Lead acetate trihydrate precursor route to synthesize novel ultrafine lead oxide from spent lead acid battery pastes

Xiaojuan Sun a, b, 1, Jiakuan Yang a, b, *, Wei Zhang a, Xinfeng Zhu a, c, Yuchen Hu a, Danni Yang a, Xiqing Yuan a, Wenhao Yu a, Jinxin Dong a, Haifeng Wang a, Lei Li a, R. Vasant Kumar d, Sha Liang a, 1

a School of Environmental Science and Engineering, Huazhong University of Science and Technology (HUST), 1037 Luoyu Road, Wuhan, Hubei 430074, PR China
b Key Laboratory for Large-Format Battery Materials and System of Ministry of Education, Huazhong University of Science & Technology (HUST), 1037 Luoyu Road, Wuhan, Hubei 430074, PR China
c Henan University of Urban Construction, Pingdingshan, Henan 467000, PR China
d Department of Materials Science and Metallurgy, University of Cambridge, Cambridge CB2 3QZ, UK

HIGHLIGHTS

- The Pb(CH₃COO)₂·3H₂O precursor was prepared from the spent lead battery pastes.
- Novel lead oxide products were prepared from the precursor in N₂ and air.
- The assembled batteries show a good cyclic stability in 80 charge/discharge cycles.

GRAPHICAL ABSTRACT

Abstract

A novel green recycling process is investigated to prepare lead acetate trihydrate precursors and novel ultrafine lead oxide from spent lead acid battery pastes. The route contains the following four processes. (1) The spent lead pastes are desulphurized by (NH₄)₂CO₃. (2) The desulphurized pastes are converted into lead acetate solution by leaching with acetic acid solution and H₂O₂; (3) The Pb(CH₃COO)₂·3H₂O precursor is crystallized and purified from the lead acetate solution with the addition of glacial acetic acid; (4) The novel ultrafine lead oxide is prepared by the calcination of lead acetate trihydrate precursor in N₂ or air at 320–400°C. Both the lead acetate trihydrate and lead oxide products are characterized by TG-DTA, XRD, and SEM techniques. The calcination products are mainly α-PbO, β-PbO, and a small amount of metallic Pb. The particle size of the calcination products in air is significantly larger than that in N₂. Cyclic voltammetry measurements of the novel ultrafine lead oxide products show good reversibility and cycle stability. The assembled batteries using the lead oxide products as cathode active materials show a good cyclic stability in 80 charge/discharge cycles with the depth of discharge (DOD) of 100%.

Article info

Article history:
Received 16 April 2014
Received in revised form 6 June 2014
Accepted 1 July 2014
Available online 14 July 2014

Keywords:
Spent lead acid battery
Novel ultrafine lead oxide
Lead acetate trihydrate
Thermal decomposition
Electrochemistry test

1. Introduction

Globally, lead-acid battery constitutes the largest volume among secondary batteries arising from the advantages of low cost, good
stability, and high recovery ratio of over 97% of the spent batteries. Lead acid batteries account for nearly 80 wt% of the total lead consumption [1–3]. While the recovery of spent lead–acid battery is the most successful example among all commercial batteries throughout the world, any contamination during discarding, recovery or recycling the spent lead–acid batteries has drawn serious attention due to their toxicity to the environment [4–6]. A typical spent lead acid battery mainly consists of four components: spent electrolyte (11–30 wt%), lead alloy grid (24–30 wt%), lead pastes (30–40 wt%), and polymeric materials (22–30 wt%) [7]. Among these, lead paste is the most difficult to deal with because of the presence of active lead compounds in relatively stable state. A typical composition of a spent paste is lead sulphate (nearly 60%), lead (IV) dioxide (nearly 28%), lead (II) oxide (nearly 9%), metallic lead (nearly 3%) and a small but significant concentration of impurities such as iron, antimony, tin and barium [7,8]. Environmentally sensitive recovery of spent lead–acid battery pastes has attracted considerable interest from researchers [9–11].

The traditional pyrometallurgical route, which is the most widely used in the recovery of secondary lead resource, can emit large quantities of SO2 gas and lead dust, causing threat to the environment [12–14]. Moreover, the pyrometallurgical process requires a lot of energy for the decomposition of lead sulfate above 1000 °C, thus it will consume non-renewable resources of coal, coke, oil or natural gas.

