

Short communication

A novel cureless paste for positive plates in valve-regulated batteries

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Abstract

A new manufacturing technique for positive plates for valve-regulated lead–acid batteries has been developed. This involves a novel paste-preparation method which employs hydrogen peroxide to replace the traditionally used sulfuric acid. After pasting, the plates can be assembled into groups and placed directly into a battery case. Formation can then be performed without the plates undergoing the conventional curing process. Such a non-curing process could reduce production time and costs. More importantly, the resulting plates provide good flexibility which is particularly suitable for spirally-wound battery designs. © 2003 Elsevier B.V. All rights reserved.

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1. Introduction

Lead–acid battery plates have been produced from ‘leady oxide’ for many years [1]. Leady oxide is typically a mixture of 70–80 wt.% lead monoxide and 20–30 wt.% lead particles (‘free lead’) [2]. Conventionally, pastes for positive and negative plates are formed by mixing water and sulfuric acid with leady powder and small quantities of various additive materials. The metallic lead content has to be reduced to 5 wt.% or less after the curing process. A higher content of free lead may result in swelling, warping and/or extensive sludge formation during the formation of positive plates [3]. Though the paste manufacturing processes is generally satisfactory, there are still many aspects that can be improved. For example, the paste must be subjected to curing and drying processes during which temperature and humidity have to be carefully controlled. These processes are time consuming (24–48 h) and require considerable space and energy, and hence increase product cost. Furthermore, the resulting plates are rather rigid and stiff, which makes them suitable for conventional flat-plate battery configurations but not for spirally-wound batteries which require flexible plates [4].

The research reported here describes a novel method of paste preparation for positive plates. The method employs hydrogen peroxide in place of sulfuric acid, and the physical, chemical compositional, structural and morphological properties of the resultant paste are investigated systemati-

cally. The feasibility of applying this new paste in batteries without the conventional curing process is demonstrated.

2. Experimental

2.1. Preparation of positive plate

Pastes based on the use of hydrogen peroxide were prepared by mixing 100 g leady oxide (with 22.5 wt.% free lead, provided by Equal Shine Industry, Hong Kong) with 11 cm³ of hydrogen peroxide solution of different concentration (2, 5, 8 or 10 vol.%) and 13 cm³ distilled water. The procedure involved placing the required amount of leady oxide in container and adding about three-quarters of the required water as quickly as possible (<2 min). The hydrogen peroxide solution was then introduced at a slow rate (over a period of 20 min) and with good dispersion over the paste. Finally, the remainder of the water was added to the mix, and agitation was continued for about 5 min before measurement of the paste density.

The conventional H₂SO₄-based paste was prepared by mixing 100 g leady oxide (as described above) with 5.6 cm³ sulfuric acid (1.40 relative density) and 12.5 cm³ distilled water. The procedures are the same as the method used for preparation of paste based on hydrogen peroxide.

The paste densities were adjusted to 4.0 g cm⁻³. Lead-coated glass-fiber mesh (with a single filament diameter of 0.75 mm) was cut into 40 mm × 35 mm pieces to be used as grids for the test cells. The free lead in the leady oxide and in the pastes was analyzed using a gravimetric

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method. All the plates were pasted manually and had a thickness of 1.2 mm. The paste weight was 10 g per plate.

After pasting, the conventional H₂SO₄-based plate was cured at 50 °C and 95% relative humidity for 48 h in temperature-controlled water bath and then dried at 60 °C for 24 h.

2.2. Material characterization

The free lead contents of the leady oxide and paste were analyzed by means of a gravimetric method. The PbO₂ content of the formed pastes was determined with a titrimetric method. The plates were removed at different formation stages. After the plates were washed and dried, the paste was ground and weighed for titration. Before and after cell formation, the cured and non-cured pastes were subjected to X-ray diffraction (XRD, Philips, model PW1010) for phase analysis. The phase compositions were determined by using the advanced Traces Program [5]. The morphology of the plates was examined with a scanning electron microscope (SEM, Leica, model 440). The specific surface area (BET) of the electrode active materials was measured with a nitrogen adsorption analyzer (Nova, model 1000).

