

# Optimization of charge parameters for lead–acid batteries used in photovoltaic systems

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## Abstract

The lead–acid batteries used in the photovoltaic (PV) systems are subjected to penalizing operating conditions. The recharge is badly controlled since it depends on the weather conditions. These particular operating conditions induce unusual degradations of the active material compared to more traditional applications like SLI batteries. Consequently, when used in PV applications, lead–acid batteries show a shorter lifetime than they could reach.

The management of the recharge of the photovoltaic lead–acid batteries is a major issue for the optimization of their lifetime. Today, complex methods of end of recharge, such as complements of recharge using current pulses, are increasingly widespread. Many parameters can be adjusted (frequency, duty cycle, voltage threshold for beginning the pulsed phase . . .) but no reliable data are available in the literature.

The study that follows deals with the experimental optimization of these various parameters (under well defined operating conditions). In the same time, a specific software has been developed in our laboratory and helps to understand why these pulses increase the charge acceptance of the lead–acid battery.

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*Keywords:* Lead–acid battery; Photovoltaic systems; Charge; Battery management; Pulsed current; “Hard” sulphation

## 1. Introduction

Lead–acid batteries integrated into photovoltaic (PV) systems suffer from a lack of reliability leading to heterogeneous lifetimes (going from 3 to 14 years). In the more penalizing cases, the battery must be replaced frequently and the storage system corresponds to half the global system cost after 20 years of service. Outstanding and durable lead–acid battery management is then necessary to obtain reliable storage function and thus, reliable PV systems.

Battery management concerns both the charge and the discharge of the battery but most efforts concern the charging phase and lots of charge management strategies can be observed in the literature. Most of the time, they come from the automotive application, which working conditions strongly differ from PV applications. These managements must then

be optimized to PV range, both for the daily and periodic managements for rehabilitation. The daily management, which is the purpose of this work, is mainly divided into two kinds: the ampere-hour management and the voltage management.

The ampere-hour management consists in calculating the number of ampere-hours needed to fully charge the battery. This management is the less widespread strategy [1,2], in so far as it is necessary to set an overcharge coefficient to balance the gassing reaction, the overcharge coefficient depending on the battery technology and ageing.

The voltage management assigns predefined voltage thresholds, which cannot be exceeded, in order to limit specific degradations of corrosion and drying out at high voltage and “hard” sulphation at low voltage. The main voltage managements are the on/off [3–6], floating [7–9] and pulse width modulation (PWM) [10–14] strategies.

The PWM management appears to be an effective alternative compared to other strategies and tends to spread. It is more and more studied for PV applications and seems to

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be really attractive for the charge of lead–acid batteries in so far as the accumulators would be better charged with this strategy. However, even if some studies try to explain the phenomena induced in such a case [15], the electrochemical reasons of the gain obtained and the characteristic parameters of such a management are still undefined.

The purpose of this paper is then to present a new kind of management, which can be described as a “combined” strategy of pulsed current associated to ampere-hour management, in order to obtain the benefit of these two kinds of strategies.

The present paper shows how the “combined” management we propose is favorable to the lead–acid battery both in a physical and a chemical way and explains why we observe benefits in terms of restored capacity and “hard” sulphation amount.

## 2. Experimental

The experiments are performed on battery elements, consisting of one positive tubular electrode and two negative prismatic electrodes separated by a Daramik® separator. The different components are provided by CEAC-EXIDE and were conditioned by charge/discharge cycles until reaching a constant initial capacity value. After being submitted to the cycling procedure described afterwards, an optical study was performed on the positive active material as well as a chemical quantification of the sulphate content of the positive active material.

Table 1

Parameters of the pulsed current phase and comparison with PWM charge procedure

	PWM	Pulsed current phase
Voltage	Constant	Free
Height of the current pulses	Constant	Constant ( $I_{10}$ )
Frequency ( $F$ )	Fixed	Variable (1–500 Hz)
Duty cycle ( $r$ )	Variable	Variable (0.5–0.875)
End of charge	Imprecise	Number of ampere-hour

### 2.1. Cycling procedure

The “combined” procedure, formerly described in [16,17] and summarized here in Fig. 1 is then applied to the elements. A reference cell is also realized with the same electrodes. The reference experiment consists in applying the same phase A (stopped when  $U$  equals  $U_s$ ), and a phase B, where the current is constant and equal to  $I_{10}$ , until reaching 0.15 time the initial capacity ( $C_{init}$ ) of the cell. Five parameters were identified as possible parameters to modify and study during the pulsed current phase of this “combined” procedure. Table 1 shows these five parameters, the ones chosen for optimization and the main differences with a classical PWM strategy. Only two of them were studied here: the frequency of the pulses (noted  $F$ ) and the duty cycle ( $r$ ) corresponding to the duration of the pulses ( $t_{ON}$ ) multiplied by the frequency  $F$ .