More recently increasing attention has been paid to the recovery of spent lead–acid battery pastes through alternative hydrometallurgical process. The most used hydrometallurgy method, which consists of pretreatment, desulfurization, reduction and electro-winning process, can avoid SO2 and lead dust emission problems [15,16]. However, the energy efficiency of electro-winning process is low, with a higher total energy consumption compared with traditional pyrometallurgical route. The suggested leaching solutions of H2SiF6 or HBF4 can lead to emission of fluorine in the environment which is also unacceptable.

Given the disadvantages in the traditional pyrometallurgical and electro-winning methods, several new hydrometallurgy approaches have been developed. Attempts have been tried to leach the components (PbSO4, PbO2 and PbO) of spent lead pastes by citric acid and sodium citrate as reported in our previous studies [10,11,17]. In this leaching process, the lead citrate precursor is separated from the leaching solution by simple crystallization. The ultra-fine lead oxide powder can be obtained through calcination of lead citrate at a temperatures less than 400 °C. In order to improve the desulfurization efficiency of spent lead pastes, spent lead pastes were firstly converted into the desulfurized pastes with desulfurizing agents, then the desulfurized pastes were leached with citric acid solution to generate lead citrate [18]. In order to improve the speed of leaching reaction and decrease the consumption of citric acid, a modified version using acetic acid and sodium citrate leaching system was developed for the recovery of spent lead pastes [19]. However, in these previous researches, the impurities in spent lead pastes can easily join and contaminate the lead citrate precursor, leading sometimes to an unacceptably high content of the impurities in the final leady oxide. And then, the capacity retention ratio of the batteries manufactured with the leady oxide as the active material of the cathode decreases rapidly after 20–30 cycles. The impurities in the leady oxides could lead to the deterioration of the cycle life performance of the batteries [20]. Moreover, the leaching agents of citric acid and sodium citrate are relative more expensive than other organic or inorganic acids.

The objective of this work was to seek a more efficient method to obtain high-performance leady oxide with lower content of impurities by applying high-purity lead acetate trihydrate as a precursor. Flow sheet of this process was schematically shown in Fig. 1. The suggested method can be described as “paste to paste” recycling. In this novel approach, the high-cost leaching reagents of citric acid and sodium citrate were substituted by the cheaper acetic acid. Furthermore, the impurities in spent pastes could be effectively separated by the three filtering-separating procedures. The morphology, mineral phases and electrochemical performances of lead oxide products prepared in N2 or air were characterized, and batteries were fabricated by the new lead oxide products to examine the battery performance.

2. Experimental

2.1. Reactants and raw materials

The samples of spent lead acid battery pastes were provided by Hubei jinyang Metallurgical Co. Ltd., China, where typically spent lead battery pastes are pyrometallurgically treated to recover lead as a metal using a conventional smelting process. Lead pastes from the spent lead-acid pastes were made available for this work after a separation process using Engitec Technologies Company CX.
crushing and sorting system. The lead paste samples were washed with distilled water until pH of the washed water was above 6.5. Dried lead paste powders which passed through 120-mesh screens were used as raw materials in this study. The chemical compositions of lead and main metallic element in the used lead pastes are shown in Table 1. The antimony in spent lead-acid battery grid may enter into lead paste during the crushing process in the sorting system. Since the crushing and sorting equipment is made of iron and steel, Fe as an impurity can easily enter into the lead paste. For the next leaching step, the solid cake was washed with distilled water and separated from the mother liquor, since most of impurities comprising Fe, Sb, and Cu, etc. were soluble and retained in the mother liquor. At different molar ratios of glacial acetic acid to lead in the collected filtrate after the leaching process, the yield efficiency of Pb(CH$_3$COO)$_2$·3H$_2$O product and the pH of mother liquor were determined. The yield efficiency of Pb(CH$_3$COO)$_2$·3H$_2$O product was calculated by Equation (2):

\[
\text{Yield efficiency of Pb(CH$_3$COO)$_2$·3H$_2$O product} = \frac{\text{The mass of Pb(CH$_3$COO)$_2$·3H$_2$O product (g)}}{\text{Stoichiometric maximum yield of Pb(CH$_3$COO)$_2$·3H$_2$O product (g)}} \times 100\%
\]

The obtained 93.2 g desulphurized lead pastes were used in the following leaching procedure with 3 mol L$^{-1}$ acetic acid and 30%W/V H$_2$O$_2$ at a stirring speed of 400 rpm. Various molar ratios (0.75, 1.0, 1.5, 2, 2.5, and 3) of acetic acid to total Pb in desulphurized lead pastes, expressed as CH$_3$COOH/Pb, were investigated. After leaching for 6.0 h, all components in the solid desulphurized lead pastes were reacted with the leaching solution containing acetic acid and hydrogen peroxide. Only a small amount of un-reacted solid components remained, which were filtered and separated from the leaching solution. The leaching experiments were conducted in triplicate, and the mean values were calculated. The filtrate was collected for the next step in the overall procedure.

