

## Effect of additives in compressed lead–acid batteries

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### Abstract

The innovative solution proposed in this paper to improve both cycling life and performances of a very low cost lead–acid battery is the combination of the compression concept and the use of micro-porous additives added in the active mass.

The influence of different rates of compression (10–100 kPa) applied on 2 V pre-industrial modules slightly modified has been studied in accelerated cycling test as well as the effect of different kinds of additives on 2 V lab cells performances in a compressed application.

It appears that a pressure minimum of 10 kPa is necessary to stabilise the performances and multiply, by close to 10, the cycling life of the modules. Nevertheless, a 100 kPa pressure allows to perfectly maintain the electrode integrity during the cycling test and prevent effectively the shedding phenomenon.

The idea of the insertion of porous additives into the active mass has been validated during this study since a significant improvement of the cell performances has been observed with two kind of additives tested: Zeolite and Carbon Graphite.

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### 1. Introduction

Since the appearance of the first battery in 1860 [1], we are trying to improve the lead–acid batteries in terms of both cycling life and performances.

One of the well-known life limiting factors of a lead–acid battery is the active material damage during cycling due to the expansion of the active mass [2]. This problem has often been tackled from a mechanical angle where two kind of constraints could be distinguished: the passive containment of the active mass and the active application of a mechanical pressure.

- The passive containment of the positive active material is born with the first tubular design in 1910, where the paste is contained at first in a tube of rubber materials then in a gauntlet, developed by Boriolo [3]. Another way to limit

the expansion of the active material is the pocketing of the electrode in a porous separator [4] commonly used since 1975 with the coming of polyethylene separators.

- The idea of an active application of mechanical pressure has been proposed in 1978 by Alzieu et al. [5]. Experiments on a conventional flooded battery have been realized thanks to the development of an external compression system and a multi-layer separator. The main positive result of this test campaign is the significant increase in cycling life of the tested cells [6]. The significant effects of compression have been confirmed with different batteries designs [7–10].

In other respects, the low performances of lead–acid batteries are usually attributable to an effective use of only 1/3 of the active mass [11] because of acid diffusion problems in the plate. One of the ideas often proposed is to improve the active material porosity thanks to a modification of the paste manufacture. Nevertheless, this method is quite difficult to use without dramatic texture change of the paste limiting the pasting stage. Another way to improve the active material

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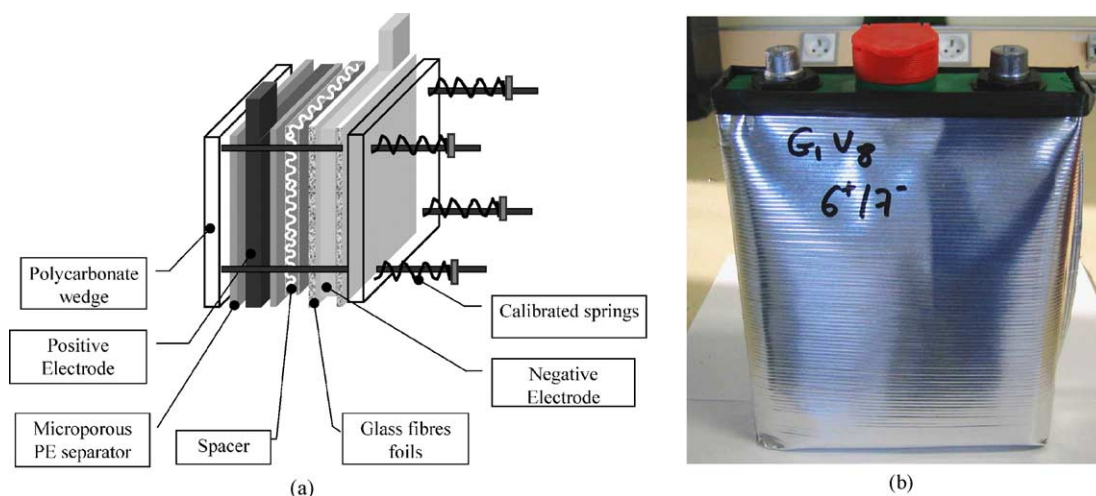


Fig. 1. Schematic representation of the assembly used in a compressed application (a), 2 V cell inserted in a coffee bag envelope (b).

properties is the use of additives, which could have a significant effect on its properties, porosity, density, etc. Numerous kinds of additives [4] have already been tested in order to improve the performances of lead–acid batteries and, despite a significant increase of the performances at the beginning of the battery life, the main long-term drawback met with additives added in the active mass is an increase of the decohesion phenomenon leading to an acceleration of the capacity loss [12].

