

Short communication

## Positive thin electrodes obtained from hydrothermally synthesized 4BS for lead-acid batteries

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### Abstract

Tetrabasic lead sulfate,  $4\text{PbO}\cdot\text{PbSO}_4$  (4BS), was prepared from an aqueous suspension of leady oxide by using a simple hydrothermal method. Digesting the paste at a moderate temperature ( $125^\circ\text{C}$ ) and heating for a short time (30 min) ensured the obtainment of particles of small, uniform size. The material was deposited on a lead alloy substrate 0.2 mm thick by spraying from aqueous suspensions. The deposits were highly uniform and homogeneous, with a coating thickness of  $100\ \mu\text{m}$ . A multi-step charge algorithm involving no preliminary soaking provided the best  $4\text{BS} \rightarrow \text{PbO}_2$  conversion. The resulting electrodes delivered a capacity of  $115\ \text{Ah kg}^{-1}$  with excellent capacity retention over more than 500 cycles at 100% depth of discharge (DOD).

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**Keywords:** Tetrabasic lead sulfate; Thin electrodes; Lead acid batteries

### 1. Introduction

The use of tetrabasic lead sulfate (4BS) instead of tribasic lead sulfate (3BS) as an intermediate species in the positive electrode is regarded as effective way of avoiding a premature capacity loss (PCL) in lead/acid batteries [1,2]. Cured plates containing large amounts of 4BS exhibit good mechanical strength and a long cycle life. These assets are generally ascribed to the “metasomatic process” involved in the first oxidation process [3], by which 4BS is converted into a large number of fine  $\text{PbO}_2$  crystals that gather into porous agglomerates and mimic the overall shape of the precursor 4BS crystals. This results in a mechanically stronger lead dioxide structure than that obtained from a 3BS phase. However, large 4BS crystals require a very long formation time for complete oxidation to  $\text{PbO}_2$  in order to obtain plates with a sufficiently high initial capacity. This made the presence of 4BS in battery paste undesirable in the past. The Bell process [4] overcame the difficulties in the electroformation process and facilitated the use of 4BS as an active material for positive electrodes. In the lead acid battery industry, the 4BS

phase is obtained at temperatures above  $80^\circ\text{C}$  either during the paste preparation or the curing process. This material not only lengthens battery life, but also affords more flexible preparation conditions. In fact, a number of methods have been developed for the preparation of 4BS-based positive plates aimed at increasing the capacity delivered by the battery and its cycle life [5–7].

Crystal size and the electroformation process are two major targets in optimizing 4BS-based positive automotive-battery plates. In this work, we revisited the use of 4BS in positive electrode with emphasis on the synthetic procedure, electrode design and electroformation process. The compound was prepared by using a hydrothermal method that affords easy control of particle size. Also, it shortens the preparation time compared with other alternative choices such as the Evachtherm® method of Pavlov and Ruevski [8] and the milling-based method of  $\text{PbO}$  and  $\text{PbSO}_4$  mixtures developed by Grugeon-Dewaele et al. [9]. Our electrodes were prepared as thin electrodes (0.22 mm thick including the paste and substrate) by using a spray deposition method from aqueous suspensions. This method had previously been successfully used to prepare thin electrodes from conventional positive active materials and nanometric  $\text{PbO}_2$  [10,11]. The effect of preliminary soaking and the electroformation algorithm are described.

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## 2. Experimental

Tetrabasic lead sulfate was prepared by hydrothermal synthesis from a mixture of leady oxide (composition 72%  $\alpha$ -PbO and 28% Pb) and sulfuric acid under stoichiometric conditions in 75 ml of water in a Berghof high-pressure autoclave. The temperature and time used in the different experiments were 125–200 °C and 30–120 min, respectively. The 4BS precipitate obtained was filtered, washed several times with distilled water and dried in a vacuum oven at 60 °C for 3 h. X-ray powder diffraction (XRD) patterns were recorded on a Siemens D5000 diffractometer, using Cu K $\alpha$  radiation and a graphite monochromator. Particles morphology was examined in scanning electron microscopy (SEM) images obtained with a Jeol JMS 6400 microscope. The average particle size was calculated by using the VISILOG 6.0 software, and the composition of the lead compounds detected in the XRD patterns was determined with PEAKS<sup>®</sup> [12].