The leaching efficiency for lead in desulphurized lead paste was calculated by Equation (1):

\[
\text{Leaching efficiency of lead} = \frac{(V_1 \times C_2)/(W_1 \times C_1)}{100\%}
\]

In Equation (1), $W_1$ (g) is the mass of the desulphurized lead pastes; $V_1$ (L) is the volume of filtrate solution, $C_1$ (wt %) is the mass percent of lead in the desulphurized lead pastes, $C_2$ (g L$^{-1}$) is the lead concentration in the filtrate solution. The concentration of lead in the digestion solution of desulphurized lead pastes and filtrate solution was measured by AAS (novAAA400, Analytik Jena AG).

2.4. Synthesis of Pb(CH$_3$COO)$_2$·3H$_2$O from the filtrate after the leaching process

The glacial acetic acid was then added to a 50 ml solution of the collected filtrate to crystallize Pb(CH$_3$COO)$_2$·3H$_2$O from the mother liquor. Thus crystal could be filtered and separated from the mother liquor of the filtrate, since most of impurities comprising Fe, Sb, and Cu, etc. were soluble and retained in the mother liquor. At different molar ratios of glacial acetic acid to lead in the collected filtrate (expressed as CH$_3$COOH/Pb in the filtrate), the yield efficiency of Pb(CH$_3$COO)$_2$·3H$_2$O product and the pH of mother liquor were determined. The yield efficiency of Pb(CH$_3$COO)$_2$·3H$_2$O product was calculated by Equation (2):

\[
\text{Yield efficiency of Pb(CH$_3$COO)$_2$·3H$_2$O product} = \frac{\text{The mass of Pb(CH$_3$COO)$_2$·3H$_2$O product (g)}}{\text{Stoichiometric maximum yield of Pb(CH$_3$COO)$_2$·3H$_2$O product (g)}} \times 100\%
\]

2.5. Thermal analyses of Pb(CH$_3$COO)$_2$·3H$_2$O crystal precursor

The thermal analysis of crystal precursor was conducted by thermogravimetric – differential thermal analysis (TG-DTA) using Diamond (Platinum-Selmer equipment Co. Ltd., Shanghai), under air or nitrogen gas at a heating rate of 5 °C min$^{-1}$ from room temperature to 500 °C.

2.6. Calcination of Pb(CH$_3$COO)$_2$·3H$_2$O

Calcination temperature of Pb(CH$_3$COO)$_2$·3H$_2$O crystal was determined based on TG-DTA data. In N$_2$, the lead acetate precursors were calcinated at 205 °C, 265 °C, 320 °C, 370 °C and 400 °C for 1 h, at each temperature. In air, the lead acetate precursors were calcinated at 205 °C, 260 °C, 295 °C, 350 °C and 400 °C for 1 h, at each temperature.

2.7. Characterization of materials

Powder X-ray diffraction (XRD) data were collected from powder samples of Pb(CH$_3$COO)$_2$·3H$_2$O crystal product and the combustion products using a X’Pert PRO XRD (Philips, PANalytical B.V., Holland) with Cu Ka radiation and $\lambda = 1.5418$ Å at scanning rate of 0.28° per second for 2θ in the range from 5° to 75°.

Table 1

<table>
<thead>
<tr>
<th>Compositions (wt%)</th>
<th>Pb</th>
<th>Cu</th>
<th>As</th>
<th>Zn</th>
<th>Sb</th>
<th>Fe</th>
<th>Cd</th>
</tr>
</thead>
<tbody>
<tr>
<td>Percentage</td>
<td>76.600</td>
<td>0.008</td>
<td>0.040</td>
<td>0.003</td>
<td>0.240</td>
<td>0.100</td>
<td>0.002</td>
</tr>
</tbody>
</table>
Morphology studies were carried out with scanning electron microscopy (ULTRA PLUS-43-13, Germany) operated at 10 kV after coating the samples with gold. EDX spectra of the calcined products from lead acetate precursors were collected on an ultra-thin window (UTW) X-ray detector equipped with SEM.