This study proposes an innovative solution in order to improve both cycling life and performance of a very low cost lead–acid battery by combining the compression concept and the use of porous additives. Indeed, the paste cohesion will be maintained owing to the compression system and the electrode porosity will be both improved and maintained during cycling thanks to the addition of porous compounds, which will create acid reservoirs within the active material, favouring the diffusion process. The first results concerning the influence of the compression and the addition of different additives selected on the cell behaviour are presented in this paper.

## 2. Experimental

### 2.1. Pre-industrial 2 V modules preparation

Two volt modules are realized with low cost electrodes resulting from the rolled technology followed by Xmet ‘Propenzi’ process and usually used in a starting lighting ignition (SLI) applications. Several plates stacks are taken on the production batteries line and modified for a compressed application thanks to the insertion of a multi-layer separator as described Fig. 1a. Each constituent element of this separator has a particular function:

- The micro-porosity of the polyethylene separator put around the positive electrode allows to facilitate the oxygen release.

- The use of glass fibre separator on the negative electrode prevents the crushing of the negative active mass.
- The insertion of a corrugated polyethylene spacer guarantees an electrolyte reservoir between the two electrodes

The modified electrode stacks are inserted in a flexible envelope made from ‘coffee bag’ materials (Fig. 1b). This material is a current consumer product usually used in the packaging of foodstuff. Its low cost material is composed of two thermo-soldering polypropylene foils surrounding thin aluminium foil allowing a perfect imperviousness to gas and water.

Finally, two polycarbonate wedges are set out parallel to the electrode stack and the pressure is applied on the dry cells thanks to the use of calibrated springs (Fig. 1a). Two compression rates are tested: 10 and 100 kPa<sup>1</sup>.

### 2.2. Laboratory modified 2 V cell preparation

#### 2.2.1. Additives selected

The selection of additives depends on numerous criteria in terms of porosity, resistance to acid and positive potential, dimensions, purity, weight, cost, etc. Three kinds of additives have been retained for this first experiments campaign namely silica-based additives, zeolite and carbon materials.

**2.2.1.1. Silica-based additives.** The silica-based additives have been chosen because of their high chemical and electrochemical inertia. The two samples tested were powders and fibres in shape.

The micro-porous silica powder has been furnished by Daramic. It is commonly used in the manufacture of separators. It consists of particles agglomerates of which the grain size is close to 3  $\mu\text{m}$  with about 90% of porosity.

The glass fibre samples (Hollingsworth&Vose Co.) are characterised by a specific area above 0.3  $\text{m}^2 \text{g}^{-1}$  and

<sup>1</sup> Equivalence: 100 kPa = 1 bar = 14.503 PSI = 29.625 In. Hg.

Table 1  
Cycling conditions applied to the pre-industrial modules

Discharge	$C_2$ up to $U_{lim} = 1.25$ V
Charge	Step 1: $I$ constant = $I_2$ up to $U_{lim} = 2.65$ V Step 2: $I$ constant = $I_{15}$ up to 115% Ah

particles with an average diameter included between 0.25 and 10  $\mu\text{m}$  and by a high length up to 50  $\mu\text{m}$ .

**2.2.1.2. Zeolite.** This compound is one of the more common products used in catalysis applications and it has been retained because of its high open porosity. The zeolite chosen is the ZSM-5 type (Utikon-zeochem) with a pore diameter close to 0.5 nm. Its particle size has not been characterised yet.