Positive plates 1 cm<sup>2</sup> in size were prepared by spraying an aqueous suspension of the active material (15 g of 4BS in 25 ml H<sub>2</sub>O) over both sides of lead alloy sheets [Pb–Sn (1.14%)–Ca (0.03%)] 0.2 mm thick, following a procedure described elsewhere [10]. The substrate was heated at 115 °C during deposition. The amount of 4BS deposited was 20 mg cm<sup>-2</sup>. The experimental cell consisted of one positive and two negative electrodes. The small negative plates were cut from conventional negative S.E.A. Tudor's plates (Exide Technologies). AGM separator was supplied by Bernard Dumas. All electrochemical measurements and cycling tests were carried out by using a Solartron 1470A battery test system. Sulfuric acid of 1.15 sp.gr. was used as electrolyte during the formation stage. Cells were disassembled, washed and stuffed with 1.28 sp.gr. electrolyte for cycling tests. A Hg/Hg<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>SO<sub>4</sub> (sp.gr. 1.28) reference electrode was used and all voltammetric potentials reported here are referred to it. The electrochemical formation of 4BS was accomplished by overcharging the cell up to 250% of its theoretical capacity. The depth of discharge (DOD) was 100% and a cut-off voltage of 1.6 V used as limiting factor in all tests. Cells were subsequently charged at 110% of the capacity measured in the previous discharge.

## 3. Results and discussion

Time, temperature and stirring were the factors to be controlled during the hydrothermal synthesis of the 4BS phase from stoichiometric mixtures of leady oxide and sulfuric acid. Fig. 1 shows the XRD patterns for the product obtained by heating at 200 °C for 1 h without and with stirring. Only traces of PbO under the former conditions were detected; this phase, however, disappeared when the synthesis was assisted by stirring. The strongest reflections corresponded to the [1 1 0], [−3 2 0] crystallographic planes (Fig. 1b), which suggests crystal growth along the  $\langle hk0 \rangle$  direction and the potential presence of needle-shaped particles as shown below. Table 1 shows the contents in the different phases as calculated from the XRD patterns. In the absence of stirring, the amount of PbO decreased as the temperature increased irrespective of the heating time. Additional basic

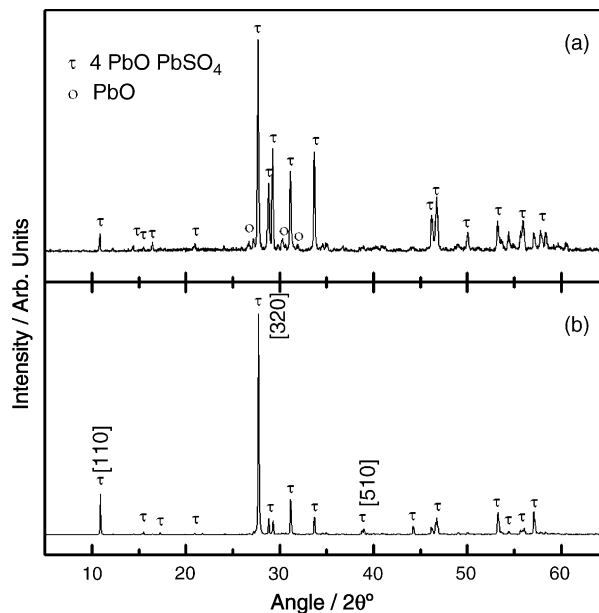


Fig. 1. XRD patterns for samples obtained by hydrothermal synthesis at 200 °C for 1 h (a) without and (b) with stirring.

sulfates such as 1BS were also detected. With stirring, only the 4BS phase was detected in the final product, whichever the time and temperature.

