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# Stannous sulfate as an electrolyte additive for lead acid battery made from a novel ultrafine leady oxide



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### HIGHLIGHTS

- The optimal addition of  $SnSO_4$  in electrolyte of lead acid battery is 2.24 mmol L<sup>-1</sup>.
- The novel leady oxides are used as active material of working electrode.
- The novel leady oxides are used as active material of positive plate.
- SnSO<sub>4</sub> as an electrolyte additive could effectively decrease crystal particles in active materials.
- SnSO<sub>4</sub> as an electrolyte additive has a positive effect on restriction of irreversible sulfation.

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## ABSTRACT

The effects of SnSO<sub>4</sub> as an electrolyte additive on the microstructure of positive plate and electrochemical performance of lead acid battery made from a novel leady oxide are investigated. The novel leady oxide is synthesized through leaching of spent lead paste in citric acid solution. The novel leady oxides are used to prepare working electrode (WE) subjected to electrochemical cyclic voltammetry (CV) tests. Moreover, the novel leady oxides are used as active materials of positive plate assembled as a testing battery of 1.85 A h capacity. In CV tests, SEM/EDX results show that the major crystalline phase of the paste in WE after CV cycles is PbSO<sub>4</sub>. The larger column-shaped PbSO<sub>4</sub> crystals easily generate in the paste of WE without an electrolyte additive of SnSO<sub>4</sub>. However, PbSO<sub>4</sub> crystals significantly become smaller with the addition of SnSO<sub>4</sub> in the electrolyte. In batteries testing, SEM results show that an electrolyte additive of SnSO<sub>4</sub> could effectively decrease PbO<sub>2</sub> particle size in the positive active materials of the teardown battery at the end of charging procedure. It is indicated that an electrolyte additive of SnSO<sub>4</sub> could have a positive influence on restraining larger particles of irreversible sulfation in charge/discharge cycles of battery testing.

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## 1. Introduction

Recently nano-structured materials have been attracting much interest because they are distinguished from the conventional materials by their small particle size and large specific area giving rise potentially to remarkable electrochemical performance in electrodes [1,2]. Some researchers have reported the synthesis of nano-structured leady oxide for application as active materials in lead acid battery. Salavati et al. [3] reported that nano-size lead oxide powder with an average particle size of 35 nm could be synthesized by decomposing lead oxalate at 500 °C. Karami et al. [4,5] synthesized uniform leady oxide nanostructures by the sonochemical method. The electrochemical tests showed a large discharge capacity and excellent cycle characteristics, however the starting materials they used are pure chemical reagents, i.e.  $Pb(NO_3)_2$ . In our previous researches [6,7], lead citrate  $(Pb_3(C_6H_5O_7)_2 \cdot 3H_2O)$  was synthesized from spent lead acid battery pastes in citric acid system, and nano lead oxide with particle size of 100-200 nm was obtained from calcination-combustion of lead citrate.

Based on self-synthesized leady oxides, the initial capacity of lead acid battery is excellent, while the cycle life is relatively poor [8,9]. Some other researches [10,11] were conducted to synthesize nanostructured lead oxide through chemical reaction. The nanostructured lead oxide, as anode and cathode of lead-acid batteries. also showed relatively poor cycle life compared with traditional lead-acid batteries made from ball-milled leady oxide [12.13]. In order to improve the cycle performance of novel lead-acid batteries, some solid or liquid additives were reported to be added into the electrolyte. Yang [14] demonstrated that the addition of SnSO<sub>4</sub> as an electrolyte additive significantly improved the performance of deep cycle batteries, and also effectively improved the battery charging acceptance and reduced water loss. However, they used the traditional lead acid battery in factory as subjects, rarely described the influence mechanism of SnSO<sub>4</sub> and did not take into account the morphology changes of the active materials. H<sub>3</sub>PO<sub>4</sub> as electrolyte additive was studied in the electro-mobile and the leadacid battery electrochemistry field [15,16]. The results show that H<sub>3</sub>PO<sub>4</sub> can reduce the dependence of discharge capacity on the charge/discharge rate and improve the discharge capacity.