**2.2.1.3. Carbon materials.** Those products have been selected because of their electronic conduction properties among others. The two carbon samples chosen are nanotubes (cirimat Icmie, Toulouse) and graphite powder (SG) presenting a high specific area close to 570 and 40  $\text{m}^2 \text{g}^{-1}$ , respectively. Nevertheless, those materials are not stable versus positive potential and will be only used in the negative electrode.

### 2.2.2. Electrode preparation

The modified electrode preparation consists of the addition of 1–2 wt.% of additives into the original paste formulation. Only the water quantity is adjusted in order to maintain a satisfactory texture for the pasting operation. Then, naked rolled grids with a 16  $\text{cm}^2$  area are coated with the modified paste. Finally the electrodes are dried during a curing stage: these are put in a steam room at 60 °C during 24 h with 100% of humidity and then 24 h dry.

The cells are composed of the assembly of three plates in which the modified one is surrounded by the two other polarities and the multi-layer separator is inserted between the plates. The cells are tested in a compressed application with a 100 kPa constraint.

## 2.3. Electrical tests

### 2.3.1. Pre-industrial modules

The pre-industrial modules are tested with an accelerated cycling procedure favouring the shedding phenomenon (Table 1). The test is stopped when the discharge capacity is lower than 50% of the initial one.

### 2.3.2. Laboratory cells modified by additives

In order to underline the effect of the additives on the electrical performance of the modified cells, a characterisation procedure is applied with different discharge rates:  $C_{10}$ ,  $C_5$  and  $C_2$  (Table 2). The test is stopped when the performances are stabilised, i.e. after 5 cycles at least.

Table 2  
Characterisation procedure applied to the laboratory cells modified by additives

Discharge	$C_{10}$ up to $U_{lim} = 1.4$ V	X 5
Charge	$I$ constant = 0.5 $I_{10}$ up to 115% Ah	
Discharge	$C_5$ up to $U_{lim} = 1.4$ V	X 5
Charge	$I$ constant = 0.5 $I_{10}$ up to 115% Ah	
Discharge	$C_2$ up to $U_{lim} = 1$ V	X 5
Charge	$I$ constant = 0.5 $I_{10}$ up to 115% Ah	

## 3. Results

### 3.1. Compression effect

#### 3.1.1. Electrical behaviour

Fig. 2 represents the evolution of the relative discharge capacity during the accelerated cycling test. For an uncompressed configuration, the reference achieves only 70 cycles before reaching the stop conditions. For both compressed designs, a good stabilisation of the capacity is observed during 300 cycles, then a slight decrease of the performances appears. The stop condition is reached after 500–700 cycles. Moreover, a high compression rate application (100 kPa) leads to a low capacity loss with stabilised performances close to only 90% of the initial capacity.

#### 3.1.2. Post mortem analysis

A post mortem analysis has pointed out the cells failure mode. As seen in Fig. 3a, without compression, the positive electrodes have suffered more damage since the active materials are completely broken away from the grids. With a low compression rate (10 kPa), the positive plates are less defaced (Fig. 3b). The active material is rather soft and shedding is observed only on the edges of the plates. A higher pressure (100 kPa) leads to the integrity of the electrodes being perfectly maintained (Fig. 3c).

Finally, for both compressed applications, the formation of foam at the top of the electrode stack causes short-circuits responsible for the premature and of the cycling tests (Fig. 4).

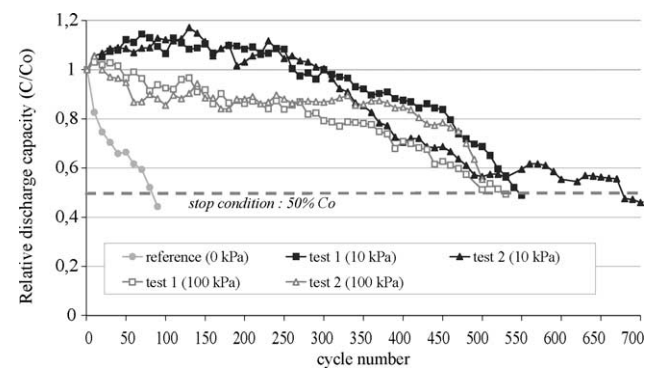


Fig. 2. Relative discharge capacity evolution during the cycling test of the pre-industrial modules.

