

# A comparative study of pulsed current formation for positive plates of automotive lead acid batteries

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## Abstract

Positive plate formation with pulsed current is investigated under a wide range of pulse characteristics and compared with continuous current formation. The results indicate that pulsed current formation has a higher faradaic efficiency for conversion into lead dioxide than formation with continuous current. On the other hand, with pulsed current, there is always some residual tetrabasic lead sulfate, not observed on plates formed with continuous current. Pulsed current formation yields higher  $\beta$ -PbO<sub>2</sub>/ $\alpha$ -PbO<sub>2</sub> ratio than continuous current formation, and is more efficient at longer times of formation. © 2002 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Formation, one of the final steps in battery production, is carried out by applying a charge to the cured plates immersed in sulfuric acid solution. Traditionally, this charge is applied under controlled current and temperature. Although the current may be varied over a period of time, it is essentially continuous. Pulsed current has been used extensively in battery charging schemes [1–3] allowing a very short time for recharge. There has been a lot of interest in the use of pulsed current in the battery formation [4,5] in order to reduce the production costs. It is expected that pulsed current formation may allow an increase in faradaic efficiency and/or reduction in the time of formation, but only a few reports in the literature address this question.

Of the two kinds of plate present in batteries, the positive plate is more difficult to form. In other words, conversion of cured positive plate to PbO<sub>2</sub> is more demanding than conversion of cured negative plates to spongy lead. Hence, if any advantage may be obtained with pulsed current formation, it should be achieved at the positive plate. In this article we report results of positive plate formation, under laboratory conditions, with pulsed current over a wide range of pulse profiles.

## 2. Experimental

Cells were assembled with one positive plate inside a polyethylene envelop (0.28 mm thick) inserted between two negative plates. The dimensions of all plates were 140 mm × 95 mm. The cell was placed inside a small Plexiglas container measuring 154 mm × 115 mm × 16 mm.

A sulfuric acid solution of density 1.14 g/ml was used to fill the cell and no temperature control was attempted. A total charge of 21.6 Ah was used. This is a reduced value, chosen in order to avoid complete formation of the plates, which would make it difficult to observe the effect of different experimental conditions on formation results. Formation was carried out according to a full 2 × 3 × 3 factorial design, with levels defined as follows:

- total time: 10 and 20 h;
- pulse profile: 1:1, 1:3, and 3:1;
- pulse length: 4, 400 and 4000 ms.

Here ‘pulse profile’ is the ratio between the time with current switched on and the time with current switched off. For a given total time, each profile requires a different current to keep constant the total charge applied to the cell. The currents for all experimental conditions investigated are shown in Table 1.

The complete formation procedure consisted of placing the cell in the Plexiglas container, filling it up with 180 ml of sulfuric acid solution and allowing a rest period of 15 min, after which the pulses were applied with a BOSS 20 × 20

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Table 1  
Currents used for pulsed formation in different pulse profile

Total time (h)	Pulse profile	Current (A)
10	1:1	4.32
20	1:1	2.16
10	1:3	2.88
20	1:3	1.44
10	3:1	8.64
20	3:1	4.32

bipolar power supply controlled by a microcomputer, and monitored with a digital oscilloscope. At the end of formation time, the positive plate was removed and rinsed in water until neutral pH was obtained. Pellets were removed from different regions of the plate and dried in an oven at 100 °C for at least 2 h. The pellets were then ground and sieved to a 200 mesh powder. X-ray diffraction analysis of this powder was obtained in a D5000 Siemens diffractometer with Cu K $\alpha$  as radiation source. Quantitative interpretation of the diffractogram was carried out by means of the PEAKS software [6]. One positive unformed plate of the same batch used in these experiments was also analyzed by X-ray diffraction.

Another experiment was performed under a constant current of 1.0 A and a temperature of 30 °C, to allow a comparison between pulsed and continuous current formation. In both formation procedures, the initial plate composition was 3BS = 3.6%, 4BS = 69.7%, 1BS = 2.6% and  $\alpha$ -PbO = 24.2%.