In general, there are more attentions on the cycle performance of the novel lead acid battery, and influence mechanism of the additives in electrolyte is not clear currently. Bhattacharya [17] suggested that Sn<sup>2+</sup> is adsorbed on the plate to improve the plate corrosion resistance by changing the structure of the surface layer of PbSO<sub>4</sub>. Wei [18] studied the effect of SnSO<sub>4</sub> on deep-discharge capacity of lead acid battery using cyclic-voltammetry method. The study showed that Sn<sup>2+</sup> ions could be reduced to tin on the negative plates, or could be oxidized to Sn<sup>4+</sup> species on the positive plates, which are beneficial to the operation of lead acid batteries. Liu [19] found that with the addition of moderate dose Na<sub>2</sub>SO<sub>4</sub> in electrolyte, the capacity and charge acceptance of lead battery can be improved, and the water loss of battery can be reduced, so as to prolong the cycle life of the battery. Chahmana [20] studied the effect of various ions containing Sn<sup>2+</sup>, Sb<sup>3+</sup>, Co<sup>2+</sup>, Mg<sup>2+</sup> and Al<sup>3+</sup> in electrolyte on the formation of PbO<sub>2</sub>. Some metal ions enhanced the proportion of PbO<sub>2</sub> in gel area which could improve the cohesiveness with other materials. In battery testing or usage, active material loss, early capacity loss, and irreversible sulfation are three main reasons of the battery failure [21–23]. Some battery failed since the large particle of PbSO<sub>4</sub> could not turn into PbO<sub>2</sub> timely, namely irreversible PbSO<sub>4</sub>. This kind of irreversible PbSO<sub>4</sub> commonly causes lead acid battery failure. The additives in electrolytes have influences on the performance of lead acid battery, especially on the transformation of PbSO<sub>4</sub> into PbO<sub>2</sub> in the active material of positive plate. However, the effects of the additives in electrolytes on the morphologies of lead sulfate have seldom been investigated.

In this paper, self-synthesized leady oxides were used as active materials to make the working electrode (WE) in the threeelectrode system and the positive plate in the testing battery. Electrolytes with the addition of different concentration of  $SnSO_4$  were used to study the influence of  $SnSO_4$  as an electrolyte additive in both CV testing and battery testing. The properties of the resulting leady oxide product, microstructure, electrochemical and battery performances of the as-prepared samples were discussed. The flow sheet for this route is shown in Fig. 1.

#### 2. Experimental

#### 2.1. Materials and chemicals

Spent lead acid battery pastes were provided by Hubei Jinyang Metallurgical Co., Ltd., China. The chemical compositions of the spent lead acid battery pastes are shown in Table S3 in Supplementary information.

Sodium citrate (Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>·2H<sub>2</sub>O, 99% purity), citric acid (C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>·H<sub>2</sub>O, 99.5% purity), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, 30% purity), stannous sulfate (SnSO<sub>4</sub>, 99% purity) and concentrated sulfuric acid (98% purity) were obtained from Sino-pharmaceutical Company of China.

### 2.2. Preparation of novel leady oxide

Self-synthesized leady oxides used as active materials were prepared by two steps. In the first step, 100 g of spent lead pastes were added to a leaching solution containing specific amount of sodium citrate, citric acid and 30 W/V% hydrogen peroxide [24]. The conditions of leaching process are provided in Supplementary



Fig. 1. The flow sheet of experiments.

information. In this step, the lead citrate precursor was formed as a white precipitate. Leaching experiment was carried out under constant stirring at speed of 650 rpm to maintain full suspension of the slurry. After leaching in homoeothermic water bath at 50 °C for 20 h, the lead citrate were washed with distilled water, vacuum filtrated and dried at 100 °C. In the second step, the lead citrate precursor was calcined in tube furnace in a static air at 375 °C for 1 h and novel leady oxide products were obtained.

#### 2.3. Preparation of working electrode and electrochemical testing

The novel leady oxide was used as active material in the paste of WE in a three-electrode system. The WE made from novel leady oxide and corresponding three-electrode system are presented in Fig. 2. The counter electrode (CE) was double platinum electrode, and the reference electrode (RE) was an Hg/Hg<sub>2</sub>SO<sub>4</sub>/K<sub>2</sub>SO<sub>4</sub> (sat.) electrode. WEs (26.5 mm  $\times$  28.5 mm) for cyclic voltammetry (CV) testing were prepared with some procedures including pastemixing, paste-curing, washing and drying treatment [9]. The detailed procedure for the preparation of WE is provided in Supplementary information. CV was carried out using VMP-2 electrochemical workstation from Bio-logic Science Instruments SAS. A scanning speed of 10 mV  $s^{-1}$  was used within a potential range of +0.5 to +1.5 V. The electrolyte was 3 mol L<sup>-1</sup> sulfuric acid solution with addition of different concentration of SnSO<sub>4</sub>. Various amount of SnSO<sub>4</sub> was added into 50 mL sulfur acid solution respectively, and after stirring for 5 min until SnSO<sub>4</sub> was completely dissolved to obtain homogenous electrolytes with different dosage of SnSO<sub>4</sub>. The WE symbol and corresponding concentration of SnSO<sub>4</sub> in electrolyte are shown in Table 1.