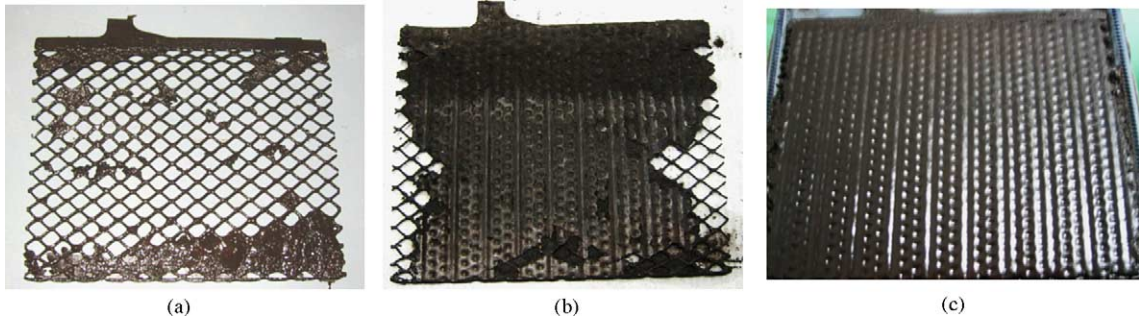


Fig. 3. Photographs of positive electrodes compressed at 0 kPa (a), 10 kPa (b) and 100 kPa (c) after the accelerated cycling test.



Fig. 4. Photograph of short-circuit at the top of the electrode stack in a compressed application.

### 3.2. Effect of additives

Fig. 5 shows the average discharge capacity at different discharge rates obtained with the modified positive electrodes. Thus, compared to the reference, the electrical behaviour of the cell modified with silica-based additives is not satisfactory. Indeed the powder used has a negative effect whatever the discharge rates and fibres seem to have no particular influence. Nevertheless, the test with zeolite is very interesting since the performances are up by close to 20% on the reference whatever the discharge rate.

Fig. 6 presents the performances obtained at different discharge rates with negative modified electrodes. The two carbon-based additives tested allow to improve the cell performances whatever the discharge rates. But the best behaviour is obtained with graphite powder since the performances are up to 20–50% on the reference depending on the discharge rate. The best improvement is obtained with the higher discharge rate, i.e. C<sub>2</sub>.

## 4. Discussion

This study has shown the significant effect of the compression application on a flexible module composed of thin plates stack slightly modified with a multiplication by close

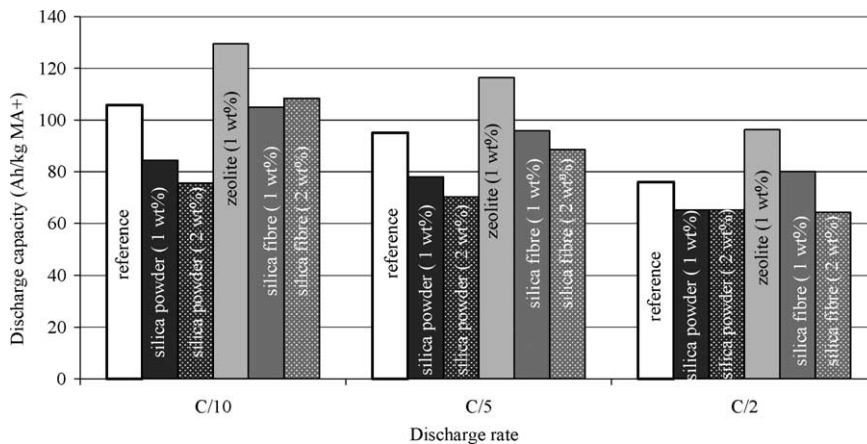


Fig. 5. Average discharge capacity at different discharge rates of the cells with modified positive electrodes.