Particle size varied with the heating temperature. The characteristic needle-shaped particles of 4BS phase (Fig. 2a and b) increased in length and width as the synthesis temperature was raised from 125 to 200 °C. Fig. 3 shows the size distribution corresponding to the length of needle for samples obtained with stirring at two different temperatures. Higher temperatures resulted in a wide, non-uniform distribution of sizes, which ranged from 10 to 40  $\mu$ m. The range was much shorter, size distribution more uniform and the maximum below 15  $\mu$ m at the lower temperature. The sample obtained at 125 °C was therefore chosen for the subsequent electrochemical studies on the assumption that the electroformation to PbO<sub>2</sub> would be favoured by a decreased particle size.

The deposits, which were obtained by spraying an aqueous suspension of the 4BS compound over the lead alloy, were highly uniform and homogeneous, with a coating thickness of ca. 100  $\mu$ m (Fig. 2c). Various formation algorithm based on a constant current density were tested with a view to maximizing the efficiency of the 4BS  $\rightarrow$  PbO<sub>2</sub> transformation. Also, the influence of soaking on the formation process was examined.

Table 1  
Phase contents (wt.%) in various hydrothermally prepared samples as determined from their XRD patterns

Temperature (°C)	Time (h)	Phases
125	1	4BS (84) + PbO (16)
200	1	4BS (96) + PbO (4)
200	2	4BS (93) + 1BS (7)
125 <sup>a</sup>	0.5	4BS
200 <sup>a</sup>	1	4BS

<sup>a</sup> Stirring–assisted synthesis.

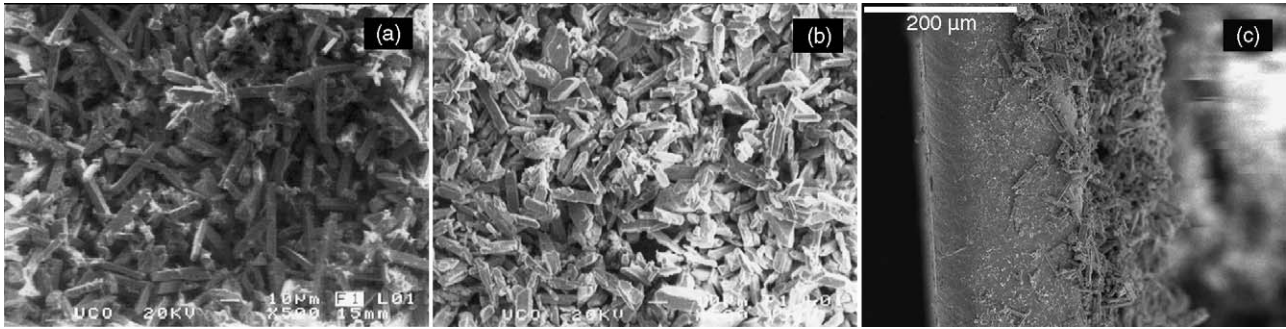


Fig. 2. SEM images of samples obtained by stirring-assisted hydrothermal synthesis at 200 °C (1 h) (a) and 125 °C (0.5 h) (b). (c) Cross-sectional view of the 4BS coating.

Table 2  
Charge algorithms used for the 4BS to PbO<sub>2</sub> transformation

Charge algorithm	Number of steps	% Electrochemical formation	Time (h)
A	1		6
B	2	60 <sup>a</sup>	8
		40	12
C	6	2	0.25
		3	0.5
		15	1
		55	2
		Rest	0.83
		25	1.5

<sup>a</sup> Percentage referred to the total overcharge.

Table 2 shows the charge algorithms used during the formation process and Table 3 the composition of the different phases found in the electrodes after the formation process. The effect of soaking for 30 min prior to the formation stage on the final composition of the charged electrodes is also shown. None of the tests provided 100% conversion to PbO<sub>2</sub>. The best results were obtained with the multi-step algorithm C. Moreover, preliminary soaking step raised the sulfate content and detracted from the 4BS → PbO<sub>2</sub> transformation. Thus, not only pre-soaking,

