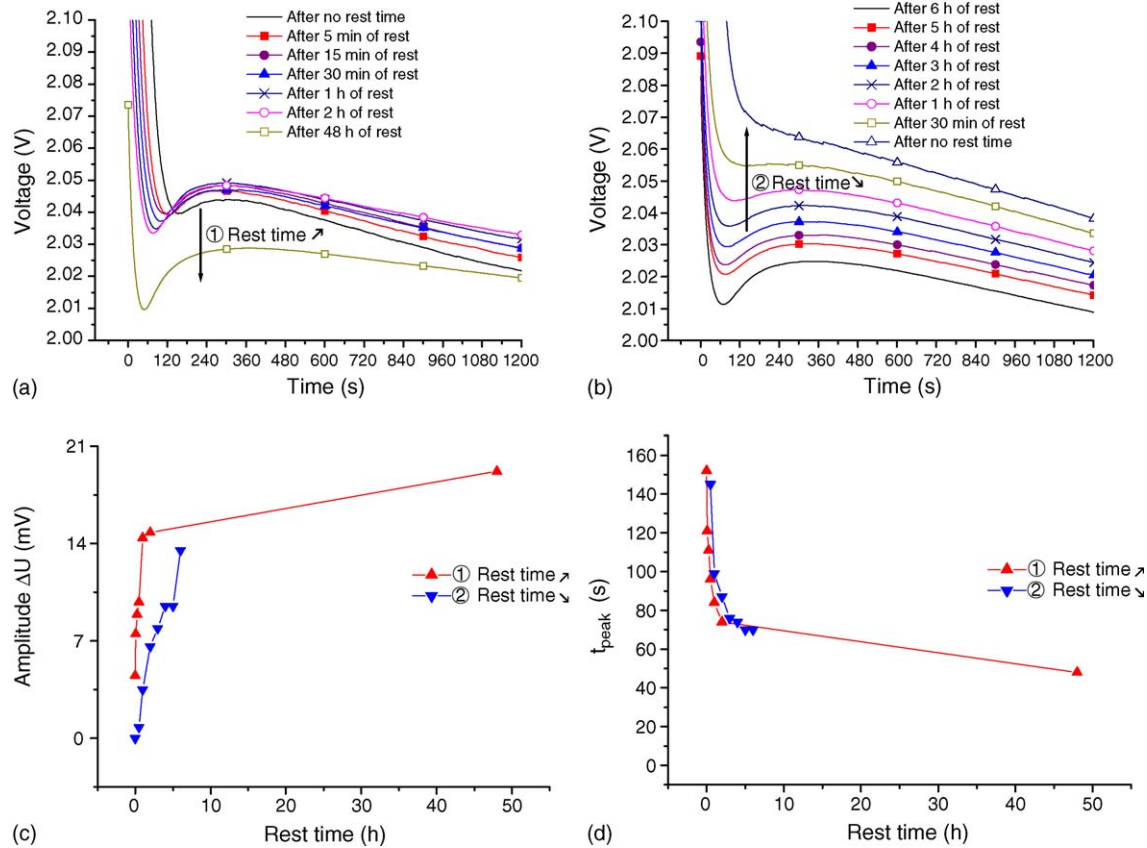


Fig. 9. Evolution of the “discharge coup de fouet” when the rest time preceding the galvanostatic polarisation increased (a) or decreased (b), and amplitude  $\Delta U$  (c) and peak time  $t_{peak}$  (d) of the phenomenon.

lation system allows the “discharge coup de fouet” amplitude to be reduced significantly, which supports again the hypothesis of a mechanism based on mass transport. If the rest time preceding the galvanostatic polarisation has a significant influence on the discharge and on the charge “coup de fouet” amplitude  $\Delta U$ , the peak time  $t_{peak}$  was, also, influenced, as shown in Figs. 9d and 10d. A similar behaviour was observed for the plateau time  $t_{plateau}$ .

In addition, the method linking  $U_{peak}$  and the capacity  $C$  (or  $U_{plateau}$  and  $C$ ) proposed by some authors [1,8–10] is again questionable since it can lead to erroneous evaluations of  $C$  if the rest time is not controlled, particularly if a short rest time is performed.