2.3. Cell performance

2.3.1. Cell assembly

The positive plates were directly assembled in test cells without a curing. Each positive plate was placed between two commercial negative plates with separators (absorptive glass-mat, AGM) in between. The plate group was inserted into a commercial battery case, and two separate polycarbonate fixing sheets were added to provide the required plate-group pressure. An amount of H₂SO₄ solution (1.23 relative density) equivalent to 15 cm³ Ah⁻¹ was added and the total cell volume was held constant (plates, separator and electrolyte). The cell was then sealed, and a rubber valve fitted.

2.3.2. Formation

After soaking the plates in electrolyte for 2 h cell formation was conducted at a constant current density of 25 mA g⁻¹. The formation was program controlled with 1 h step followed by a 10 min rest, for a total of 24 repeats (h). Since the capacity of the negative plate was substantially greater than that of the positive plate, the cell was positive limited. The total input capacity was always kept at 600 mAh g⁻¹ versus the positive active material, i.e. 2.5 times the theoretical value for converting PbO to PbO₂.

2.3.3. Discharge properties

After cell formation, the cells were discharged at a current density of 35 mA g⁻¹ and the time for the terminal voltage to fall to 1.70 V was determined. The product of the current and the time gave the discharge capacity. The battery was then returned to full charge.

3. Results and discussion

3.1. Preparation of pastes and plates

Conventional H₂SO₄-based paste was prepared by mixing leady oxide with H₂SO₄. Since the free lead content after paste-mixing was still much higher than 5 wt.%, the content was reduced during the curing-drying process. Under suitable humidity and temperature conditions, the free lead in the paste reacts with oxygen from air, i.e.



The H₂O₂-based paste was prepared by mixing leady oxide with H₂O₂ solution. The following reactions may occur in the paste-mixing process:



Hydrogen peroxide solution is a strong oxidant. When leady oxide was mixed with H₂O₂ solution, the free lead was oxidized to monoxide during the paste-mixing process.

3.2. Analysis of free lead content and surface area

The free lead contents in the pastes are listed in Table 1. The data show that for the cured conventional H₂SO₄-based paste, the free lead content is 2.5 wt.%. The free lead content of the non-cured, hydrogen peroxide pastes decreases as the concentration of H₂O₂ is increased. Except for 2% H₂O₂, the free lead content is below 5 wt.%. These results indicate that 5% hydrogen peroxide solution is sufficient to reduce the free lead content in the paste to an acceptable level. This suggests that hydrogen peroxide is able to convert the free lead to lead oxide (see Eq. (3)) during paste mixing without requiring a curing process.

The specific surface areas of the pastes, before and after formation, were analyzed and are also given in Table 1. The specific surface area of the conventional H₂SO₄-based paste is higher than that of the H₂O₂-based pastes.

Table 1
Physical properties of pastes

Sample	Free lead (wt.%)	Specific surface area (m ² g ⁻¹)	
		Before formation	After formation
H ₂ SO ₄ -based paste (after curing)	2.5	1.25	4.2
H ₂ O ₂ -based paste			
2 vol.%	5.4	1.06	3.12
5 vol.%	4.1	1.10	3.36
8 vol.%	4.0	1.05	3.26
10 vol.%	3.8	10.8	3.43

