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### A novel leady oxide combined with porous carbon skeleton synthesized from lead citrate precursor recovered from spent leadacid battery paste



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#### HIGHLIGHTS

- Leady oxides synthesized from lead citrate precursor in different atmosphere.
- Porous carbon in leady oxides was firstly investigated.
- Mass percentage of Pb metal and carbon in leady oxides can be controlled.
- A calcination theory model of mass-transfer controlled is proposed.

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#### G R A P H I C A L A B S T R A C T



#### ABSTRACT

A novel nanostructured leady oxides comprising porous carbon skeleton has been synthesized by thermal decomposition of lead citrate precursor, recovered from spent lead-acid battery paste. The influences of  $O_2$  percentage in the calcination atmosphere ( $O_2/N_2$  mixture) and the temperature on leady oxide product characteristics are studied by chemical analysis, scanning electron microscopy (SEM) and X-ray diffraction (XRD). The major crystalline phases of the products are identified as lead oxides, metallic Pb, and carbon. Porous carbon is observed as skeletons within the leady oxide (PbO containing some Pb metal) particles. Mass percentage of Pb metal in the leady oxide increases with increasing the proportion of oxygen in the calcination atmosphere. However, the amount of carbon decreases from approximately 8.0 to 0.3 wt%, and the porous carbon skeleton structure is gradually damaged with oxygen concentration increasing. A model about the thermal decomposition of lead citrate precursor is firstly proposed to elucidate these observations. The nanostructured leady oxides combined with porous carbon can be directly used as precursor of active materials in a new lead acid battery.

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#### 1. Introduction

During the last few years, the synthesis of nanostructured leady oxides materials has attracted considerable attentions [1–5], because it can be applied as active materials in lead-acid batteries, in terms of improving the electrochemical performance with high surface area [6]. Nanostructured leady oxides could be obtained by several

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Fig. 1. The flow sheet of experiments.

processing techniques including ball milling [7], hydrothermal [8–11], sonochemical [4,12–18], microwave irradiation [19] and thermal decomposition [1,5,20–24].

Leady oxides constitute a variety of valence states of Pb (II, III and IV) and thus different crystallite structures, depending upon the preparation parameters such as temperature. Leady oxides with various nanoscale structures can be obtained from different lead precursors via various methods. The lead precursors can be classified into inorganic salts and organometallic compounds. Lead salts precursors consist mainly of lead carbonate [25], lead hydroxide [3,6,8,26], lead nitrate [27] and lead hydroxycarbonate [19]. The mechanism of lead salts precursors decomposition is commonly a simple endothermic reaction, which can be easily controlled. There are only few available inorganic lead salt precursors, thus the range of structure of leady oxide products is limited.

Lead organometallic precursors offer greater variety and more possible options for making nanostructured leady oxides when compared with lead salts precursors. The lead organometallic precursors include not only simple organic precursors such as lead acetate [9,11,28] and lead oxalate [29], but also some novel organometallic compounds which are reported recently [15,18,24]. Metallic Pb and residual carbon normally exist in the leady oxides calcination products, because the formation of residual carbon under reducing atmosphere is unavoidable during thermal decomposition of lead organometallic precursors [20,30,31].

PbO with a certain amount of Pb metal, traditionally so-called leady oxide, is a desirable precursor of the production of active material for lead-acid batteries. Carbon is also a common additive in lead-acid batteries in both electrodes. The mass ratio of PbO to total leady oxide product is defined as oxidizability, which is important because leady oxides with oxidizability above 70 wt % are typical precursor of the production of active material for lead-acid batteries. Usually, the amounts of Pb metal and carbon in active materials exhibit significant influences on the performance of lead-acid batteries. For example, 0.1–2% wt % of carbon addition in the positive active material (PAM) or negative active material (NAM) of a lead acid cell could improve both the discharge capacity and the lifecycle performance [32]. The amount and the type of carbon material additives could be controlled in order to guarantee the performance enhancement [32]. In this study, the decomposition of lead citrate usually yielded leady oxide comprising porous carbon, which could possibly be applied as a novel carbon enhanced active material for lead acid batteries, with no need to add extra carbon in the paste precursor.

In this study, lead citrate precursors ( $Pb_3(C_6H_5O_7)_2$ ·3H<sub>2</sub>O) were synthesized from spent lead-acid battery pastes. The precursors were calcined in different gaseous atmospheres, to investigate thermal decomposition mechanism. Mass ratios of PbO, Pb metal, and residual carbon in the calcination products, the crystalline phase constitutions, and microstructures were characterized and the thermal decomposition mechanism is proposed.