The CV cycle number of each WE is 250 times, and the total scanning time of the all CV cycles is about 12.5 h. When CV tests finished at the end of discharging procedure in the 250th CV tests, the WE was washed with distilled water for 5 min until the electrolyte in WE surface was cleaned and then dried in oven. After dried, the teardown pastes scraped from a half plate of WE were ground and used in XRD analysis, and the surface of the teardown pastes scraped from the other half plate of WE were used in SEM analysis.

#### 2.4. Preparation of the positive plate and testing battery assembly

The novel leady oxide was used as active material in the paste of positive plate. The positive plates (39.5 mm  $\times$  65.6 mm) for designed 2 Ah testing battery were prepared with the same procedures as WE. The detailed battery assembly procedure is also



Fig. 2. The schematic diagram of three electrode system (a) and working electrode (b).

#### Table 1

Concentration of  $SnSO_4$  added to the electrolyte in three-electrode system and testing battery.

| WE symbol<br>in CV tests | Battery symbol in<br>testing battery | Concentration of $SnSO_4$ (mmol $L^{-1}$ ) | Volume of electrolyte<br>in testing battery (mL) |
|--------------------------|--------------------------------------|--|--|
| Sn-0                     | B-Sn-0                               | 0  | 47   |
| Sn-1                     | B-Sn-1                               | 0.45                                       | 47   |
| Sn-2                     | B-Sn-2                               | 2.24                                       | 47   |
| Sn-3                     | B-Sn-3                               | 4.48                                       | 47   |
| Sn-4                     | B-Sn-4                               | 22.40                                      | 47   |

provided in Supplementary information. On the basis of numerous preliminary experiments, an ideal strength of pasted positive plate could be prepared with the novel leady oxide of optimum amount of 25 g for each piece of the positive plate. The theoretical capacity of assembled battery corresponding to 25 g novel leady oxide as active material is 1.85 Ah. The grids were low antimony alloys of Sn (0.28–0.32 wt%) Al (0.015–0.020 wt%)–Ca (0.09–0.10 wt%)–Pb provided by Inter Power Co., Ltd., China. In the battery assembly step, each positive plate was coupled with two commercial negative plates made from ball-milled leady oxides soaking in an electrolyte which contains sulfur acid solution (1.335 g cm<sup>-3</sup>) and different content of SnSO<sub>4</sub>. The battery symbol and corresponding concentration of SnSO<sub>4</sub> in electrolyte are also shown in Table 1.

#### 2.5. Battery testing

The battery testing includes initial capacity and cycling test using Land battery testing device (CT2001B). The charging conditions of initial capacity and cycling test are the same. First placing for 30 min and charging at a constant current of 200 mA until voltage reached 2.45 V. After that, charging at a constant voltage of 2.45 V for 12 h and placing for 2 h. The initial capacity of the battery was tested at a constant discharge current of 100 mA until terminal voltage reached 1.75 V. Both the charging and the discharging cycle tests were performed repeatedly at a constant discharge current of 200 mA with a cut-off terminal voltage of 1.75 V (depth of discharge, DOD = 100%).

### 2.6. Battery torn down

After a certain times charge/discharge cycles, we tore the batteries down after a final charging procedure. The teardown positive plate was washed in distilled water for 5 min until electrolyte in surface was washed away, and dried in oven at 75 °C for 10 h. First, the expansion rate of the plate after drying was measured. The expansion rate of the plate was calculated by Equation (1):

Expansion rate of the plate (%) = 
$$\frac{T_1 - T_2}{T_2} \times 100\%$$
 (1)

where,  $T_1$  (mm) is the thickness of the teardown plate;  $T_2$  (mm) is the initial thickness of plate before the charging/discharging cycles. The thickness of the teardown positive plate is the average of measuring value of upper, middle, and lower section.

The contents of  $PbSO_4$  and  $PbO_2$  in positive paste which were scraped from the teardown positive plates were measured. Powder XRD analysis and SEM of the teardown positive active materials were also investigated.