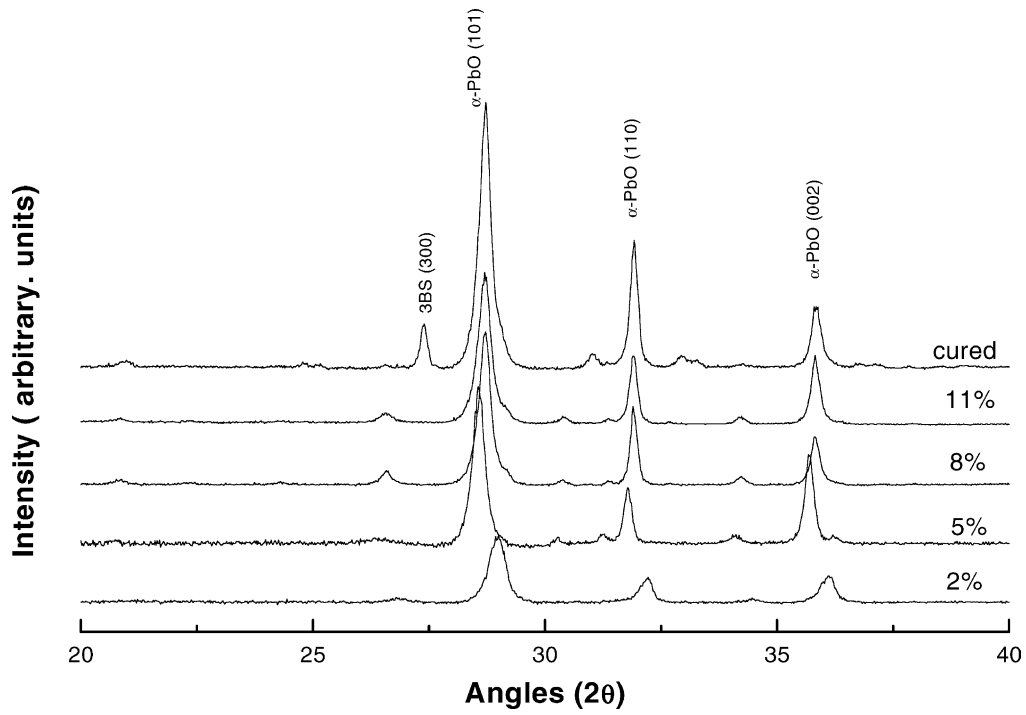


Fig. 1. X-ray diffraction patterns of pastes before formation.

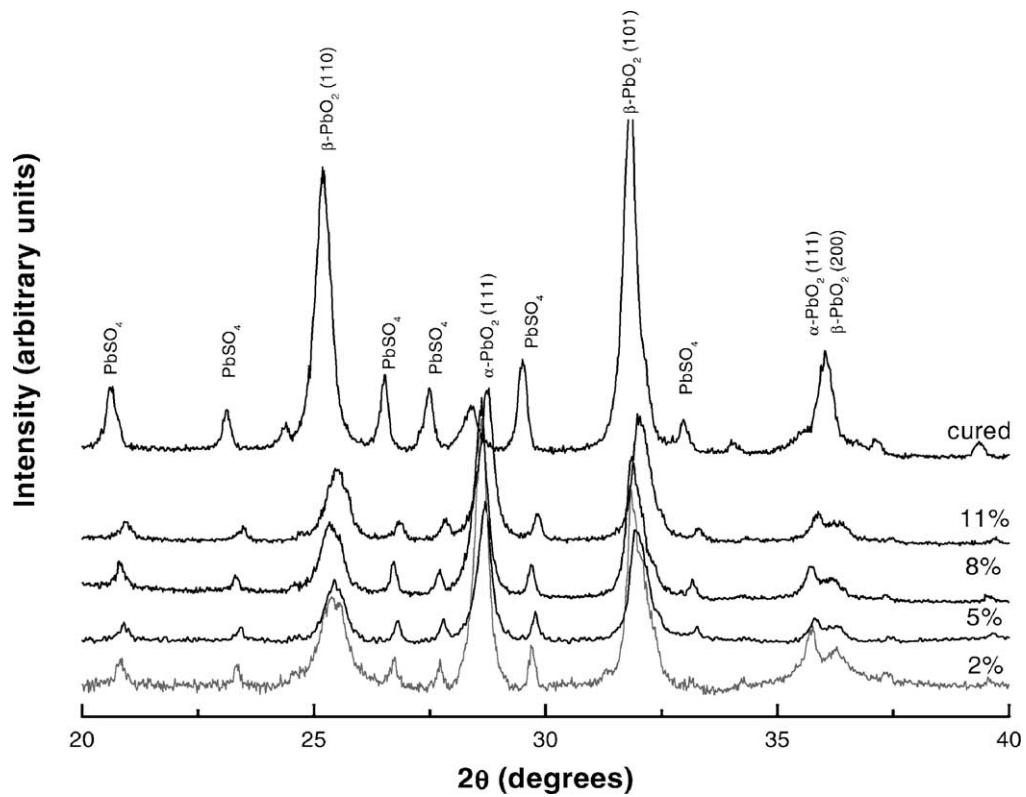


Fig. 2. X-ray diffraction patterns of pastes after formation.