A smaller cell (1/4 of the above) was used to follow the potential–time behavior in the initial stages of formation.

Current (1.08 A) was applied with a 273A EG&G/PAR potentiostat/galvanostat and a cadmium wire was used as reference electrode. Symmetrical pulses (pulse profile 1:1) were used with pulse length of 1 and 20 s.

### 3. Results and discussion

As the composition given above shows, the positive cured plates are rich in tetrabasic lead sulfate (4BS). The results for all the conditions of pulsed current formation are given in Table 2. The plate formed under continuous current formation yielded the following composition:  $\beta$ -PbO<sub>2</sub> = 35%,  $\alpha$ -PbO<sub>2</sub> = 22%, ( $\beta$ -PbO<sub>2</sub>/ $\alpha$ -PbO<sub>2</sub> = 1.6), PbSO<sub>4</sub> = 11%,  $\alpha$ -PbO = 31%.

Comparison of continuous and pulsed formation, shows that total PbO<sub>2</sub>, in many cases, is higher and that there is always some 4BS remaining (with amounts spread over a relatively wide range) for pulsed formation, whereas, for continuous formation the only remaining unformed compounds are lead oxide ( $\alpha$ -PbO) and neutral lead sulfate (PbSO<sub>4</sub>). These results show clearly that pulsed current formation is more efficient in terms of total PbO<sub>2</sub> than continuous current formation.

A geometrical representation of the results, given in the cube diagram of Fig. 1, helps to visualize how the formation conditions (under pulsed current) affect the total PbO<sub>2</sub> content. It can be seen clearly, that the formation time of 20 h, whose results are shown on the right-hand face, is always more efficient. The effect of pulse frequency is noticeable only for the 10 h formation time, with lower frequencies leading to higher conversions to PbO<sub>2</sub>. Since

Table 2  
Results of X-ray diffraction quantitative analysis for all experiments with pulsed formation

Experiment	Time (h)	Pulse length (ms)	Current (A)	$\beta$ -PbO <sub>2</sub> / $\alpha$ -PbO <sub>2</sub>	4BS (%)	PbO <sub>2</sub> (%)
Profile 1:1						
1	10	4	4.32	3.3	26	44
2	20	4	2.16	2.1	5	75
3	10	400	4.32	1.9	12	54
4	20	400	2.16	2.0	4	71
5	10	4000	4.32	2.9	17	53
6	20	4000	2.16	2.4	3	63
Profile 1:3						
7	10	4	2.88	2.6	19	50
8	20	4	1.44	2.3	9	66
9	10	400	2.88	4.3	11	52
10	20	400	1.44	3.1	3	74
11	10	4000	2.88	3.2	11	58
12	20	4000	1.44	2.1	3	70
Profile 3:1						
13	10	4	8.64	6.8	12	46
14	20	4	4.32	2.1	5	67
15	10	400	8.64	3.4	13	51
16	20	400	4.32	1.8	5	67
17	10	4000	8.64	2.1	12	57
18	20	4000	4.32	2.5	8	64