The range of frequency studied is from 1 to 500 Hz and the range of the duty cycle varies from 0.5 to 0.875.

The restored capacity is measured after 20 cycles with the “combined” charge procedure.

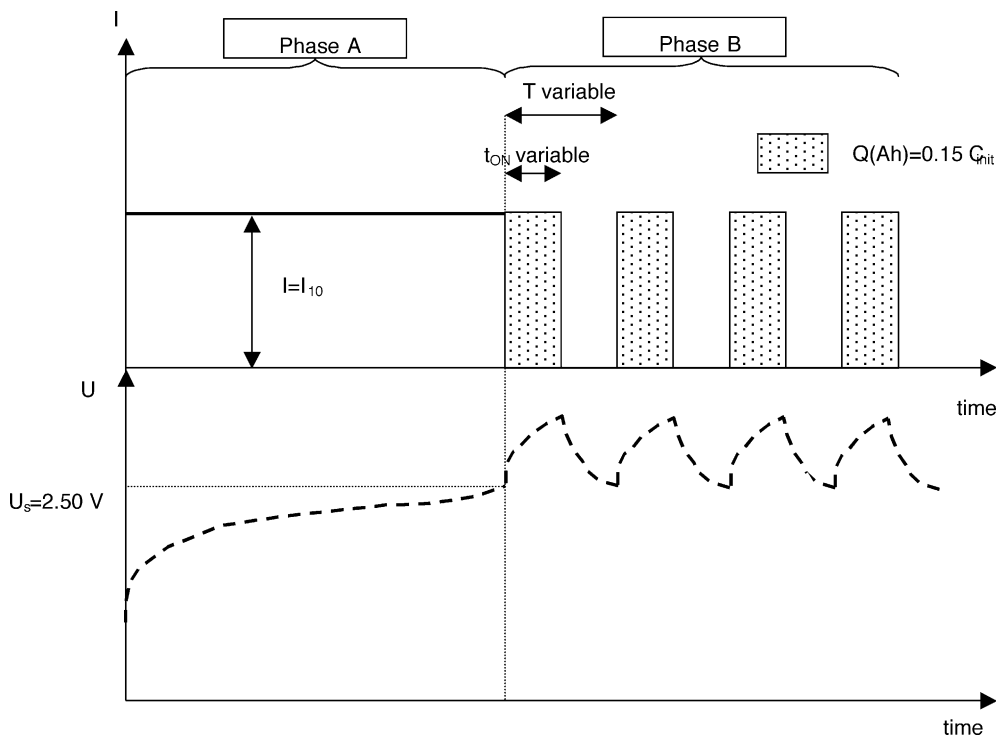


Fig. 1. Description of the “combined” procedure proposed in terms of voltage (dashed line) and current (full line).

## 2.2. Microscopical study

The microscopical study of the positive active material was realized with a JEOL JSM 25S III scanning electron microscope (SEM).

## 2.3. Chemical analysis of the active material

The photovoltaic working conditions mainly leading to sulphation, a chemical titration of  $\text{PbSO}_4$  has been realized after a full charge in order to observe “hard” sulphation (also known as irreversible sulphation). Moreover, to characterize the distribution of the sulphates, the titration has been realized for positive active material at the top and at the bottom of the plates.

## 3. Results and discussion

The typical voltage evolution during the “combined” procedure is present in Fig. 2.

During phase A, the cell voltage progressively increases until reaching the regulation point,  $U_s$  (2.50 V). Phase B is characterized by an initial voltage fall, due to the fact that the average current in the cell is less important than during phase A, the duty cycle  $r$  being inferior to unity. At the end of the charge, the voltage reached is equal to 2.80 V.