2.8. Electrochemical measurements and physicochemical properties of lead oxide products

The cyclic voltammetry (CV) curves of lead oxide powder were determined with a three-electrode system [20,21]. The working electrode was a microelectrode filled with the tested lead oxide powder. The counter electrode was a double platinum electrode, while Hg/Hg2SO4/K2SO4 (sat.) was chosen as the reference electrode. The electrolyte was sulphuric acid solution at concentration of 3.0 mol L\(^{-1}\). The CV tests were performed at room temperature (20 ± 2 °C) using VMP-2 device from USA at a scanning speed of 10 mV s\(^{-1}\) in a potential range of 0 V to +1.5 V (anodic range), while the last 7 CV curves were collected from 20 cycles. The basic physicochemical properties of lead oxide powder product such as the degree of oxidation (oxidizability), density, acid-absorption and water-absorption values were determined according to our previous literature [20].

2.9. Battery assembling and testing procedure

The method of battery assembling and testing are based on our previous work reported in the literature [20]. In battery assembling, the lead oxide powder products act as positive active material, while negative plates were provided by Wuhan Changguang Power Sources. Co. Ltd. After the mixing and pasting, curing, and formation processes, each of the dried positive plates was coupled with two commercial negative plates soaked in sulphuric acid solution. Sources. Co. Ltd. After the mixing and pasting, curing, and formation processes, each of the dried positive plates was coupled with two commercial negative plates soaked in sulphuric acid solution. The solid residue in the desulphurized lead pastes after leaching process consisted of a small amount of un-converted PbSO4 and other insoluble solid impurities.

Generally, leaching efficiency of lead in the desulphurized pastes increased with the increase of molar ratio of CH3COOH/Pb. It indicates that extraction efficiency of lead could reach up to over 95% at each molar ratio of CH3COOH/Pb provided leaching time is long enough. Even at the minimum molar ratio of CH3COOH/Pb of 0.75, the leaching efficiency of lead could also increase up to nearly 97.6% for a leaching duration of 360 min. Therefore, it shows that the leaching efficiency of lead from the desulphurized lead paste is high with the leaching system of acetic acid and hydrogen peroxide solution. The solid residue in the desulphurized lead pastes after the leaching process consisted of a small amount of un-converted PbSO4 and other insoluble solid impurities.

The reactions of lead paste with acetic acid solution and H2O2 might be presented as indicated in the following Equations (3)–(7).

\[
\begin{align*}
\text{PbO} (s) + 2\text{CH}_3\text{COOH} (aq) & \rightarrow \text{Pb(CH}_3\text{COO})_2 (aq) + \text{H}_2\text{O} & (3) \\
\text{PbO}_2 (s) + 2\text{CH}_3\text{COOH} (aq) + \text{H}_2\text{O}_2 (aq) & \rightarrow \text{Pb(CH}_3\text{COO})_2 (aq) + 2\text{H}_2\text{O} + \text{O}_2 (aq) & (4) \\
\text{PbCO}_3 (s) + 2\text{CH}_3\text{COOH} (aq) & \rightarrow \text{Pb(CH}_3\text{COO})_2 (aq) + \text{H}_2\text{O} + \text{CO}_2 (aq) & (5) \\
\text{Pb(CH}_3\text{COO})_2 (aq) + \text{PbO} (s) + \text{H}_2\text{O} & \rightarrow \text{Pb(CH}_3\text{COO})_2 \cdot \text{Pb(OH})_2 (aq) & (6) \\
\text{Pb(CH}_3\text{COO})_2 (aq) + 2\text{PbO} (s) + 2\text{H}_2\text{O} & \rightarrow \text{Pb(CH}_3\text{COO})_2 \cdot 2 \text{Pb(OH})_2 (aq) & (7)
\end{align*}
\]

With the addition of acetic acid solution and hydrogen peroxide, a large number of gas bubbles are observed to emit in the stirring vessel due to the generation of oxygen and carbon dioxide as shown in Equations (4) and (5).

When the molar ratio of CH3COOH/Pb was 0.75, the concentration of lead and pH of the solution after leaching for the different extended durations are shown in Fig. 3. The concentration of lead increased from 1.60 to 3.95 mol L\(^{-1}\) when the leaching time is increased from 10 to 360 min. The pH value simultaneously increased from 4.27 to 8.12, indicating that the acetic acid solution was almost completely consumed and reacted with the desulphurized paste.