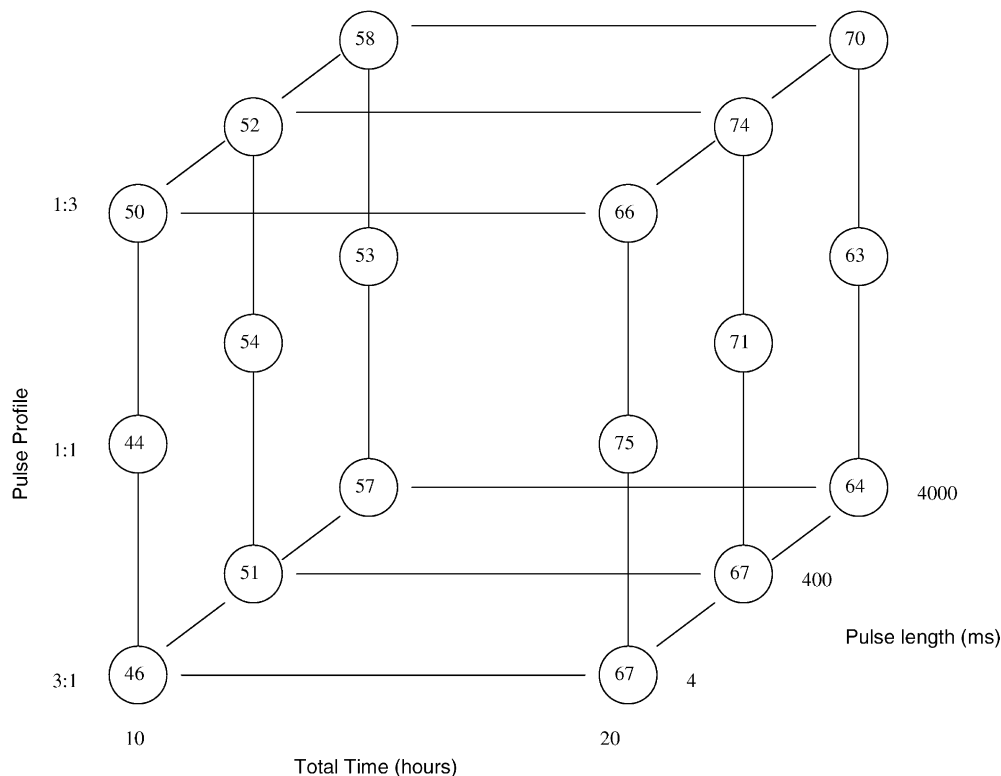


Fig. 1. Geometric representation of PbO<sub>2</sub> contents after pulsed formation in different experimental conditions.

longer formation times at constant charge imply smaller currents, it might seem that this behavior should be ascribed to the current difference. However, this is not the only effect. A comparison of the three results with pulse profile 1:1 and formation time of 10 h with those with profile 3:1 and formation time of 20 h, shows that the latter are also the better (in terms of total PbO<sub>2</sub> content), although all results were obtained with a current of 4.32 A. Thus, one can conclude that, longer periods with the current off are associated with higher formation yields.

Usually, frequencies as low as some of those used in the present work, are not considered for charging and formation of batteries [2,5]. However, our results clearly indicate that better responses are obtained with lower frequencies, especially at shorter formation times, as shown in Fig. 2. A possible explanation for this finding is as follows. As the current is applied, the electrochemical reaction converts lead sulfate to lead dioxide and sulfuric acid. With increasing concentration of sulfuric acid, formation efficiency is lowered. When the current is off, sulfuric acid is only diffusing away from the plates. As the pulse starts again, acid concentration is lower than in a continuous current formation, and therefore a higher efficiency can be achieved. In other words, the efficiency is controlled by sulfuric acid diffusion. If the diffusion rate is small, high frequency pulses would not improve formation as much as low frequency pulses. Fig. 1 suggests a slight improvement in formation efficiency at 10 h for pulse profile 1:3, where diffusion of sulfuric acid away from active material is enhanced. To investigate this

behavior an experiment with reference electrode following the potential of the positive plate during pulsed current formation was carried out. The potential–time diagrams are shown in Fig. 3. It is seen that for longer pulses (10 s) the variation of potential with time is larger than for shorter (0.5 s) pulses. Even when the curves are in the same time scale this behavior is observed. The sulfuric acid gradient caused by longer pulses is higher and responsible for the potential–time variation, indicating a slow rate of diffusion of sulfuric acid away from the plate.