After 20 cycles, restored capacities are measured (full discharge at  $I_{10}$  until reaching 1.80 V per cell). The results for the nine tested cells and the reference are presented in Table 2.

This table shows that there is no difference between the reference and the initial capacity of the cells submitted to the advanced charging procedure. Moreover, apart from the fifth cell, all the experiments present higher restored capacity after cycling with the advanced recharge procedure than the ini-

tial one, leading to a ratio (restored capacity/initial capacity) varying from 113 to 147%. The “combined” charge procedure is then very favorable in terms of restored capacity. It must also be underlined that the best results are obtained for the cells undergoing an advanced charge strategy at 1 Hz frequency, which seems to be in our experiences the optimum.

However, the measured capacity obtained after 20 cycles can be coupled with internal degradations leading to premature end life of the batteries. An internal examination of the lead–acid batteries is then necessary. The results of the chemical analysis performed on positive active material are summarized in Table 3.

Two main conclusions can be drawn regarding these results:

- What must be underscored first is that all the cells present higher sulphate content at the bottom than at the top of the plate, which is induced by a more important work of the bottom of the electrodes. This fact is induced by the partition of the current density on the plates and by electrolyte stratification. This last phenomenon is suppressed at voltage values higher than 2.80 V per cell, which is only observed at the end of charge in our experiments.
- Moreover, the reference cell shows the highest lead sulphate content, which means that the injection of current in the “combined” form presents high benefit in term of lead sulphate oxidation. This seems then to be an interesting way to fight against “hard” sulphation.

However, it must be underlined that the best-restored capacity is not correlated to the lowest average sulphation. The restored capacity corresponds to an actual state-of-health of a battery, while the average sulphation can allow a long-term prediction of the state-of-health since the shape, geographical repartition and amount of the crystals will have an impact on the future capacity loss.

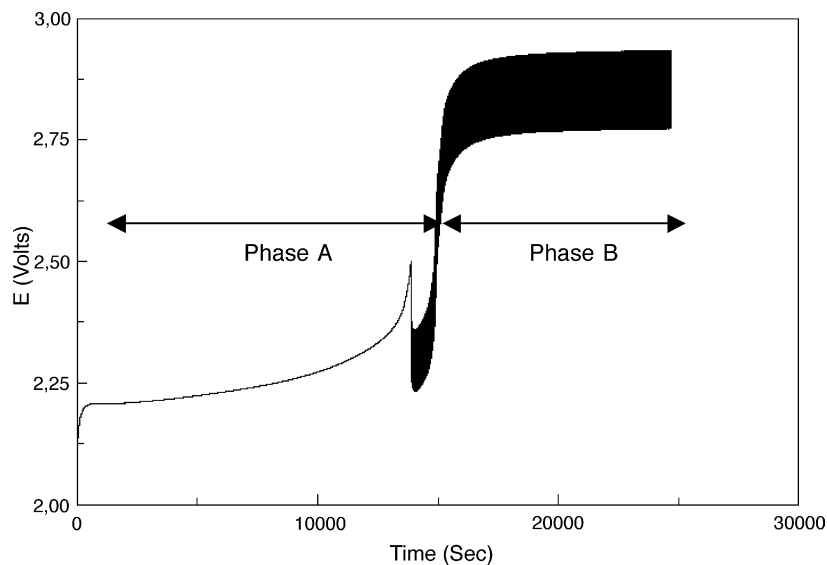


Fig. 2. Typical voltage evolution during the “combined” charge (example presented here:  $F = 1$  Hz,  $r = 0.5$ , 5th cycle).

Table 2  
Results of the restored capacities after 20 cycles

Experience	Frequency (Hz)	Duty cycle	Initial capacity (Ah) at C/10	Restored capacity (Ah) at C/10	Restored capacity/initial capacity (%)
(1)	1	0.5	25.5	37.5	147
(2)	1	0.75	18.3	26.5	142
(3)	1	0.875	28.2	36.9	131
(4)	200	0.5	24.1	30.7	127
(5)	200	0.75	26.8	26.8	100
(6)	200	0.875	29.4	33.3	113
(7)	500	0.5	28.6	34.7	121
(8)	500	0.75	27.0	33.8	125
(9)	500	0.875	27.1	31.5	116
Reference	–	–	28.0	28.3	101

The error is estimated at  $\pm 2\%$ .