3.3. Crystallization of Pb(CH3COO)2·3H2O crystal

The XRD pattern of the crystal product is shown in Fig. 4 (a), while photographic and SEM images are shown in Fig. 4(b) and (c).
The product was identified as Pb(CH$_3$COO)$_2$·3H$_2$O (JCPDS No. 00-014-0829). Thus, the reaction of glacial acetic acid and the lead acetate filtrate solution may be expressed as the Equation (8).

\[
Pb(CH_3COO)_2 \cdot 2Pb(OH)_2 (aq) + 4CH_3COOH (aq) + 5H_2O \rightarrow 3 Pb(CH_3COO)_2 \cdot 3H_2O (s) \quad (8)
\]

The effects of CH$_3$COOH/Pb in the filtrate on yield efficiency of Pb(CH$_3$COO)$_2$·3H$_2$O crystal and pH in the solution are shown in Fig. 5. As shown in Fig. 5, the mass of the Pb(CH$_3$COO)$_2$·3H$_2$O crystal product increased when CH$_3$COOH/Pb in the filtrate increased. The yield efficiency of Pb(CH$_3$COO)$_2$·3H$_2$O crystal can reach up to nearly 85.0% at a molar ratio of CH$_3$COOH/Pb in the filtrate of 1.4 and then remained constant with any further increase of the molar ratio of CH$_3$COOH/Pb in the filtrate. The pH of lead acetate solution decreased from 7.6 to 2.8 with the molar ratio of CH$_3$COOH/Pb in the filtrate increased from 0.8 to 1.6. It indicated that nearly 85.0% of lead was crystallized from the mother liquor with the formation of Pb(CH$_3$COO)$_2$·3H$_2$O.

### 3.4. Thermal analysis of the Pb(CH$_3$COO)$_2$·3H$_2$O product

The TG-DTA curves of lead acetate trihydrate in air and N$_2$ are shown in Fig. 6. According to Fig. 6, the mass loss of lead acetate

---

**Fig. 3.** Effect of leaching time on concentration of Pb and pH in the leaching solution at the molar ratio of CH$_3$COOH/Pb of 0.75.

**Fig. 4.** The XRD pattern (a), Photograph (b) and SEM image (c) of the crystal product Pb(CH$_3$COO)$_2$·3H$_2$O.

**Fig. 5.** Effect of molar ratio of CH$_3$COOH/Pb in the filtrate on yield efficiency of Pb(CH$_3$COO)$_2$·3H$_2$O product and pH in the mother solution.

**Fig. 6.** TG–DTA curves of lead acetate trihydrate precursor in N$_2$ and air.
trihydrate in air (42.0%) was more than that in N₂ (37.5%). From the DTA curve in N₂, there are five endothermic peaks at the temperatures of 64.3, 205.8, 250.6, 294, and 357.1 °C. It is indicated that lead acetate trihydrate undergoes a series of dehydrate and pyrolysis reactions which are endothermic in N₂. While there are only three endothermic peaks at the temperature of 61.4, 204.9, and 256.8 °C from the DTA curve in air; two exothermic peaks exist around 293.6 °C and 348.7 °C, which are ascribed to vigorous oxidation of C and organic matter when the temperature rises in air. The difference of thermal characteristics of lead acetate trihydrate oxidation of C and organic matter when the temperature rises in air. The XRD patterns of calcination products from lead acetate trihydrate in N₂ at different temperatures are shown in Fig. 8. The calcination products at 205 °C were Pb(CH₃COO)₂ and Pb(CH₃COO)₂·H₂O. The calcination products at 265 °C were Pb(CH₃COO)₂·2PbO and Pb(CH₃COO)₂·PbO. The calcination products at 320 °C were mainly α-PbO, β-PbO, metallic Pb, carbon and some undecomposed Pb(CH₃COO)₂. With increasing calcination temperature, it was observed that the crystalline phases of the calcined products were transformed into α-PbO, β-PbO and metallic Pb. The calcination products at 370 °C and 400 °C were mainly α-PbO, β-PbO and metallic Pb as shown in the XRD patterns. Besides, diffraction peak intensity of α-PbO is stronger than that of β-PbO, indicating that the amount of α-PbO is more than that of β-PbO. From above analyses, the Pb(CH₃COO)₂·3H₂O precursor could be completely converted into PbO and Pb products at above 370 °C. The calcination reactions might be followed by Equations 9 and 10 in N₂ gas [22].