#### 2.7. XRD analysis

The crystalline phases of leady oxides and the teardown pastes in both WE of three-electrode system and positive plate of testing battery were identified by a D/MAX 2550 X-ray diffractometer (RIGAKU Corporation, Tokyo, Japan) using Cu  $K_{\alpha}$  radiation  $(\lambda=1.54$  Å) at 300 mA and 40 kV.

### 2.8. SEM analysis

The morphologies of leady oxides, the teardown pastes in both WE of three-electrode system and positive plate of testing battery were investigated with scanning electron microscopy (SEM, Sirion 200, FEI, Holland) operated at 10 kV after coating the samples with gold. EDX spectra of the samples were collected on an ultra-thin window (UTW) X-ray detector equipped with Sirion 200 SEM.

## 3. Results and discussion

#### 3.1. Characterization of leady oxides

As shown in Fig. 3(b), the XRD patterns of self-synthesized leady oxides specimens indicate that they mainly comprise  $\beta$ -PbO and  $\alpha$ -PbO with little amount of Pb and Pb<sub>3</sub>O<sub>4</sub>. The SEM images of the self-synthesized leady oxides are shown in Fig. 3(a). The micromorphology of the leady oxides can be perceived as a porous structure with ultrafine particles, which provide more contact areas for electrochemical reaction of the active materials, and benefits for the increase of capacity.

Other physicochemical characteristics of leady oxides are summarized in Table 2. It can be seen that the apparent density of selfsynthesized leady oxide is much lower than the traditional ballmilled leady oxide, which was provided by Wuhan Changguang Power Sources. Co. Ltd. The degree of oxidation (oxidizability) ranges from about 70 to 85 wt%. Owing to the porous structure shown in Fig. 3(a), the specific surface area of self-synthesized leady oxides is much higher. Therefore the self-synthesized leady oxides exhibit much higher water absorption value and acidabsorption value than traditional leady oxide and could show higher initial discharge capacity potentially.

# 3.2. The effect of $SnSO_4$ added in electrolyte on the electrochemical performance of working electrode made from novel leady oxides

As described in Section 2.3, the prepared WE was used in a three-electrode system with different concentration of  $SnSO_4$  added in an electrolyte. Fig. 4(a) shows the 100th CV curves of WE in an electrolyte with different concentration of  $SnSO_4$ . As shown in Fig. 4(b), the ratio of charge capacity to discharge capacity of WE almost maintains 1.0 when cycle number reaches 100, which

indicates the anode reaction has achieved steady state. CV results show that with the addition of SnSO<sub>4</sub> in an electrolyte, both the reduction peak currents and oxygen evolution currents increase first and then decrease, and the reduction peak currents reach a peak within a current of -700 mA when the SnSO<sub>4</sub> concentration is 2.24 mmol L<sup>-1</sup>. The results indicate that moderate concentration of  $\rm Sn^{2+}$  could promote the reduction  $\rm Pb^{4+}$  to  $\rm Pb^{2+}.$  With lower concentration of  $\rm SnSO_4$  (0–2.24 mmol  $\rm L^{-1}$ ), the reduction reaction initiates in the voltage of 0.85 V (vs. Ref). However, the voltage moves to 0.65 V (vs. Ref) with higher concentration of SnSO<sub>4</sub>  $(2.24-22.4 \text{ mmol L}^{-1})$ . Generally, the decrease of reduction voltage in reverse scanning indicates that the reduction reaction becomes difficult to take place. Fig. S2 in Supplementary information shows the discharge capacity of WE in an electrolyte with different concentration of SnSO<sub>4</sub>. The reduction peak and oxygen peak of WE Sn-0 disappear after the 100th CV cycle, so its discharge capacity after the 100th CV cycle declines sharply to zero at the 100th CV cycle. The reason might be that sudden internal short circuit happens at the 100th CV cycle, which causes large crystals as PbSO<sub>4</sub>. And then the more irreversible PbSO<sub>4</sub> particles with larger crystal size cause the decrease of conductivity of WE and then lead to the failure of the discharging. The morphologies of the teardown paste will be investigated in the following Section. As shown in Fig. S2, the optimum SnSO<sub>4</sub> concentration in an electrolyte is 2.24 mmol L<sup>-1</sup>, and the corresponding discharge capacity of WE Sn-2 is significantly larger than that of WE with other SnSO<sub>4</sub> concentration in an electrolvte.