The flow sheet for this route is shown in Fig. 1.

#### 2. Experimental

#### 2.1. Synthesis of lead citrate precursor

Lead citrate  $(Pb_3(C_6H_5O_7)_2\cdot 3H_2O)$  was synthesized by a novel hydrometallurgical method from spent lead-acid battery paste, reported in our previous work [20]. The spent lead acid battery pastes samples were provided by Hubei Jinyang Metallurgical Co. Ltd., China. Main parameters of the hydrometallurgical processes are provided in Supplementary Information, while the outline is described below.

Trisodium citrate hydrate (Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>·2H<sub>2</sub>O, >99% purity) was used as the desulfating agent and the source of organic ligand during leaching the spent lead battery paste. Anhydrous acetic acid (CH<sub>3</sub>COOH, 99.5% purity) was used to assist rapid leaching [20]. The pH of the leaching solution was maintained at about 5.2. Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, 30%, w/v) was used as the reductant to reduce PbO<sub>2</sub> to PbO. After leaching, lead citrate was retained in the solution for 24 h for the crystals to grow, followed by filtration, washing with water and drying in air at 105 °C. The final product was used as a precursor in the following thermal decomposition experiments.

# 2.2. Preparation of porous carbon skeleton based nanostructured leady oxide

Leady oxide was synthesized by calcining 0.5 g lead citrate  $(Pb_3(C_6H_5O_7)_2:3H_2O)$  at different temperatures and in different gaseous atmospheres (with varying volumetric concentration of oxygen) for

a fixed duration of 60 min. The calcination atmosphere comprised a mixture of  $O_2/N_2$  in various volumetric proportions. Based upon preliminary TG-DTA curves of the lead citrate precursor in air, which are shown in Supplementary Information Fig. S1, three suitable calcination temperatures 370, 450 and 600 °C were chosen in this study. The volumetric percentage of  $O_2$  in  $O_2/N_2$  mixture (at a total flow rate of 500 mL/min) were 0%, 10%, 21%, 30%, 70%, and 100%, and denoted as  $O_2$ -0%,  $O_2$ -10%,  $O_2$ -21%,  $O_2$ -30%,  $O_2$ -70%, and  $O_2$ -100%, respectively.

Mass fraction of PbO in the leady oxides was measured by chemical titration. The leady oxide sample was dissolved in acetic acid solution (10% v/v), and diluted to a given volume in a volumetric flask. The Pb<sup>2+</sup> concentration was determined by EDTA titration method.

To determine the mass fraction of Pb metal in the leady oxides, leady oxides were totally dissolved in nitric acid solution (10% v/v) and the dissolved Pb<sup>2+</sup> concentration was determined by EDTA titration method to measure total Pb. The fraction of Pb metal was calculated as total Pb minus PbO determined above.

Mass of porous carbon in the leady oxides was measured by a High-frequency Infrared Carbon & Sulfur Analyzer (HCS-140, Shanghai DeKai Instrument Co., Ltd. China).

#### 2.3. Characterization of leady oxides products

The X-ray diffraction (XRD) of leady oxide products were measured using a X'Pert PRO XRD (Philips, PAN Analytical B.V., Holland) in the 2 $\theta$  range from 5° to 75°, with Cu–K $\alpha$  radiation  $\lambda$  = 1.5418 Ű. Morphologies of leady oxides products were studied with scanning electron microscopy (Sirion 200 SEM, FEI, Holland), operated at 10 kV after coating the samples with gold. EDX spectra of leady oxides products were collected on an ultrathin window (UTW) X-ray detector equipped with Sirion 200 SEM.

#### 2.4. Characterization of porous carbon in leady oxides products

Leady oxides of O<sub>2</sub>-0% at 370 °C, 450 °C and 600 °C were soaked in HNO<sub>3</sub> solutions (10% v/v) to dissolve Pb metal and its oxides. After dissolving, the solid residue was carbon. The carbon residue was filtered and separated from the solution, and washed by deionized water until pH was about 7, then dried at 105 °C before further characterization. The carbon samples prepared from leady oxide products of O<sub>2</sub>-0% at 370 °C, 450 °C and 600 °C are named C370, C450 and C600, respectively.