Finally, it must be noted that the amplitude of the “charge coup de fouet” was more important during the second phase of the experiment (i.e. when the rest time increased), which shows the difficulty in studying these phenomena. This increase seems to be related to the evolution of the active mass microstructure during cycling. This observation can be related to the fact that no “charge coup de fouet” occurred during the first cycles of the cells, in spite of the cell voltage drop observed at the end-of-discharge proving the fully discharged state of the cell, and that the amplitude of the phenomenon increased with the number of cycles. In that way, the “charge coup de fouet” could be used to follow the SOH of lead-acid cells, as suggested by Pavlov in Refs. [15] and [16].

### 3.4. Influence of the DOD on the “discharge coup de fouet”

As already shown by Pascoe and Anbuky [1], the cell voltage response (Fig. 11) of the “discharge coup de fouet” phenomenon is modified when the discharge preceding the “full” recharge is only partial (DOD lower than approximately 10% of the cell capacity). Measurements performed with a reference electrode confirm that this phenomenon, called “double dip” in Ref. [1], is related to the positive electrode only (Fig. 12), which was, also, verified on cells with a negative-limited electrode.

Here too, the method relating  $U_{peak}$  and  $C$  (or  $U_{plateau}$  and  $C$ ) [1,8–10] can be criticized again. Indeed, a full SOC is not a sufficient condition to ensure a relevant use of the “coup de fouet” parameters because of the influence of the electric history of the battery on these parameters. This is particularly problematic in the case of irregular cyclings such as those encountered in PV applications.

### 3.5. Discussion

One of the main interests of the “discharge coup de fouet” presented in the literature is its possible use to diagnose the SOH of LABs from a linear relationship between the “coup de fouet” parameters and the battery capacity [1,8–10]. However, some authors have reported conflicting results in the field [9] and various experiments presented in this paper do not confirm the