# 3.3. Microstructural analysis of the spent working electrode after CV tests

The XRD patterns of the teardown pastes in the WEs with the addition of various concentration of  $SnSO_4$  in an electrolyte are shown in Fig. 5. Since each WE was tore down at the end of discharging procedure in the 250th CV tests, the major crystalline phase in the teardown paste is PbSO<sub>4</sub>, and a little amount of unreduced PbO<sub>2</sub> and metallic Pb is identified at the end of discharging procedure.

The SEM images of the teardown paste in the outer surface of WE plates at the 250th CV cycles are shown in Fig. 6. As shown in Fig. 6(a-c), when the concentration of SnSO<sub>4</sub> was relative low at  $0-2.24 \text{ mmol L}^{-1}$ , two types of morphologies appeared in the outer surface of WE plates, which were long column-shaped and small granular-shaped crystals. As shown in Fig. 6(d-e), the new morphology appeared as flake-shaped crystals. As shown in Fig. S3, the EDX analysis result of the long column-shaped crystal show



Fig. 3. (a) The SEM image of novel leady oxide prepared at 375 °C in tube furnace; (b) the XRD pattern of novel leady oxide prepared at 375 °C in tube furnace.

#### Table 2

| The physicochemical | characteristics of the nov | al leady ovide com | nared to traditional | hall_milled leady ovide |
|---------------------|----------------------------|--------------------|----------------------|-------------------------|
| The physicoenennear | characteristics of the nov | ci icauy oxiuc com | parcu to traditional | Dan-mineu icauy oniuc.  |

| Types of lead oxide                  | Apparent Density/g cm <sup>-3</sup> | Oxidizability/% | Water-absorption value/ml kg <sup>-1</sup> | Acid-absorption value/g $kg^{-1}$ |
|--------------------------------------|-------------------------------------|-----------------|--|-----------------------------------|
| Self-synthesized leady oxide         | 1.32                                | 82.2            | 249.4                                      | 459.1                             |
| Traditional leady oxide <sup>a</sup> | 1.93                                | 83.2            | 110.0                                      | 381.3                             |

<sup>a</sup> Note: The traditional ball-milled leady oxide was provided by Wuhan Changguang Power Sources. Co. Ltd.



**Fig. 4.** The CV results of WE: (a) The 100th CV curve and (b) the ratio of charge capacity to discharge capacity of working electrodes in an electrolyte with the addition of various concentration of SnSO<sub>4</sub>.

that the major elements of large column-shaped crystal were Pb, S, and O, and the molar ratio of Pb:S:O was approximately 1:1:4, indicating that column-shaped particle was PbSO<sub>4</sub>. The flake-shaped crystal was identified as a molar ratio of Pb:S:O of approximately 1:1:7, which indicated that the flake-shaped crystal could be mainly composed of PbSO<sub>4</sub> and PbO<sub>2</sub>.

On the outer surface of WE plates, the active materials which react with sulfuric acid directly, grow up as charge/discharge cycles proceeding, and eventually form irreversible column-shaped PbSO<sub>4</sub> larger particles, as shown in Fig. 6(a). With the addition of Sn<sup>2+</sup> in the electrolyte, the proportion of PbSO<sub>4</sub> large particles significantly decreased (Fig. 6(b) and (c)). When the concentration of Sn<sup>2+</sup> was 2.24 mmol L<sup>-1</sup> in Sn-2, the PbSO<sub>4</sub> particles became fine and uniform, which was beneficial for the electrochemical performance. It is consistent with the maximum value of the discharge capacity of WE of Sn-2 with 2.24 mmol L<sup>-1</sup> of SnSO<sub>4</sub> as shown in Fig. S2. As the ionic radius of Sn<sup>2+</sup> is smaller than Pb<sup>2+</sup>, PbSO<sub>4</sub> could be generated during the reduction reaction with Sn<sup>2+</sup> as the crystal nuclei, resulting in the formation of smaller particles [17]. When the concentration of SnSO<sub>4</sub> in an electrolyte increased up to



**Fig. 5.** The XRD patterns of the teardown pastes in the working electrodes with the addition of various concentration of  $SnSO_4$  in an electrolyte at the end of discharging procedure of the 250th CV tests.

4.48–22.4 mmol  $L^{-1}$ , the outer surface of the WE plate gradually formed as a flake-shaped particle, as shown in Fig. 6(d).