\[
Pb(CH₃COO)₂ → PbO + CH₃COCH₃ + CO₂ \quad (9) \\
Pb(CH₃COO)₂ → Pb + CH₃COOH + CO₂ + H₂ + C \quad (10)
\]

The SEM images of the calcination products at different temperatures in N₂ are shown in Fig. 9. As shown in Fig. 9(a) and (b), the products show plate-like shape in the size of 10–20 μm at the calcination temperatures of 205 °C and 265 °C. In Fig. 9(c), some spherical particles of size range 200–400 nm appear at 320 °C. In Fig. 9(d) and (e), the calcination products become uniform spherical particles of 200–400 nm at 370 and 400 °C, and some larger spherical particles show the tendency of agglomeration at the higher calcination temperature of 400 °C. In general, the morphologies of the products calcinated in N₂ change from plate-like shape into spherical shape when the temperature rises from 205 °C to 400 °C. The EDX spectra of the calcination product at 400 °C in N₂ shows that the major phase is identified as lead oxide, which is consistent with the XRD results in Fig. 8.

3.6. Calcination products from lead acetate trihydrate in air

The photographs of lead oxide products in air are shown in Fig. 10. As shown in Fig. 10, the calcination products at 205 °C are
Fig. 9. The SEM images of calcination products from lead acetate trihydrate precursor in N₂ gas at different temperatures for 1 h: (a) 205 °C, (b) 265 °C, (c) 320 °C, (d) 370 °C, and (e) 400 °C.
white or grey powders, which is similar to the products calcinated at 205 °C in N\textsubscript{2}. As shown in Fig. 10(c)–(f), the colors of the calcination products turn into grey or yellow when the calcination temperatures rise up to 260–400 °C, which is much different from brown or dark color of the products calcinated at corresponding temperatures in N\textsubscript{2}. The color difference of calcination products turns to brown or dark since an amount of C residues are kept in the calcined products in N\textsubscript{2}. However, much less C residue is kept in the calcined products in air since C is easily to oxide with air.

The XRD patterns of calcination–combustion products at different temperatures in air are shown in Fig. 11. Similar to that in N\textsubscript{2}, the products were mainly Pb(CH\textsubscript{3}COO)\textsubscript{2}, 3Pb(CH\textsubscript{3}COO)\textsubscript{2}·PbO·H\textsubscript{2}O, and Pb(CH\textsubscript{3}COO)\textsubscript{2}·PbO at the calcination of 205 °C. The calcination products at 260 °C were Pb(CH\textsubscript{3}COO)\textsubscript{2}·2PbO and Pb(CH\textsubscript{3}COO)\textsubscript{2}·PbO. The calcination–combustion products at 295 °C were mainly \( \alpha \)-PbO, \( \beta \)-PbO, metallic Pb, and a small amount of un-combusted Pb(CH\textsubscript{3}COO)\textsubscript{2}. At higher temperature of 350 °C and 400 °C, the products were completely transformed into the phases of \( \alpha \)-PbO, \( \beta \)-PbO and metallic Pb. The diffraction peak intensity of \( \alpha \)-PbO is equal to that of \( \beta \)-PbO, indicating that the amount of \( \alpha \)-PbO is approximately equal to that of \( \beta \)-PbO. Any existence of carbon as in air, is removed by oxidation by Equations 11–14:

\[
2C + O_2 \rightarrow 2CO \quad (11)
\]
\[
C + O_2 \rightarrow CO_2 \quad (12)
\]
\[
PbO + CO \rightarrow Pb + CO_2 \quad (13)
\]
\[
2PbO + C \rightarrow 2Pb + CO_2 \quad (14)
\]

Thus no carbon was identified in the calcined products in air.

The SEM images of the calcination–combustion product at 205 °C shows that the major phase is plate-like shape to a ball-like shape with increasing temperature. As shown in Fig. 12(a) and (b), the calcination–combustion products shows plate-like shape in the size of 10–20 \( \mu \)m at 205 °C and 265 °C. In Fig. 12(c), the calcination products are mainly particles of 200–400 nm, with a few undecomposed substances at 295 °C. In Fig. 12(d) and (e), two different kinds of spherical particles exist in the lead products, where fewer agglomerated spherical particles of 5 \( \mu \)m are dispersed in lots of smaller spherical particles of 400–800 nm at 350 °C and 400 °C. The EDX spectra of the calcination–combustion product at 400 °C shows that the major phase of calcination–combustion product is identified as lead oxide, which is consistent with the XRD results in Fig. 11.