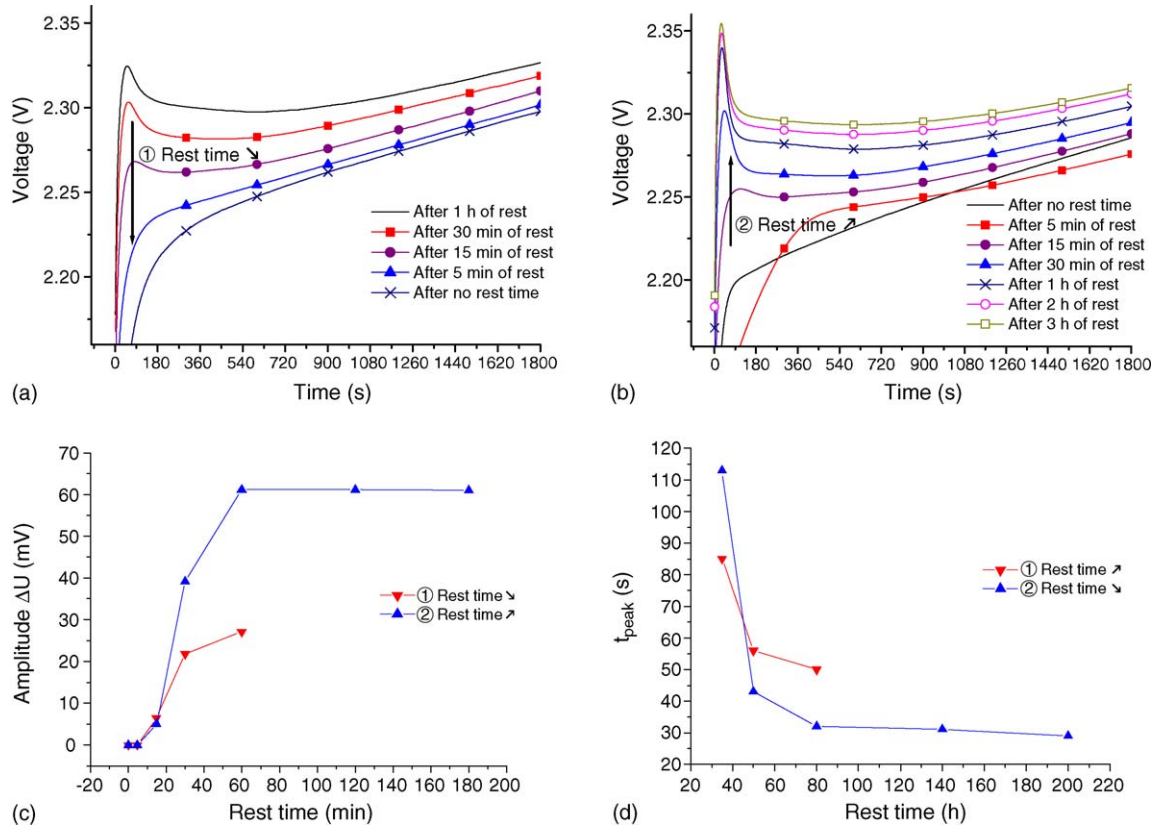


Fig. 10. Evolution of the “charge coup de fouet” when the rest time preceding the galvanostatic polarisation decreased (a) or increased (b), and amplitude  $\Delta U$  (c) and peak time  $t_{peak}$  (d) of the phenomenon.

linear relationship, as shown for instance in Fig. 13 that shows the battery capacity versus the peak voltage during the cycling of a battery in the following conditions: charge and discharge at 10 h rate, the end-of-charge being performed at a floating voltage of 15.00 V (2.50 V per cell) and the discharge being stopped at a cut-off voltage of 10.80 V (1.80 V per cell).

Nevertheless, it is interesting to note that the peak voltage evolution during the cycling of three LABs having undergone

the treatment specified above was similar (Fig. 14). This was, also, observed for the other “coup de fouet” parameters, both in discharge and in charge. This suggests that the “coup de fouet” is a deterministic phenomenon that follows specific rules.

It is shown in this paper that the “discharge coup de fouet” is not only influenced by the well-known current and temperature conditions, but also by the level of high SOC, by the rest time preceding the discharge, and by the depth of the preceding discharge. All these operating conditions, which cannot easily be controlled in the field, particularly in irregular conditions like in PV applications, explain why the relationship between the “coup de fouet” parameters and the battery capacity is sometimes not linear.

Moreover, the linear relationship mentioned by Pascoe et al. [1,8,10] seems to be related to the linear relationship between the high-frequency resistance,  $R_{HF}$  (also called internal resistance or ohmic resistance) and the capacity mentioned by other authors [17,18]. If  $R_{HF}$  is actually a function of the SOC, its value is approximately constant at high-SOC levels [19]. Therefore, the measurement of  $R_{HF}$  and the analysis of its variation over the life of the battery at high-SOC levels appear to be a more reliable method for assessing the SOH, compared to the “coup de fouet” parameters that are influenced by many conditions, as emphasized in this paper. Furthermore,  $R_{HF}$  is weakly influenced by the temperature [20] and does not require performing a discharge, which is an additional advantage on the “coup de fouet” method.

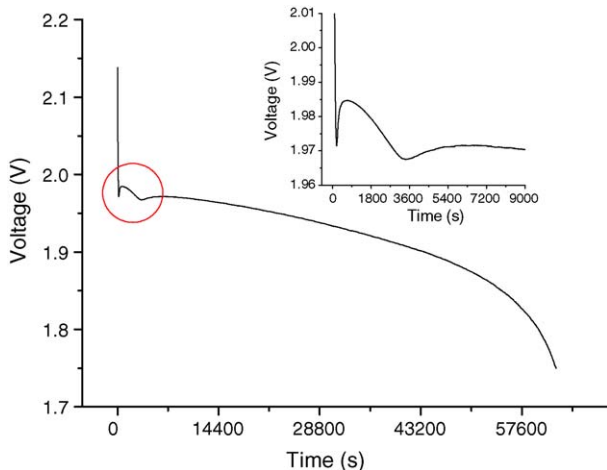


Fig. 11. “Double dip” observed at the beginning of a discharge of a lead-acid cell when the preceding DOD was only 5%.