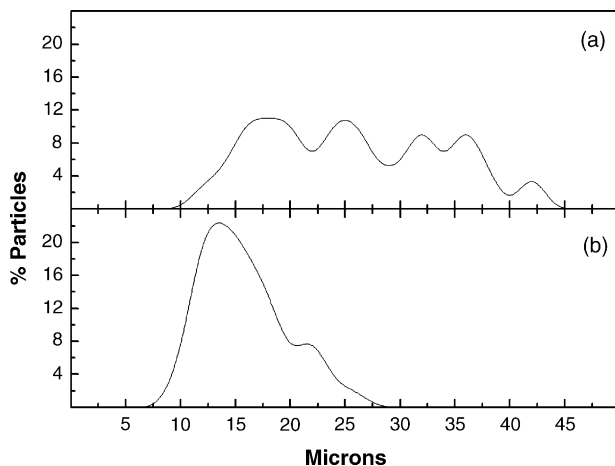


Fig. 3. Needle length distribution of 4BS compounds. Synthesis conditions: 200 °C, 1 h (a) and 125 °C, 0.5 h (b).

but also the charge algorithm used influenced the formation process. These results contradict those reported by Torcheux et al. [7]: our electrodes required no soaking to facilitate the phase transformation. This was the likely result of differences in particle size and/or electrode thickness. Thus, a thinner electrode may require brief soaking for the electrolyte to fill pores and avoid sulfation of the electrode.

The image of Fig. 4a corresponds to the A algorithm; as can be seen, large polyhedral crystals of PbSO<sub>4</sub> prevailed, consistent with the composition data of Table 3. The minor PbO<sub>2</sub> phase was detected as small particles of ill-defined geometry. It is therefore the charge algorithm rather than soaking which governs the formation of large PbSO<sub>4</sub> crystals, which are difficult to convert to PbO<sub>2</sub>. The image of Fig. 4b, which corresponds to the electrode partially formed by applying the first step of C algorithm, is consistent with this finding. Spherical agglomerates of PbO<sub>2</sub> were formed on the surface of 4BS particles that retained their typical needle shape, consistent with previous results of Pavlov and Ruevski [8]. By contrast, in pre-soaked electrodes (Fig. 4c) the needle shape of particles tended to disappear. The elongated particles observed were small polyhedral crystals of PbSO<sub>4</sub>. This phase may therefore form a passivating layer at the beginning of the formation process and subsequently hinder the transformation of 4BS to PbO<sub>2</sub> [13].

The shape of the formation profiles with and without soaking, Fig. 5, supports these conclusions. Thus, the soaked electrode took more than 1 h to start the conversion of PbO<sub>2</sub> owing to the increased electrical resistance of the PbSO<sub>4</sub> crystals. Only β-PbO<sub>2</sub> was present at the end of the formation process. The absence of α-PbO<sub>2</sub>, which was detected by other authors and located in the inner of the plate [14], may be due to the special

Table 3  
Composition obtained of electrodes formed by using various charge algorithms as determined from their XRD patterns

Charge algorithm	% PbO <sub>2</sub>	% PbSO <sub>4</sub>	% 4BS
A <sup>a</sup>	38	45	17
A <sup>b</sup>	18	61	20
B <sup>a</sup>	75	21	4
B <sup>b</sup>	70	28	2
C <sup>a</sup>	95	5	0
C <sup>b</sup>	90	10	0

<sup>a</sup> Without soaking.

<sup>b</sup> With soaking.