#### 3. Results and discussion

# 3.1. Effect of calcination atmosphere on Pb metal and residual carbon in leady oxides

Proportions of the calcination products decomposed at 370 °C in  $O_2/N_2$  mixture at different volumetric percentages of  $O_2$  are shown in Fig. 2 (a). In pure nitrogen, i.e. corresponding  $O_2$ -0% gas, the sum of mass percentages of PbO, Pb metal, and carbon is only 90 wt%, indicating incomplete decomposition and the presence of intermediate hydrocarbons. With increasing the volumetric percentage of O<sub>2</sub> in the calcination atmosphere, mass percentage of metallic Pb exhibits a surprising increase from nearly negligible value to 17.4 wt%. With increasing the volumetric percentage of  $O_2$  in calcination atmosphere, the molar ratio of PbO in total Pb of the product significantly decreases from 100 wt% to 73.7 wt%, as shown in Fig. 2 (b). It is interesting that the ratio of metallic Pb increases with increasing oxygen partial pressure in the calcination atmosphere. The formation of carbon in the calcined product can in turn influence the relative amounts of PbO and Pb. As shown in Fig. 2 (a), the amount of carbon in the calcination product decreases from 8.4 wt%



**Fig. 2.** Effects of volumetric percentage of  $O_2$  in  $O_2/N_2$  mixture on (a) mass percentage of components and (b) molar ratio of PbO to total Pb element in calcined products synthesized from lead citrate precursors at 370 °C.

to 0.3 wt% with the increase of  $O_2$  concentration in calcination atmosphere. It is notable that residual carbon still exists in 100 v/v%  $O_2$  and might have acted as a localized reducing agent (as C or CO) within the decomposing citrate particle facilitating transformation of PbO into Pb metal.

Chemical composition of the products that are decomposed at 450 °C and 600 °C in various atmosphere are shown in Supplementary Information Fig. S2. Under certain conditions, it should be noted that some of the lead oxide is present as  $Pb_3O_4$  especially with increasing temperature. At 450 °C, the variation of the ratio of Pb metal and PbO in leady oxides is similar as that at 370 °C. With increasing the proportion of  $O_2$  in calcination atmosphere, mass fraction of Pb metal increases from 0.7 wt% to 12.7 wt%, while PbO decreases from 94.4 wt% to 84.3 wt%. Samples of  $O_2$ -0% series are an exception because the fraction of residual carbon is relatively high, which is about 8 wt%. However, at 600 °C, the molar ratio of Pb metal in total Pb changes little with varying oxygen concentration.

#### 3.2. Characterization of the leady oxides calcined at 370 °C

The XRD patterns of the calcination products in  $O_2/N_2$  mixture at 370 °C are shown in Fig. 3. As shown in Fig. 3, only  $\beta$ -PbO is identified in the calcination products in  $O_2-0\%$  atmosphere (pure  $N_2$  gas), which agrees with the results from chemical analysis in Fig. 2. Leady



Fig. 3. The XRD patterns of the calcination products from lead citrate precursor at 370 °C in  $O_2/N_2$  mixture with different volumetric percentage of  $O_2$ .

oxides crystallite contains  $\beta$ -PbO,  $\alpha$ -PbO and Pb metal when prepared in a gaseous atmosphere ranging from O<sub>2</sub>-10% to O<sub>2</sub>-30%; when the proportion of O<sub>2</sub> rises to above 70%,  $\alpha$ -PbO does not exist in the calcination products any longer.  $\beta$ -PbO suggests that availability of higher oxygen concentration may result in higher local temperatures within the combusting lead citrate. Higher local temperatures within the combusting lead citrate. Higher local temperatures within an increase in the volumetric percentage of O<sub>2</sub> in N<sub>2</sub>/O<sub>2</sub> mixture, the intensity of major crystalline peak at 20 of 31.4° of Pb metal increases, indicating that the amount of Pb metal in the calcination products tends to increase, which agrees with the results in Fig. 2 (b).

The SEM images of the calcination products from lead citrate precursor at 370 °C in  $O_2/N_2$  mixture with different volumetric percentage of  $O_2$  are shown in Fig. 4. As shown in SEM images Fig. 4 (a)-1, (b)-1, (c)-1, (d)-1, (e)-1 and (f)-1, the leady oxides products are ultrafine crystal particles within the size range of 100–200 nm approximately. In the calcination products of  $O_2$ -0%, leady oxides particles are found to be uniform spheres with an average diameter of about 100 nm. The particles became elliptical cylinder or irregular shape in the calcination products of  $O_2$ -21% and  $O_2$ -30%. The particles exhibit laminated structure in the calcination products of  $O_2$ -70% and  $O_2$ -100%.