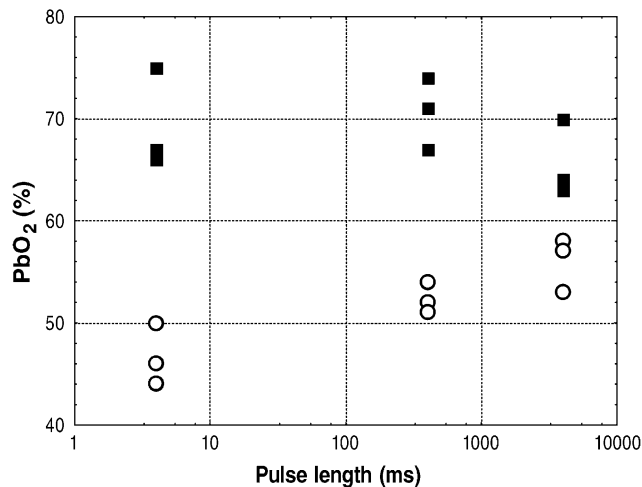


Fig. 2. PbO<sub>2</sub> content after formation plotted against pulse length. Total time of formation: (○) 10 h, (■) 20 h. Data extracted from Table 2.

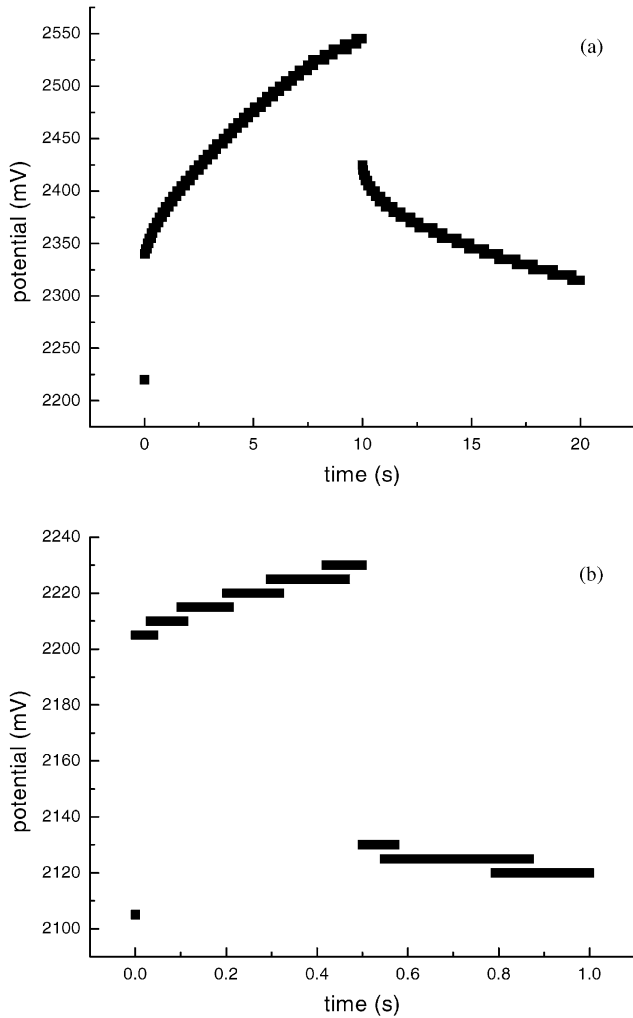


Fig. 3. Potential vs. time for positive plates subjected to symmetrical pulsed formation in the initial stages (several minutes). Pulse period: (a) 20 s, (b) 1 s.

With respect to the  $\beta$ -PbO<sub>2</sub>/ $\alpha$ -PbO<sub>2</sub> ratio, the results in Fig. 4 show a weak but clear negative correlation between this ratio and the total PbO<sub>2</sub> content. This may be an indication that the  $\beta$ -polymorph is formed earlier than the  $\alpha$ -polymorph. As the formation proceeds and total PbO<sub>2</sub> increases,  $\alpha$ -PbO<sub>2</sub> is favored and the ratio decreases. Since sulfuric acid density is lower at the beginning of formation, it may be argued that the  $\beta$ -polymorph is formed preferentially at lower sulfuric acid density values. The  $\beta$ -PbO<sub>2</sub>/ $\alpha$ -PbO<sub>2</sub> ratio for constant current formation is larger than that for pulsed current formation. It has been proposed elsewhere that the two polymorphs of lead dioxide contribute in different ways to the battery performance [7,8]. The structure of the  $\alpha$ -polymorph would be more compact and more beneficial against mass shedding than the  $\beta$ -polymorph, which has a larger surface area and may have a better performance for high rate discharge. According to this argument, plates formed under pulsed current would display a better high rate discharge performance but might have a poorer cycle life characteristic.