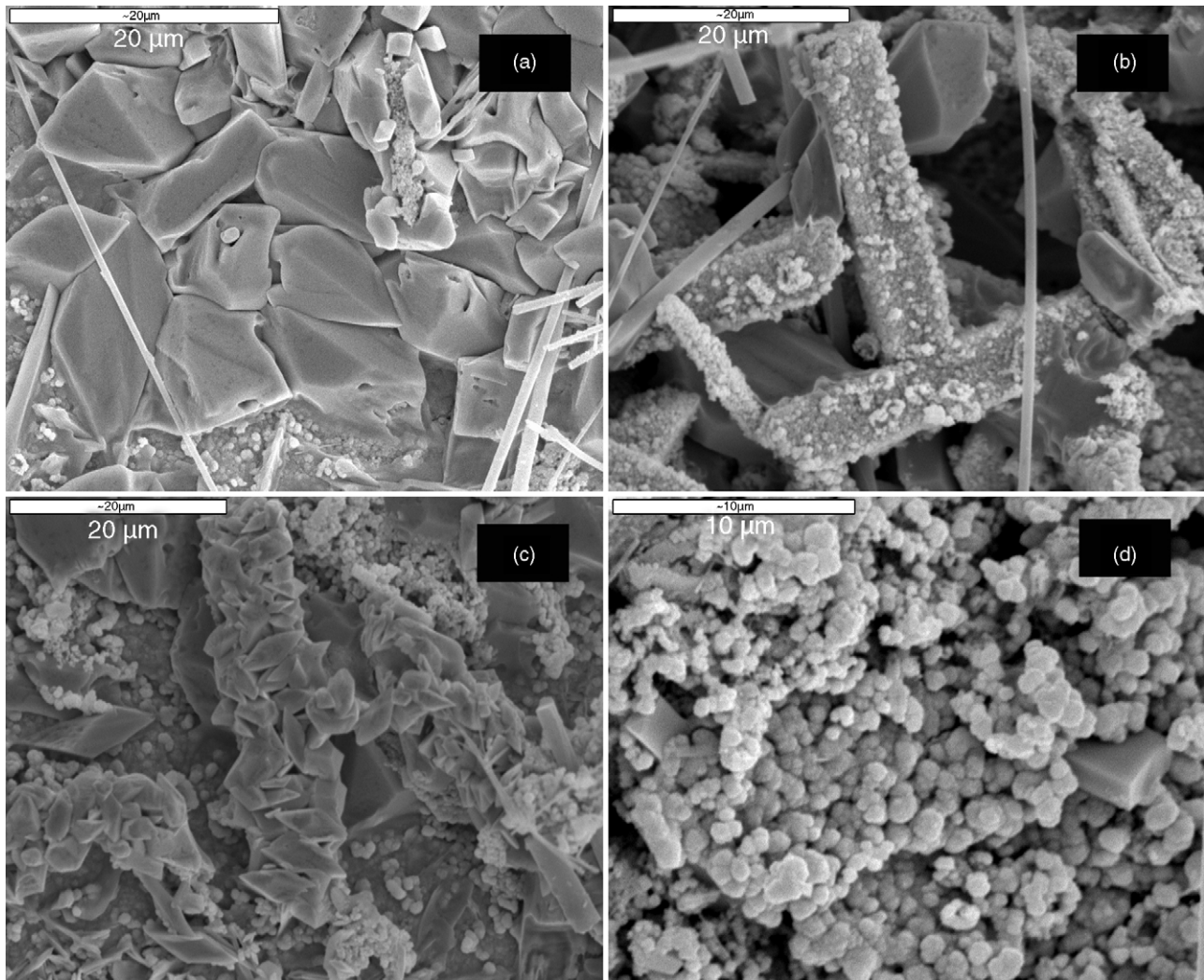


Fig. 4. SEM images of a 4BS electrode electroformed by using algorithm A (a), algorithm C for 50 min without soaking (b) and a soaked electrode (c). (d) Electrode charged at the 15th cycle.

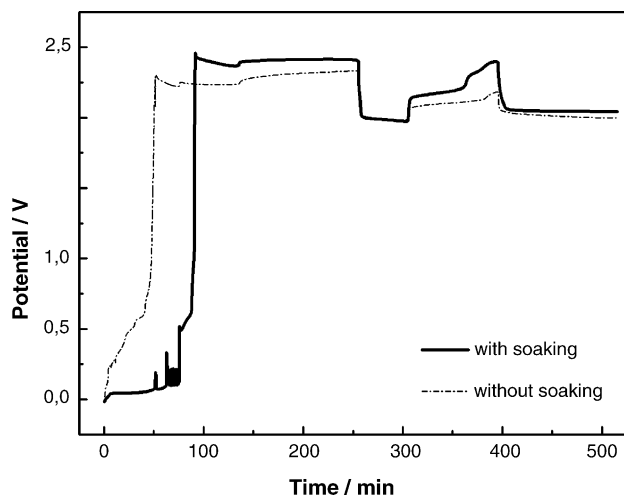


Fig. 5. Potential profiles for charge algorithm C as applied to 4BS thin electrodes.

design of our electrodes. In fact, their reduced thickness may hinder the formation of the pH gradient required to stabilize  $\alpha$ - $\text{PbO}_2$ .