These ultrafine crystal particles easily agglomerate into porous column-shape particles with a length of about 50  $\mu$ m, as shown in

SEM images Fig. 4 (a)-2, (b)-2, (c)-2, (d)-2, (e)-2 and (f)-2. As pointed by the arrow in SEM images of O<sub>2</sub>-10%, O<sub>2</sub>-21%, O<sub>2</sub>-30%, O<sub>2</sub>-70%, and O<sub>2</sub>-100%, a few smooth-surface ball-shape particles with an average diameter of about 5  $\mu$ m are dispersed between porous columnshape particles. These ball-shape particles are metallic Pb as identified by the EDX spectrum [20]. Brown [31] has reported that nucleation occurs randomly on the surfaces of the more ordered particles, and nuclei grow rapidly to form spherical products of Pb metal in the thermal decomposition of lead citrate. Moreover, carbon forms a matrix isolating lead spheres from coalescence in inert atmosphere [31]. With the increase of volumetric percentage of O<sub>2</sub> from 0% to 100%, more ball-shape particles of Pb metal appear in the SEM images, indicating that the amount of Pb metal in the calcination products increase, in accordance with the results in Fig. 2 (b).

# 3.3. Characterization of the leady oxides calcined at 450 $^\circ C$ and 600 $^\circ C$

The XRD patterns of the calcination products in  $O_2/N_2$  mixture at 450 °C are shown in Supplementary Information Fig. S3. As shown in Fig. S3, with  $O_2$  proportion above 30%, Pb<sub>3</sub>O<sub>4</sub> is identified in leady oxides. Increasing the  $O_2$  proportion results in more Pb<sub>3</sub>O<sub>4</sub>.

The SEM images of the calcination products at 450 °C in  $O_2/N_2$  mixture with different  $O_2$  percentage are shown in Supplementary Information Fig. S4. As shown in SEM images Fig. S4 (a)-1, (b)-1, (c)-1, (d)-1, and (e)-1, calcination products are ultrafine crystal particles within the size range of 100–200 nm approximately. In the calcination products of  $O_2$ -0%, leady oxides are uniform spherical particles with an average diameter of 100 nm. Particle size increases with increasing  $O_2$  proportion in calcination atmosphere from 0 v/v% to 21 v/v%, and particle size of  $O_2$ -30% more non-homogenous than  $O_2$ -21% because of the existence of Pb<sub>3</sub>O<sub>4</sub>. With increasing  $O_2$  proportion above 30%, more Pb<sub>3</sub>O<sub>4</sub> exists in leady oxides, and particle size tends to be uniform as  $O_2$ -100%.

With increasing  $O_2$  percentage from 0 v/v% to 100 v/v%, more ball-shape particles (Pb metal) appear in SEM images indicating more Pb metal in the calcination products, which is in agreement with the results in Fig. S2.

The XRD patterns of the calcination products in  $O_2/N_2$  mixture at 600 °C are shown in Supplementary Information Fig. S5.  $Pb_3O_4$ is identified in sample  $O_2$ -30% and  $O_2$ -70%. However,  $\beta$ -PbO is identified in the calcination products of  $O_2$ -100% since  $\beta$ -PbO is known to be more stable at higher temperatures.

The SEM images of the calcination products at 600 °C are shown in Fig. S6. Particle size increases with increasing  $O_2$  proportion from 0 v/v% to 100 v/v%. In images with higher magnification, in the  $O_2$ -100% sample, molten ball-shape Pb metal transforms to porous morphology perhaps due to that Pb metal is oxidized to PbO.

#### 3.4. Characterization of porous carbon skeleton in the leady oxide

Morphologies of residual carbon specimens of C370, C450 and C600 are shown in Fig. 5. As shown in SEM images Fig. 5 (a), (c) and (e), all residual carbon specimens of C370, C450 and C600 exhibit porous structure. With respect to the morphologies of leady oxides in Figs. 4, S4 and S6, it can be assumed that in Fig. 5 nanostructured leady oxide at 100 nm decorated the surface of the mesoporous carbon, which acted as the skeleton of the composite. These mesoporous carbon materials in C370 and C450 are seen to assemble as column-shape, as shown in SEM images Fig. 5 (b), (d) and (f), which is consistent with the column-shape morphologies of O<sub>2</sub>-0% leady oxides in Figs. 4 and S4. At 600 °C the higher temperature, the column-shaped skeleton structure tends to be destroyed and transforms into particles of irregular shape.