Table 2
Composition of plates before formation

Sample	Composition (wt.%)				
	Pb	3BS	α -PbO	β -PbO	Other
H ₂ SO ₄ -based paste	2.5	21.1	71.0	5.0	0.4
H ₂ O ₂ -based paste					
2 vol.%	5.4	–	85.6	3.7	5.3
5 vol.%	4.1	–	86.9	4.0	5.0
8 vol.%	4.0	–	86.2	4.7	5.1
10 vol.%	3.8	–	87.1	3.7	5.4

3.3. Phase composition

The phase changes of positive plates before and after formation were examined by XRD. The X-ray patterns of non-cured, H₂O₂-based pastes and conventional cured H₂SO₄-based paste before and after formation are shown in Figs. 1 and 2, respectively. Before formation, the cured, conventional, H₂SO₄-based plate contains leady oxide and tribasic lead sulfate (3PbO·PbSO₄·H₂O = 3BS) which are converted mainly to β -PbO₂ with a small fraction of α -PbO₂ after formation. The new H₂O₂-based plate, however, contains mainly leady oxide before formation and is converted to α -PbO₂ and β -PbO₂ after formation.

The phase composition of the pastes before formation are listed in Table 2. The free lead and the α -PbO contents of all the H₂O₂-based plates are higher than those of the conventional, H₂SO₄-based plate. By contrast, the β -PbO contents of all the H₂O₂-based plates are lower than that of the conventional H₂SO₄-based plates. It is not surprising that H₂O₂-based plates contained no 3BS, while 21.1 wt.% is found in the H₂SO₄-based plate. Among the H₂O₂-based plates, as the H₂O₂ concentration is increased, a decreased trend of free lead content and a slightly increased trend of α -PbO content are found. The β -PbO contents increase as the H₂O₂ concentration is increased up to 8%.

The phase compositions of the plates after formation are given in Table 3. The two types of plate show a marked difference in the ratio of β -PbO₂ to α -PbO₂, namely, 13.3 and less than 1.5 for H₂SO₄- and H₂O₂-based plates, respectively. Both the α -PbO and the PbSO₄ contents in the H₂SO₄-based plate are lower than those in the H₂O₂-based

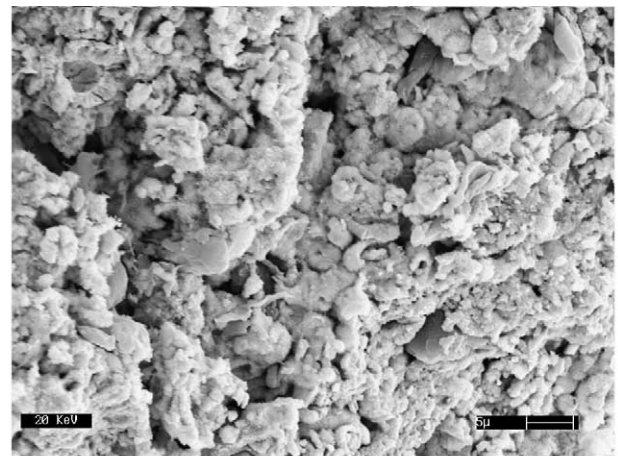
Table 3
Composition of plates after formation

Sample	Composition (wt.%)				
	α -PbO ₂	β -PbO ₂	α -PbO	PbSO ₄	Other
H ₂ SO ₄ -based paste	5.3	70.3	10.7	10.5	3.2
H ₂ O ₂ -based paste					
2 vol.%	32.1	35.3	15.9	13.3	3.59
5 vol.%	30.1	42.9	15.0	12.0	5.14
8 vol.%	29.6	39.5	13.8	12.3	4.90
10 vol.%	33.4	37.4	12.1	12.67	5.15

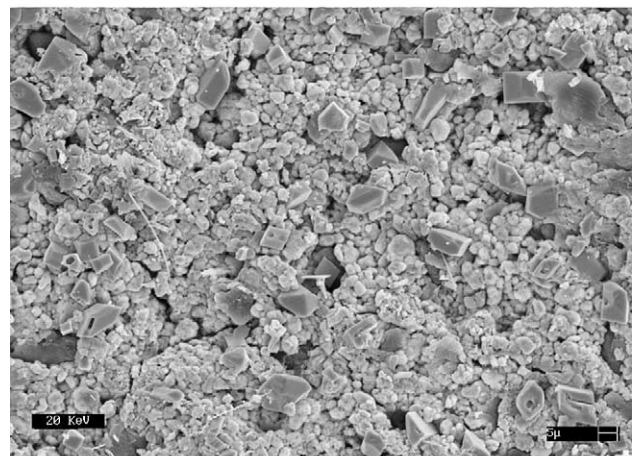
counterparts. The total PbO₂ content in the two types of plates is approximately 70 wt.%. This indicates that effective formation is achieved in both cases.