Fig. 6 shows the cyclic voltammetric curves for the electrode obtained by using algorithm C. The differences in the reduction and oxidation scans are worth special note. Thus, a broad peak consisting of two components at 1.31 and 1.38 V

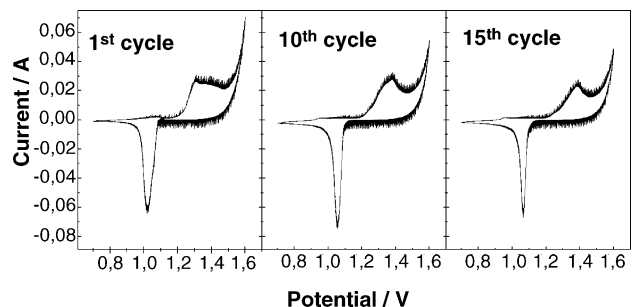


Fig. 6. Cyclic voltammetric curves for an unsoaked 4BS thin electrode formed using algorithm C.

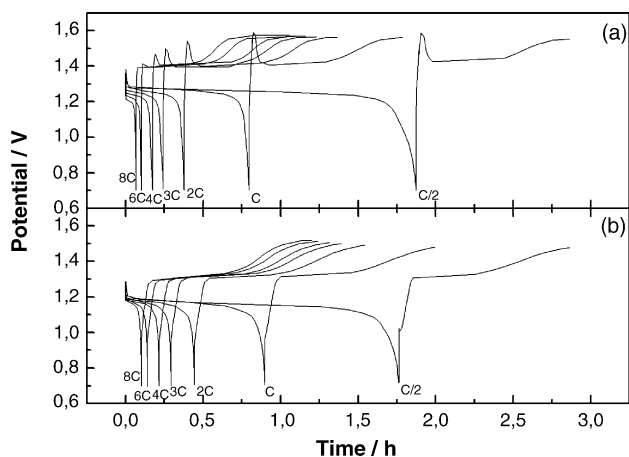


Fig. 7. Charge/discharge curves obtained at different discharge rates for a 4BS thin electrode formed using algorithm C; first cycle (a) and 15th cycle (b).

was obtained over the first few cycles. The low potential signal disappeared as the cycle number increased. One possible origin of these components is the presence of two types of  $\text{PbSO}_4$  crystals at the end of the first discharge [15], some coming from the reduction of  $\text{PbO}_2$  and others not transformed after the formation process (see Table 3). Also, differences in crystal size may account for the two-step charge process. Only one peak in the region of 1.02–1.05 V was observed in the reduction scan for the  $\text{PbO}_2 \rightarrow \text{PbSO}_4$  reaction.

Fig. 7 shows the first discharge/charge curves obtained at different rates, between C/2 and 8C, and also after the first 15 cycles. The main difference observed on cycling, was the absence of a potential peak at the onset of the charge curves. This difference in cell polarization must be related to the presence of unconverted  $\text{PbSO}_4$  after the formation process, conversion of which to  $\text{PbO}_2$  increased with increasing number of cycles. Also, the presence of  $\text{PbSO}_4$  decreased the potential of the discharge plateau under high-discharge regimes. The XRD patterns and SEM images of electrodes charged after 15 cycles (Fig. 4d) confirmed the