Table 3  
Results of “hard” sulphate titration in the positive active material after 20 cycles

Frequency (Hz)	Duty cycle	% PbSO <sub>4</sub> (plate bottom)	% PbSO <sub>4</sub> (plate top)	Averaged % PbSO <sub>4</sub>	PbSO <sub>4</sub> gradient
1	0.5	8.1	6.5	7.3	1.6
1	0.75	9.5	6.4	8.0	3.1
1	0.875	4.7	4.1	4.4	0.6
200	0.5	7.9	5.5	6.7	2.4
200	0.75	5.1	4.1	4.6	1.0
200	0.875	7.8	4.4	6.1	2.9
500	0.5	8.9	5.6	7.3	3.3
500	0.75	9.9	5.3	7.6	4.6
500	0.875	10.0	6.6	8.3	3.4
Reference	12.4	9.8	11.1	2.6	

A new parameter can then be introduced, noted  $\kappa$ , corresponding to the ratio (% restored capacity/% PbSO<sub>4</sub>). This dimensionless parameter gives us global information on the positive electrode. The evolution of  $\kappa$  is presented in the Fig. 3. It clearly appears that the best

positive plate behavior is obtained at the lower frequency studied (1 Hz) and at a duty cycle of 0.875. The optimum management is then realized for this couple of parameters and corresponds to the maximum of the parameter  $\kappa$ .

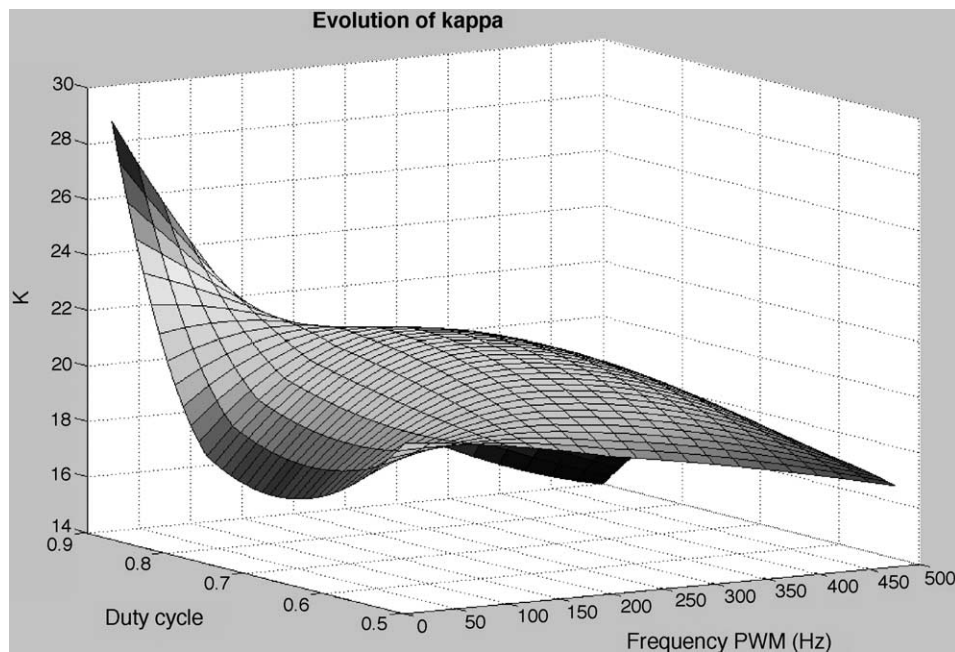


Fig. 3.  $\kappa$  Evolution as a function of the frequency and the duty cycle.