3.4. Scanning electron microscopy

Scanning electron micrographs reveal that the morphology of H₂O₂-based plates prepared at the four H₂O₂ concentrations is similar before and after formation. Micrographs of H₂SO₄- and H₂O₂-based (5%) plates after formation are shown in Fig. 3. The H₂O₂-based plate is prone to form spherical agglomerates, which appear denser than the agglomerates on the surface of the H₂SO₄-based plate. This difference in crystal morphology can be explained by the different phase transformation mechanisms during the plate formation. The non-cured (H₂O₂-based) plate may be formed from its original state, mainly from PbO → Pb²⁺ → PbO₂, without going through the sequence of PbO → 3BS → PbO₂. This could involve a smaller change in volume during the formation and would be favorable for reducing the volume change during subsequent charge–discharge cycling.



(a)



(b)

Fig. 3. Scanning electron micrographs of plates after formation: (a) H₂SO₄-based plate; (b) H₂O₂-based plate.

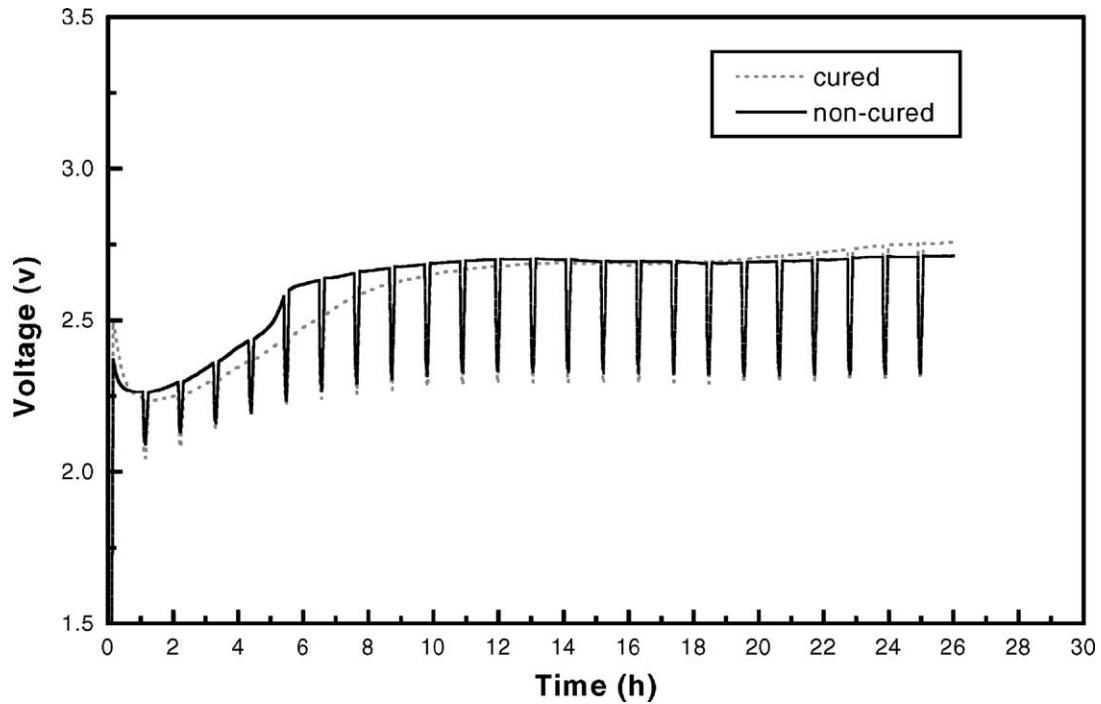


Fig. 4. Cell voltage profiles of a conventional cured plate and non-cured plate during formation.