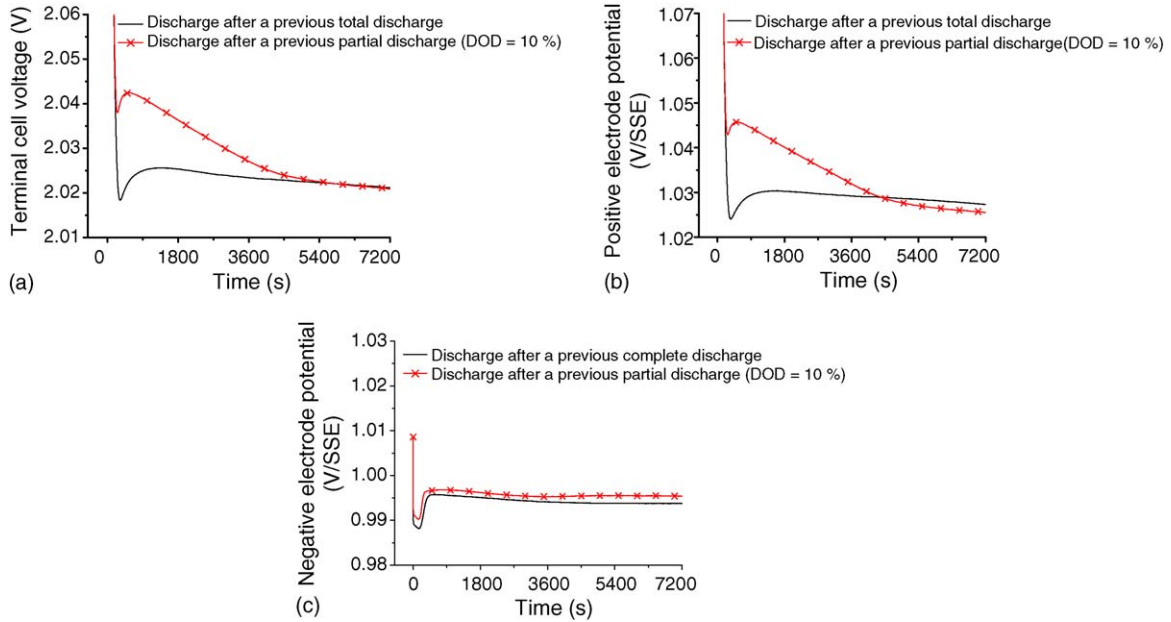


Fig. 12. “Discharge coup de fouet” and “double dip” at: (a) the cell terminals and (b) at the positive electrode. “Discharge coup de fouet” at the negative electrode (c).

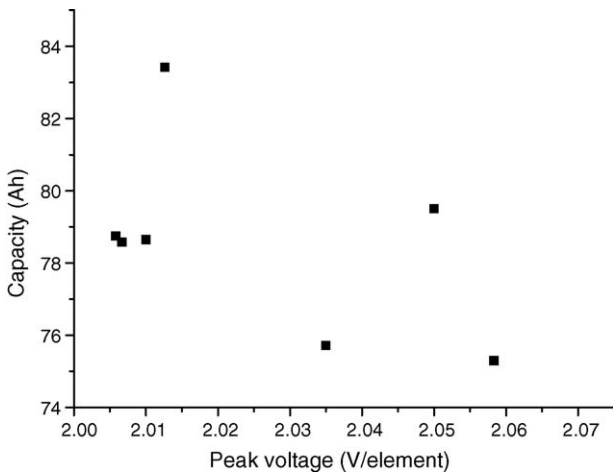


Fig. 13. Cell capacity as a function of the cell peak voltage.

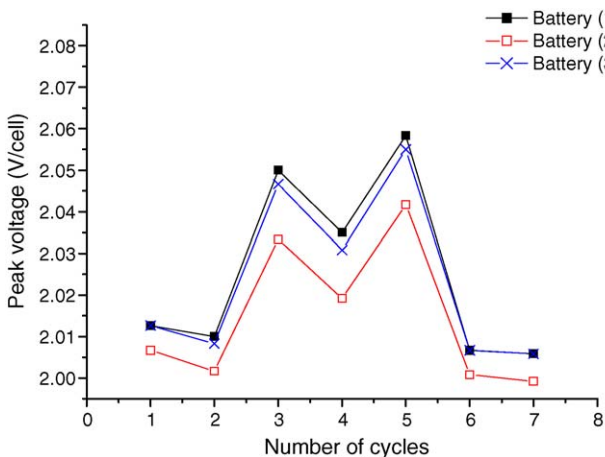


Fig. 14. Peak voltage evolution during a similar and simultaneous cycling of three batteries.