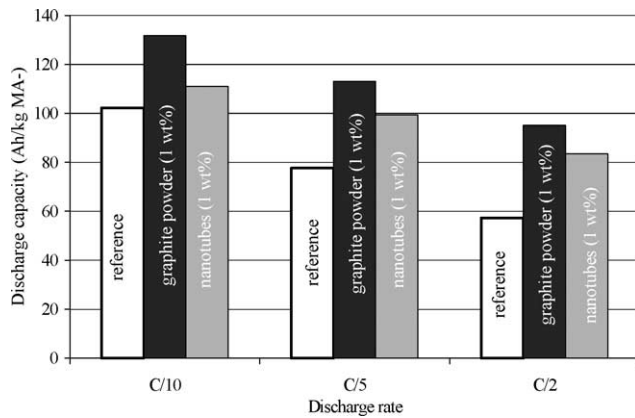


Fig. 6. Average discharge capacity at different discharge rates of the cells with modified negative electrodes.

to 10 of their cycling life in aggressive cycling conditions. In accordance with several authors [8,13,14], the post mortem analysis shows the significant influence of the pressure on the positive plate evolution. The expansion of the active materials is limited, suppressing the shedding phenomenon responsible for the dramatic capacity loss of the cell in such cycling conditions.

Besides, as noticed by other authors [15,16], a low rate of compression (10 kPa) already allows a significant increase of the cycling life. But the post mortem analysis of our cells shows that a low pressure is not sufficient enough to maintain the positive electrode in a good structural state. Moreover, the important effect of a high pressure on the active mass cohesion and the premature end of the test because of short-circuit are arguments to prefer a high rate of compression.

The decrease of the capacity observed with a high pressure (100 kPa) is in accordance with Chang's studies [7]. This behaviour can be attributable to the effect of the constraint on the active mass evolution. Indeed, the pressure could contribute to the crushing of the porous volume of the active mass limiting the acid diffusion process in the electrode and in the same way the amount of useful active materials. Consequently, the capacity is lower because the pressure is high.

The use of porous additives seems to be a pertinent answer to this last problem but the negative effects of silica-based additives on the positive electrode show the difficulties to find a suitable additive for a compressed application.

Some hypothesis could be advanced in order to explain this behaviour. Indeed, the porosity of the silica powder is rather doubtful and the small aggregate size of the powders could contribute to filling up the existing porosity of the paste and to diminish the amount of useful active mass.

Concerning the fibres, the low surface area of this additive does not favour the creation of acid reservoirs inside the paste, thus the amount of useful active mass is not improved—explaining the insignificant influence of this element on the electrical performance of the cell.

Nevertheless, the addition of zeolite allows to validate the idea of putting additives with high porosity in a compressed

application. Indeed, it seems that its open porosity is sufficiently large ( $\varnothing_p \sim 0.5$  nm) to absorb the electrolyte and to favour diffusion inside the active mass. In other respects, the influence of the pressure application on the active mass cohesion and consequently on its conduction properties could be discussed. Thus the increase of the performances observed with a low rate of discharge, where the acid diffusion problems are less important, could be partially attributable to an improvement of the active mass conduction in a compressed application.

Concerning the tests on the negative electrodes, the good performances, in particular with a high discharge rate, obtained with carbon materials could be attributed to the high specific surface of this products influencing the acid diffusion process by acting as an 'electro-osmotic' agent [17]. This first experiment campaign does not allow to specify the share of the influence of the conduction properties of this product on the improvement of the cell performances.

## 5. Conclusions

This study has shown the positive effect of the pressure application on industrial 2 V cells slightly modified in term of both cycling life and capacity. The satisfactory performances obtained with the slightly compressed cells raise the interest to find the optimum of the compression to apply and other tests with pressure lower than 100 kPa are necessary.

The idea of using porous additives in the active materials in order to improve the capacity of the compressed cells has been validated during this first experiments campaign. Two additives have been retained: zeolite, in the positive paste, and graphite powder, in the negative paste, because of their significant influence on the electrical performance of the tested cells.

These last results encourage us to start a second test campaign with other additives and in particular with the Diatomite family. Diatomite is a silica-based porous rock, which comes from the accumulation of fossilized diatom's skeletons. These compounds are available in a large range of aggregate size and seem to fulfil numerous criteria in order to be successfully used in a compressed application.

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