### 3.7. Physicochemical properties and electrochemical characterization of lead oxide products

As shown from Table 3, the oxidizability of lead oxide products prepared in different calcination atmosphere is much higher than traditional ball-mill leady oxide products for which data was provided by Wuhan Changguang Power Sources. Co. Ltd. The oxidizability of lead oxide products prepared in N\textsubscript{2} is higher than in products in air with a small margin. As shown in Equations 11–14, the reduction reaction of PbO with solid carbon or CO gas in air atmosphere could result in the consumption of PbO, causing a lower oxidizability of leady oxide product in air than that in N\textsubscript{2}.

The enhanced water absorption of lead oxide products may be due to smaller-sized structure of prepared products compared with traditional ball-mill leady oxide products since specific surface area of prepared products is much larger than traditional ball-mill products. The acid-absorption value is affected by the oxidizability of leady oxides and the particle size of leady oxides, because higher oxidizability and smaller particle size of leady oxide products result in higher acid-absorption value [20,23]. As shown in Table 3, the acid-absorption value of lead oxide products prepared with N\textsubscript{2}...
Fig. 12. The SEM images of calcination products from trihydrate precursor in air at different temperatures for 1 h: (a) 205 °C, (b) 260 °C, (c) 295 °C, (d) 350 °C, and (e) 400 °C.
is higher than that with air. As shown in Figs. 9 and 12, the particle size of lead oxide products in N₂ is much smaller than in air, and the oxidizability of lead oxide products in N₂ is the maximum, which may contribute to the higher acid-absorption value of lead oxide products in N₂.

The last 7 CV curves in the CV tests of lead oxide prepared in N₂ (a) and air (b) are shown in Fig. 13. As shown in Fig. 13, the CV curves of the two kinds lead oxide product are similar, with four clear peaks and relatively stable peaks positions, indicating that the lead oxide product has good stability in electrochemical reactions.

The oxidation of PbO to α-PbO₂ which is described in peak (i) occurs at around +1.02 V (vs reference electrode), while oxidation of PbSO₄ to β-PbO₂ in peak (ii) occurs at around +1.3 V (vs reference electrode) [24,25]. Under the high potential, evolution of oxygen from the aqueous system takes place around +1.5 V (vs reference electrode), with the reaction being, 2H₂O → O₂ + 4H⁺ + 4e⁻. On the reverse scanning from potential +1.5 V, the reduction reaction of α-PbO₂ and β-PbO₂ to PbSO₄ occurs at about +0.9 V in peak (iii). The reduction peak (iii) in Fig. 13(b) is apparently larger than that of Fig. 13(a), which indicates a better charge and discharge performance of the lead oxide product prepared in air than that prepared in N₂. As shown in Fig. 14, the discharge capacity of two different products improved as cycle count increased, while lead oxide product prepared in air showed higher discharge capacity than that in N₂.

### 3.8. Battery performance

Fig. 15 shows the XRD patterns of plate samples made from lead oxide products in N₂ before and after the formation process. The sample before the formation process mainly contains 4PbO-PbSO₄ (4BS) and α-PbO. The ripe plates after the formation process mainly comprise β-PbO₂, PbSO₄ and small amount of 3PbO-PbSO₄·H₂O (3BS). After the formation process, the main phase of plates turns into β-PbO₂. Fig. 16 shows the SEM images of plates made from lead oxide product prepared in N₂ gas before and after the formation process. As shown in Fig. 16(a), the plate before the formation process looks like the typical microstructure of 4BS and PbSO₄. However, the microstructure of the ripe plate shows fine spherical particles of β-PbO₂ with a diameter of 10–50 nm shown in Fig. 16(b).

### Table 3

<table>
<thead>
<tr>
<th>Calcination atmosphere</th>
<th>Calcination temperature/°C</th>
<th>Apparent density/g cm⁻³</th>
<th>Degree of oxidation/%</th>
<th>Water-absorption value/ml kg⁻¹</th>
<th>Acid-absorption value/g kg⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>370</td>
<td>1.70</td>
<td>99.1</td>
<td>347.6</td>
<td>532.8</td>
</tr>
<tr>
<td>N₂</td>
<td>400</td>
<td>1.68</td>
<td>99.2</td>
<td>352.0</td>
<td>554.2</td>
</tr>
<tr>
<td>Air</td>
<td>350</td>
<td>1.52</td>
<td>95.8</td>
<td>312.2</td>
<td>476.3</td>
</tr>
<tr>
<td>Air</td>
<td>400</td>
<td>1.47</td>
<td>96.0</td>
<td>332.7</td>
<td>492.6</td>
</tr>
<tr>
<td>Traditional leady oxide*</td>
<td></td>
<td>1.93</td>
<td>83.2</td>
<td>110.0</td>
<td>381.3</td>
</tr>
</tbody>
</table>