In general, the microstructure results show that electrolyte additive of SnSO<sub>4</sub> had a significant effects on the morphology of lead sulfate crystals in WE plate after numerous CV tests. The results indicated that the optimum dosage of electrolyte additive of SnSO<sub>4</sub> in Sn-2 sample could potentially have a positive influence on restriction of crystal growth of column-shaped PbSO<sub>4</sub> and restraining irreversible sulfation larger particles in charge/discharge cycles of testing battery.

# 3.4. The effect of SnSO<sub>4</sub> added in electrolyte on the battery performance of testing battery

Fig. S4 shows the change of 10 h capacity retention ratio of the testing batteries accompanying the cycle number with different concentrations of  $SnSO_4$  added in an electrolyte along.  $C_1$  is the initial 10 h rate capacity of battery, and  $C_n$  is the n times of 10 h rate capacity of battery. From Fig. S4, the capacity retention ratio of all batteries remained about 80% before 40 cycles, and dropped to below 80% in the subsequent cycles. After the 10th charging/discharging cycles, battery B-Sn-2 showed relatively better property in the capacity retention ratio and the discharge stability. It is consistent with the optimum  $SnSO_4$  concentration in an electrolyte for Sn-2 shown in Fig. S2.

# 3.5. Microstructural characteristics of the pastes of positive plates in the teardown batteries

After certain times of charge and discharge cycles, batteries of B-Sn-0, B-Sn-1, B-Sn-2, and B-Sn-4 were tore down after a final charging procedure. Because the discharge duration of each battery



**Fig. 6.** The SEM images of the teardown paste in the outer surface of working electrode plates at the 250th CV cycles: (a) Sn-0 without SnSO<sub>4</sub>; (b) Sn-1 with 0.45 mmol  $L^{-1}$  SnSO<sub>4</sub>; (c) Sn-2 with 2.24 mmol  $L^{-1}$  SnSO<sub>4</sub>; (d) Sn-3 with 4.48 mmol  $L^{-1}$  SnSO<sub>4</sub>; and (e) Sn-4 with 22.40 mmol  $L^{-1}$  SnSO<sub>4</sub> in an electrolyte.

is much different, the different cycles result in correspondingly different teardown numbers. Table S4 shows the content of  $PbSO_4$  and  $PbO_2$  in the pastes of positive plate and the expansion rate of the positive plate in the disassembled batteries.

The content of PbO<sub>2</sub> in the paste of positive plate after torn down exceeds 70%. The content of 78% in battery B-Sn-2 was the highest, which indicated that the conversion ratio of PbSO<sub>4</sub> to PbO<sub>2</sub> was relatively higher. The expansion rate of positive plate was between 2 and 4 %.

As shown in Fig. S5, major crystalline phases of the teardown paste in positive plates were identified as PbO<sub>2</sub> and PbSO<sub>4</sub>.

SEM images of the positive pastes from the teardown battery are shown in Fig. S6. With the increase of the dosage of  $Sn^{2+}$  in an electrolyte, the particle size of the crystals in the teardown pastes significantly decreased. As shown in the EDX spectra of Fig. S7, the major elements of large particles were Pb and O with a molar ratio of Pb:O of 1:2.7, indicating the large crystal particles were PbO<sub>2</sub>. In the battery positive reaction,  $\mathrm{Sn}^{2+}$  was oxidized to  $\mathrm{Sn}^{4+}$  and precipitation to SnO<sub>2</sub> species in positive active material. SnO<sub>2</sub> may act as nuclei for the formation of PbO<sub>2</sub> and decrease the particle size of  $PbO_2$  for  $Sn^{4+}$  have a smaller crystal cell compare to  $Pb^{4+}$  [18,25]. The results show that even lower concentration of Sn<sup>2+</sup> could apparently decrease the particle size of PbO<sub>2</sub> crystals after the oxidation reaction at the end of charging procedure. It is consistent with the influence of electrolyte additive of SnSO<sub>4</sub> on the morphology of lead sulfate in WE after CV tests in Fig. 6. At the same time, in the battery negative reaction when adding SnSO<sub>4</sub> in the electrolyte, the reaction of  $Sn^{2+}$  reduction to metallic Sn is prior to the reaction of PbSO<sub>4</sub> reduction to Pb for the electrode potential of  $Sn^{2+}/Sn$  (-0.13 vs. NHE) is more positive than the electrode potential of  $PbSO_4^{2+}/Pb(-0.359 \text{ vs. NHE})$  [18,26]. Sn will precipitate from the solution during the redox reaction inside the battery and grow with a dendrite mode, and this phenomenon raised the risk of micro-short circuit [15].