3.5. Plate formation

The voltage behaviour during battery formation for a cured H_2SO_4 -based plate and a non-cured H_2O_2 -based plate prepared with 5% H_2O_2 are shown in Fig. 4. The formation voltage is lower for the cured plate. This indicates a higher formation efficiency for the cured plate. The voltage curve

for the non-cured plate crosses that for the cured plate at a formation time of about 18 h. This may be due to the fact that the cured plate is better formed at this stage, and a large proportion of the current supports gassing, which occurs at a higher voltage. To support this conclusion, an experiment was conducted in which the formation processes of the cured and non-cured plate were interrupted at given settings of

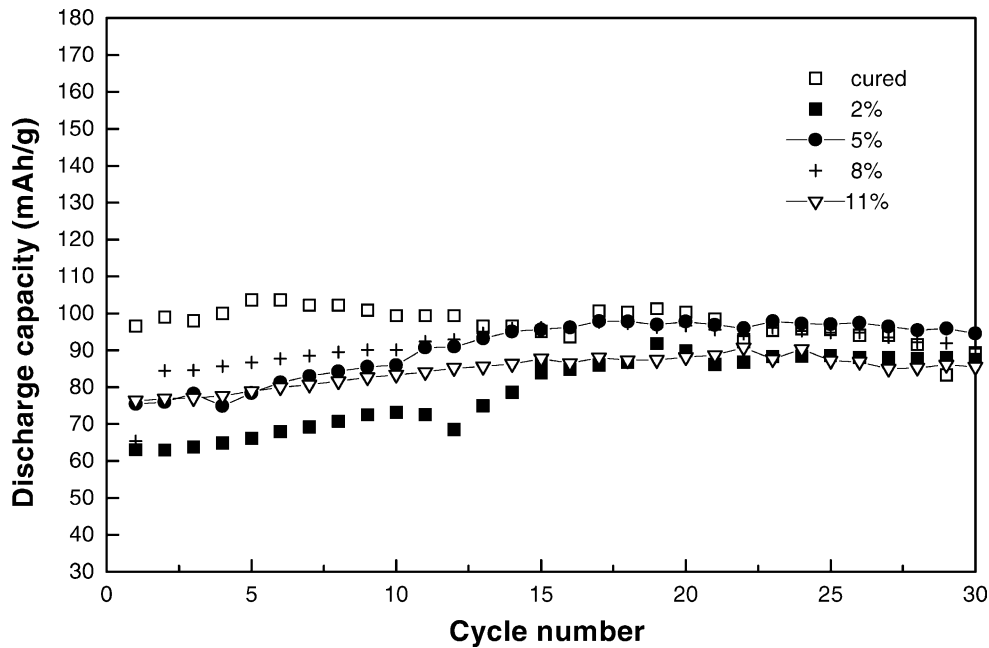


Fig. 5. Discharge capacity vs. cycle number for cured and non-cured plates. The latter plates are prepared with different concentration of hydrogen peroxide solution.

Table 4
Effect of input capacity on formation efficiency

Input capacity (%)	Cured plate		Non-cured plate (5% H ₂ O ₂)	
	PbO ₂ (wt.%)	Utilization (%)	PbO ₂ (wt.%)	Utilization (%)
75	37.1	28.3	35.5	26.9
100	41.3	32.9	38.2	31.1
150	51.5	36.5	51.3	35.5
200	71.8	38.1	68.9	35.8
250	72.9	39.3	68.9	37.9

input capacity. The plates were removed and tested for reserve capacity, or washed, dried and analyzed for chemical composition. The results are summarized in Table 4. The non-cured, H₂O₂-based plate shows lower PbO₂, and lower reserve capacity at all stages of formation. Since the values of these two parameters indicate the formation efficiency, it is clear that the non-cured plate has a slightly lower formation efficiency.

3.6. Discharge of positive plates

The plots of discharge capacity versus the cycle number for the cells made from conventional cured and non-cured plates are given in Fig. 5. The initial capacities of the non-cured, H₂O₂-based plates are all lower than those of the cured, H₂SO₄-based plate. This observation may be at-

tributed to the lower formation efficiency of the non-cured plate. After 15 cycles, the discharge capacities of the H₂O₂-based plates prepared with 5 and 8% H₂SO₄ content increase to a level which is similar to that of the cured plate.

4. Conclusions

Non-cured, H₂O₂-based plates can be prepared as readily as conventional cured plates under the same process, but their capacities are slightly lower. The use of hydrogen peroxide solution to replace conventional sulfuric acid solution can convert free lead to lead oxide during paste mixing, so that the curing process can be eliminated. This technique can greatly simplify the manufacturing process, and reduce production time and cost. This technique provides the plate with sufficient flexibility for fabrication of batteries with a spirally-wound cell configuration.

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