No explanation of the charge and discharge “coup de fouet” phenomena can be validated or invalidated at this time. Nevertheless, and contrary to the literature considerations, our interpretation is that mass-transport limitations are probably involved in the mechanism. During the first instants of the discharge, the electrode porosity, which is maximum at that time, could involve a sudden depletion of  $\text{HSO}_4^-$  ions in the pores, inducing a concentration overvoltage as a consequence. A discharge at a low current regime during 30 min followed by a discharge at a higher current regime shows a “discharge coup de fouet” during the second phase of the discharge only (Fig. 15), which tends to confirm the diffusion limitation theory rather than the other explanations.

Similarly, during the first instants of the recharge, the pores partly closed could involve an increase in the  $\text{HSO}_4^-$  concentra-

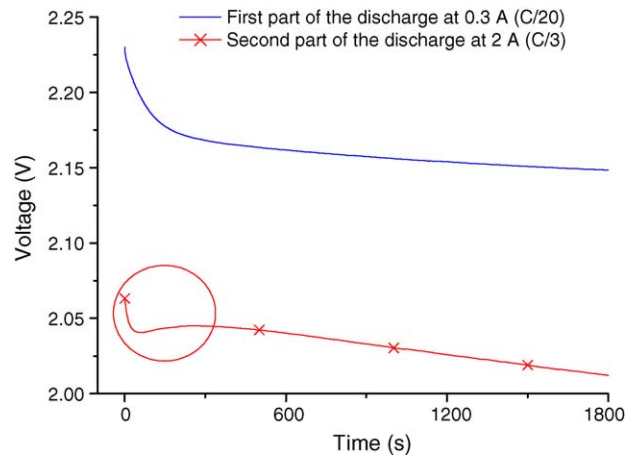


Fig. 15. Evolution of the cell voltage during a discharge, first at a low current regime (C/20) without any “coup de fouet”, and second at a high current regime (C/3) with a “coup de fouet” of low amplitude.

tion in the pores and, then, the cell-voltage increase observed, until the opening of the pores and the homogenization of the electrolyte proceed.

#### 4. Conclusions

This paper presents a study of the “coup de fouet” phenomenon observed at the beginning of the discharge or the recharge of LABs. The results show that in both cases the terminal cell voltage always reflects the positive electrode behaviour, even when a double dip occurs or when the negative electrode is the limiting electrode. Nevertheless, it is important to mention that the negative electrode, also, presents these two phenomena although its contribution on the terminal cell voltage is insignificant in that case.

These discharge and charge “coup de fouet” can be related to the high- and low-SOC levels, respectively. They are, therefore, particularly interesting in the aim of detecting these boundary levels, which constitute important parameters in any charge controller or battery management system.

Results presented in this paper show a very similar behaviour between the charge and the discharge “coup de fouet”, which suggests a common origin. Furthermore, all these results cannot be explained by the commonly accepted interpretations, which are based on crystallization effects for the “discharge coup de fouet” and on the  $\text{PbSO}_4$  resistance for the “charge coup de fouet”. Mass-transport limitations in the pore electrolyte, probably due to the electrode texture, are likely to take a significant part in the origin of these phenomena. Impedance spectroscopy and porosity measurements are currently carried out in order to attempt to determine the origin of the phenomena observed more precisely.

Finally, the method suggested in the literature to diagnose the SOH of LABs from the “discharge coup de fouet” voltage values is shown to be inappropriate in the case of irregular cycling, such as in PV applications. Indeed, the rest time before each galvanostatic polarisation, the high-SOC level, and the DOD reached before the “full” recharge, have a significant influence on this phenomenon, in addition to the well-known influence of the current and the temperature on the cell voltage. Moreover,

the linear relationship between the “discharge coup de fouet” voltage values and the capacity would come mainly from the evolution of the internal resistance. Monitoring this resistance appears then to be a more reliable method for estimating the SOH since it is independent of the operating conditions.

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