The solubility of SnSO<sub>4</sub> in 1 mol·L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> at 25 °C is 0.33 g·mL<sup>-1</sup>; therefore SnSO<sub>4</sub> added in the sulfuric acid solution could be fully dissolved. The positive discharge reaction of the lead acid battery could be described as Equation (2), and the electrode potential of *Em* of reaction in 1 mol·L<sup>-1</sup> acid solution is 1.685 V (vs. NHE). The electrode potential of Sn<sup>4+</sup>/Sn<sup>2+</sup> (Equation (3)) is 0.15 V (vs. NHE, in 1 mol·L<sup>-1</sup> acid solution), and it is prone to the reaction described as Equation (4) for 1.685 V (vs. NHE, in 1 mol·L<sup>-1</sup> acid solution), which is more positive than 0.15 V when SnSO<sub>4</sub> was added in the electrolyte.

 $PbO_2 + SO_4^{2-} + 4H^+ + 2e^- = PbSO_4 + 2H_2O$ (2)

$$Sn^{2+} = Sn^{4+} + 2e^{-}$$
(3)

$$PbO_2 + SnSO_4 + 4H^+ = PbSO_4 + 2H_2O + Sn^{4+}$$
(4)

$$Pb + SO_4^{2-} = PbSO_4 + 2e^-$$
(5)

$$Sn^{4+} + 2e^{-} = Sn^{2+} \tag{6}$$

$$Pb + SO_4^{2-} + Sn^{4+} = PbSO_4 + Sn^{2+}$$
(7)

The negative discharge reaction showed as Equation (5) and the electrode potential *Em* of reaction is -0.356 V (vs. NHE, in 1 mol·L<sup>-1</sup> acid solution). Sn<sup>4+</sup> in an electrolyte could permeate the membrane to the negative plate and participate in the reaction showed as Equation (6), while the electrode potential of *Em* is -0.15 V (vs. NHE, in 1 mol·L<sup>-1</sup> acid solution). It is prone to the reaction described as Equation (7) for -0.356 V (vs. NHE, in 1 mol·L<sup>-1</sup> acid solution), which is more negative than -0.15 V. Sn<sup>4+</sup>

was reduced to  $\text{Sn}^{2+}$  in this reaction of Equation (7). This infinite cycle increases the battery self-discharge [27]. Therefore, excessive  $\text{Sn}^{2+}$  in an electrolyte will deteriorate the battery cycle performance. In general, the optimum dosage of  $\text{SnSO}_4$  in an electrolyte is 2.24 mmol·L<sup>-1</sup>.

### 4. Conclusions

In this paper, a novel leady oxide was prepared via a low temperature calcination of lead citrate precursor, and a new lead acid battery was manufactured by the novel leady oxide. The paper focused on the effect of SnSO<sub>4</sub> as an electrolyte additive on the electrochemistry performance and microstructural characteristics of lead acid battery made from novel leady oxide.

- (1) The as-prepared novel leady oxide with the ultrafine particle size has 70–85 wt% PbO. Compared to traditional ball-milled leady oxide, novel leady oxide samples show lower apparent density, higher acid absorption and higher water absorption values, and potentially exhibit excellent initial electro-chemical performance.
- (2) CV results show that with the optimal addition of  $SnSO_4$ (2.24 mmol L<sup>-1</sup>) in an electrolyte, the WE shows the highest discharge capacity. The major crystalline phase of the pastes in WE are PbSO<sub>4</sub> and a little amount of PbO<sub>2</sub> and metallic Pb at the end of discharging procedure in the 250th CV tests, and the PbSO<sub>4</sub> crystal particles apparently become smaller with the addition of SnSO<sub>4</sub> in an electrolyte.
- (3) Battery testing results reveal that the optimal addition of  $SnSO_4$  in electrolyte is 2.24 mmol  $L^{-1}$ , and an electrolyte additive of  $SnSO_4$  could effectively decrease  $PbO_2$  crystal particle size in the positive active materials of the teardown battery at the end of charging procedure. It indicates that  $SnSO_4$  as an electrolyte additive could restrain larger particles of irreversible sulfation in charge/discharge cycles of testing battery.

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#### Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jpowsour.2015.03.125.

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