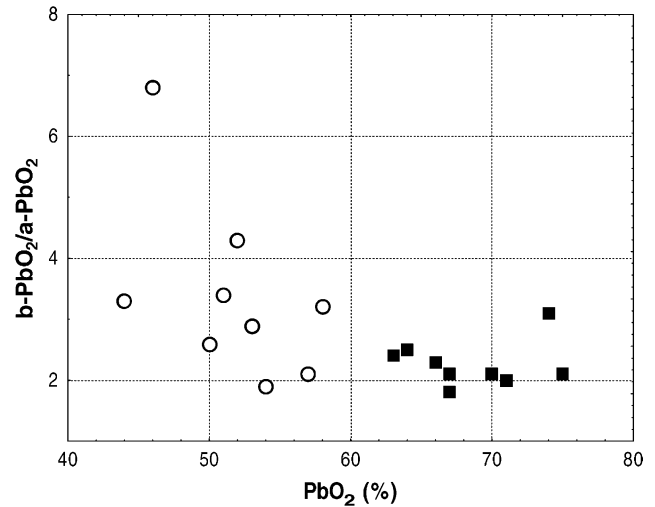


Fig. 4. Ratio of  $\beta$ -PbO<sub>2</sub>/ $\alpha$ -PbO<sub>2</sub> vs. total PbO<sub>2</sub> for pulsed formation. Total time of formation: (○) 10 h, (■) 20 h. Data extracted from Table 2.

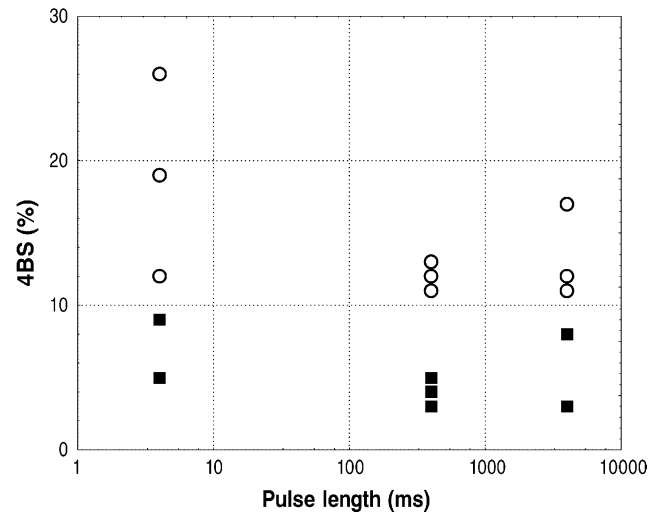


Fig. 5. Tetrabasic lead sulfate (4BS) content vs. pulse length for pulsed formation. Total time of formation: (○) 10 h, (■) 20 h. Data extracted from Table 2.

The persistence of 4BS in pulsed formation is presented in Fig. 5. It is clear that longer formation time and larger pulses lead to lower 4BS amounts. Although it may be argued that 4BS is more difficult to form, a detailed study of acidity should be performed to confirm this effect.

#### 4. Conclusions

Different pulsed current formation conditions for positive plates have been studied. Longer formation times and low frequencies (for short formation times) are the best conditions in terms of PbO<sub>2</sub> yield. Pulsed formation for tetrabasic rich cured plates is more efficient than continuous formation.

With pulsed current formed plates there is always some residual tetrabasic lead sulfate. Pulsed formation yields higher  $\beta$ -PbO<sub>2</sub>/ $\alpha$ -PbO<sub>2</sub> ratio than continuous formation. The  $\beta$ -polymorph seems to be formed preferentially in the initial stages of formation.

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