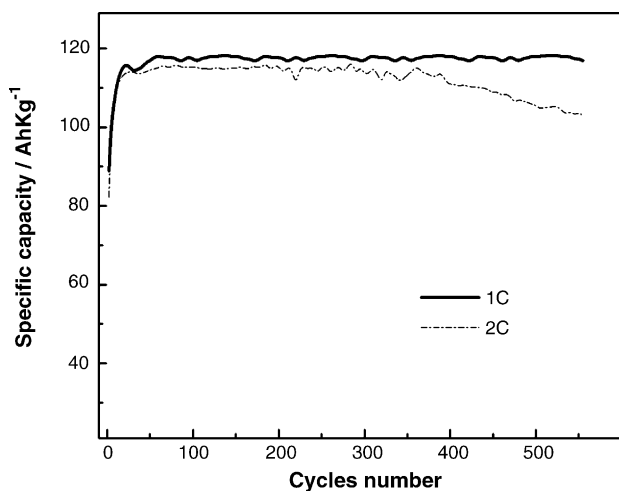


Fig. 8. Plot of discharge capacity vs. cycle number. Cell test conducted at different discharge rates.

formation of  $\text{PbO}_2$  as the sole phase. In this step, the 4BS thin electrodes retained a constant discharge potential on discharging under high-discharge regimes.

Fig. 8 shows the results of the cycling tests at two different discharge rates (1C and 2C). These electrodes delivered the highest specific capacity after the first few cycles. The capacity values obtained at both discharge rates were consistent with those for 4BS phases prepared in other ways [9]. The design of the electrode and the formation charge algorithm used are the origin of the excellent electrochemical performance obtained. The electrodes exhibited good capacity retention on cycling; thus, they retained values around  $115 \text{ Ah Kg}^{-1}$  on prolonged cycling.

#### 4. Conclusions

An hydrothermal method was used to prepare pure lead tetrabasic sulfate. The preparation time is much shorter than in other procedures; also, by using appropriate experimental conditions, particle size can be easily controlled. Thick coatings of active material in aqueous suspensions were deposited by spraying over a lead alloy substrate at  $115^\circ\text{C}$ . No curing or drying was required under these conditions. Only a multi-step charge algorithm for the electroformation process ensured efficient conversion of 4BS into  $\text{PbO}_2$ . On the other hand, pre-soaking detracted from the electrochemical response of the electrode. Cells made from these electrodes exhibited good cycling properties and delivered acceptable capacity values ( $115 \text{ Ah Kg}^{-1}$ ) even at high discharge rates.

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#### References

- [1] D. Pavlov, N. Kapkov, J. Electrochem. Soc. 137 (1990) 21.
- [2] I. Dreier, F. Saez, P. Scharf, R. Wagner, J. Power Sources 85 (2000) 117.
- [3] J. Burbank, J. Electrochem. Soc. 113 (1966) 10.
- [4] R.V. Biagetti, M.C. Weeks, Bell Syst. Tech. J. 49 (1970) 1305.
- [5] D. Pavlov, N. Kapkov, J. Power Sources 31 (1990) 189.
- [6] L.T. Lam, H. Ozgum, L.M.D. Cranswick, D.A.J. Rand, J. Power Sources 42 (1993) 55.
- [7] L. Torcheux, J.P. Vaurijoux, A. de Guibert, J. Power Sources 64 (1997) 81.
- [8] D. Pavlov, S. Ruevski, J. Power Sources 95 (2001) 191.
- [9] S. Grugeon-Dewaele, S. Laurelle, F. Joliveau-Vallat, L. Torcheux, A. Delahaye-Vidal, J. Power Sources 72 (1998) 126.
- [10] A. Caballero, M. Cruz, L. Hernán, J. Morales, L. Sánchez, J. Power Sources 113 (2003) 376.
- [11] J. Morales, G. Petkova, M. Cruz, A. Caballero, Electrochem. Solid State Lett. 7 (2004) A75.
- [12] R.J. Hill, I.C. Madsen, J. Electrochem. Soc. 131 (1984) 1486.
- [13] S. Grugeon-Dewaele, J.B. Leriche, J.M. Tarascon, A. Delahaye-Vidal, L. Torcheux, J.P. Vaurijoux, F. Henn, A. de Guibert, J. Power Sources 64 (1997) 71.
- [14] D. Pavlov, G. Papazov, V. Illiev, J. Electrochem. Soc. 119 (1972) 8.
- [15] Z. Takeara, J. Power Sources 85 (2000) 29.