* The traditional ball-mill leady oxide was provided by Wuhan Changguang Power Sources. Co. Ltd.
Cycle performance of batteries manufactured by lead oxide products in N\textsubscript{2} and air is shown in Fig. 17\textit{(a)} and \textit{(b)}, respectively. The capacity retention ratios of the assembling batteries made from the two kinds of lead oxide products show a good cyclic stability in 80 charge/discharge cycles with the depth of discharge (DOD) of 100%. The cycle performance of the assembled batteries in this study is significantly better than our previous study using the novel lead oxide recovered from the spent lead pastes with the acetic and sodium citrate leaching process. It might be related to lower concentration of impurities in the novel ultrafine lead oxide products with the lead acetate trihydrate precursor route than in the previous acetic and sodium citrate leaching route. Impurities in the recovered leady oxides have potential influences on the performance of the new lead-acid battery. In a further study we will investigate the typical impurities in the novel ultrafine lead oxide products, i.e., Fe, Sb, and Ba. The stable cycle performance may be due to favorable properties of lead oxide products in this method for the recovery of the spent lead-acid battery paste.

4. Conclusions

Pure Pb(CH\textsubscript{3}COO)\textsubscript{2}\cdot3H\textsubscript{2}O crystal has been prepared from spent lead acid battery pastes by desulphurization, leaching by acetic acid solution and crystallization procedure by glacial acetic acid. The Pb(CH\textsubscript{3}COO)\textsubscript{2}\cdot3H\textsubscript{2}O crystal is found to be pure, and can be readily separated from the mother liquor.

The preparation of lead oxide product was carried out by calcining Pb(CH\textsubscript{3}COO)\textsubscript{2}\cdot3H\textsubscript{2}O crystal in N\textsubscript{2} or in air. In N\textsubscript{2}, the major phases of the calcination products at a temperature of above 320 °C for 1 h were \textit{\alpha}-PbO, \textit{\beta}-PbO, with a small amount of metallic Pb, and the amount of \textit{\alpha}-PbO is larger than that of \textit{\beta}-PbO. The product morphology consisted of uniform spherical particles with a size range of 200–400 nm at typical calcinations temperatures of 370 °C and 400 °C. In air, at the calcination temperature of over 295 °C for 1 h the major phases of the products were still \textit{\alpha}-PbO, \textit{\beta}-PbO, with a small amount of lead, and the amount of \textit{\alpha}-PbO is approximately equal to that of \textit{\beta}-PbO. The morphology is converted from plate-like shape to spherical shape with increasing temperature. At the calcination temperature of 350 °C and 400 °C, few larger agglomerated spherical particles of 5 \textmu m are dispersed in a matrix of smaller spherical particles of 400–800 nm.

The basic physicochemical properties of lead oxide powder product show higher degree of oxidation, acid-absorption and water-absorption than traditional ball-mill leady oxide products, with lower apparent density. The CV curves of novel ultrafine lead oxide shows good reversible ability and cycle stability (above 20 cycles), and lead oxide product prepared in air exhibited higher electrochemical properties than that prepared in N\textsubscript{2}.

The assembled batteries made from the two kinds of lead oxide products prepared in both N\textsubscript{2} and air show a good cyclic stability in 80 charge/discharge cycles at a depth of discharge (DOD) of 100%.

Acknowledgments

The authors would like to express their thanks to the International Technology Cooperation Plan of Innovation Fund, HUST (2013ZZGH015), the Wuhan Planning Project of Science and Technology, China (2013060501010168, 2013011801010593, and 2014030709020313), and the national science and technology support program (2014BAC03802). The authors would like to extend their thanks to Analytical and Testing Center of Huazhong University of Science and Technology (HUST) that supplied the facilities for materials analysis during this research. The authors would like to extend thanks to the raw materials and financial support from Hubei Jinyang Metallurgical Co. Ltd., China. We also show thanks to the support of Wuhan Changguang Power Sources Co. Ltd.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jpowsour.2014.07.007.
References