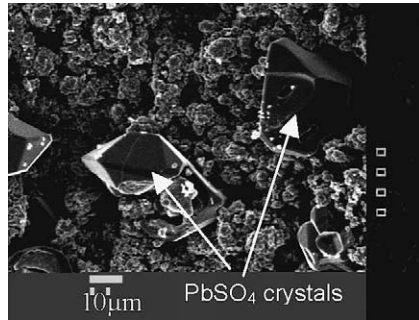


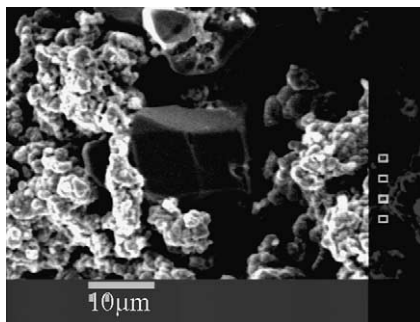
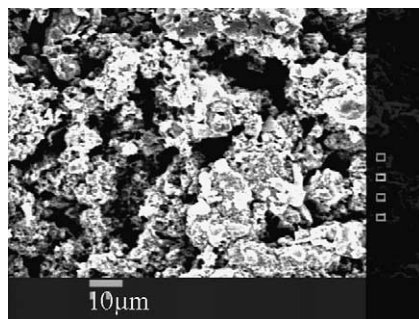
Plate 1. Reference cell.

However, even if the  $\kappa$  parameter seems to be good state-of-health indicator it must be underscored that its determination involves a post-mortem titration, which does not allow an in situ study.

For explaining the impact of the “combined management” on the active materials, the physical and chemical analyses have also been coupled with a microscopical characterization (SEM). Plates 1–3 show respectively, the positive active material of the reference cell and of the experiments (3) and (6), the last two experiments showing the highest and lowest  $\kappa$  values, respectively corresponding to the best and worst behavior observed.

From these pictures, several conclusions can be drawn:

- The most homogeneous active material (homogeneous size and distribution in the plate) is observed for experiment (3). Moreover, experiment (6) and the reference cell show par-

Plate 2.  $F = 500$  Hz,  $r = 0.875$  (experiment (6)).Plate 3.  $F = 1$  Hz,  $r = 0.875$  (experiment (3)).

tial de-cohesion of the active material, certainly resulting in a loss of capacity in comparison to experiment (3).

- The high frequency of experiment (6) and the constant current have favored the creation of large sulphate crystals, which size can reach up to  $20 \mu\text{m}$  for the reference cell. Moreover, some crystals seem to be isolated from the active material, which could explain why the lead sulphates are not easily oxidizable to  $\text{PbO}_2$ .

As a consequence, the microscopical study confirms the first conclusions, and permits to partially explain the frequency role: the 1 Hz frequency allows higher coherence of the active material and limits the large lead sulphate crystals, which are thermodynamically more difficult to re-oxidize.

#### 4. Conclusions

The objective of this study was to develop and optimize a new charge strategy, mainly to protect the battery from hard sulphation. In that way, we have associated the benefits of pulsed current management and ampere-hour management. With two variable parameters, we have shown that a 1 Hz frequency and a 0.875 duty cycle led to an optimum behavior in terms of restored capacity and residual hard sulphate. However, whatever the parameters tested, all the studied cells present the same final voltage. As a consequence, the voltage is not an efficient parameter to evaluate the state-of-health of the battery. The cell behavior is then linked to particular internal states of the active material that cannot be deduced directly from voltage or current measurements.

The study presented here only allows an experimental optimization of the two parameters tested. However, a global optimization of this kind of management implies a good understanding of the electrochemical phenomena, which take place during the charge of the battery. An electrochemical and microscopic modeling of the battery behavior seems then as a necessary tool, in order to understand why the pulsed current is more favorable than a constant current management during the charge and to optimize intelligent management strategies during both the charge and the discharge.

Therefore, CEA-LSEC is developing a software, named ‘Modélisation des Accumulateurs au Plomb-Acide Sulfurique par la Technique des Equations Couplées’ (MA-PASTEC) that models the battery from an electrochemical and physical point of view. This software is now in development but the first results tend to show that the active material at the positive and negative electrode would be better charged with the pulsed current: the charge of the active material would be more homogeneous leading to a better work of the battery.

However, these first results have to be confirmed and correlated to X-ray diffraction in order to make sure that the main effect is not due to a change of the ratio ( $\alpha\text{-PbO}_2/\beta\text{-PbO}_2$ ) [18], which would positively modify the electrical proper-

ties of lead–acid batteries but lead to a shorter lifetime of the battery. These experiments are presently undergoing.

### Acknowledgements

The authors are thankful to ADEME (French Agency for Environment and Energy Management), who has co-funded this work.

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