Fig. 4. SEM images of the products decomposed at 370 °C in O<sub>2</sub>/N<sub>2</sub> mixture with different volumetric percentage of O<sub>2</sub>: (a) 0%; (b) 10%; (c) 21%; (d) 30%; (e) 70%; (f) 100%.

The porous carbon C600 is also identified as the mixture of C element containing a small amount of O as shown by EDX spectra in Fig. 5 (g) and (h). The XRD patterns shown in Fig. 6 demonstrate that the mesoporous carbon is amorphous. Raman spectra (Fig. S7) of the porous carbon displayed D and G bands at 1370 and 1590 cm<sup>-1</sup> for C450, 1347 and 1600 cm<sup>-1</sup> for C600, respectively. Generally speaking, the appearance of the D peak corresponds to the presence of a disordered carbon structure, which is consistent with above XRD patterns. The IR spectra (Fig. S8) exhibits some residual organic groups such as:  $-CH_3$  at 3420 and 1381 cm<sup>-1</sup>;  $-CH_2$  at 2927 and 1333 cm<sup>-1</sup>; -COO- at 1611 and 1423 cm<sup>-1</sup>. As the calcination temperature increases, the peaks of the organic groups become weakened.

#### 3.5. Thermodynamics and kinetics analysis

In our previous study [20], it is proposed that the calcination of  $Pb_3(C_6H_5O_7)_2$ ·3H<sub>2</sub>O in air had two stages. First stage is decomposition of citrate from pyrolysis of citrate forming C, CO/CO<sub>2</sub>, H<sub>2</sub>O and PbO; and the second stage is the reactive combustion of remaining C and H at temperatures of higher than 350 °C.

The following Reactions (1)–(6) are considered relevant in the present system:

 $2PbO(s) + C(s) = 2Pb(1) + CO_2(g)$ (2)

 $PbO(s) + CO(g) = Pb(1) + CO_2(g)$  (3)

 $2C(s) + O_2(g) = 2CO(g)$  (4)

$$C(s) + O_2(g) = CO_2(g)$$
 (5)

$$2 Pb (1) + O_2 (g) = 2PbO(s)$$
(6)

Fig. 7 shows the standard  $\Delta G^0$  of Reactions (1)–(6) in the temperature range from 350 °C to 800 °C (HSC CHEMISTRY 6.0).

Based on the chemical formula for lead citrate as  $Pb_3(C_6H_5O_7)_2 \cdot 3H_2O$ , there is enough O per mole of  $Pb_3(C_6H_5O_7)_2 \cdot 3H_2O$ in thermal decomposition to generate 3 mol of PbO, 8 mol  $H_2O(g)$ and 3 mol of  $CO_2$  (g), leaving 9 mol of C available either to form  $CO_2$ (with oxygen) or stay as C (in absence of oxygen). Under pyrolysis, a theoretical composition of C in the PbO + C is calculated as 13.8 wt%, but in practice CO can also be generated thus more of the C can partially react with the oxygen present in the citrate. Experimental observation of 8 wt % C under nitrogen provides evidence for this supposition. Under this scenario, there is no combustion of C, only endothermic decomposition. If the temperature is at the lower end, the reaction of PbO with C is kinetically hindered although thermodynamic driving force for decomposition of PbO to Pb metal with C and CO does exist. As the temperature increasing, amounts of Pb metal (but still in small amounts) appear to increase under pure nitrogen. With increasing concentration of oxygen in the gaseous atmosphere, more C in citrate is directly combusted, generating heat and thus locally increasing the temperature. At higher temperatures CO is thermodynamically more stable than CO<sub>2</sub> and PbO reduction is both thermodynamically and kinetically more favorable directly with C (Fig. 7), enhanced by the close proximity of PbO, C and heat generated within the decomposing citrate matrix itself.

Since most of the lead citrate is decomposed in between 350 and 450 °C, fixing the furnace temperature at 370 and 450 °C has similar patterns, as C material is still available. Holding the furnace temperature at 600 °C, which is above the decomposition temperature, most of the C is already combusted and some of Pb metal formed can be oxidized back especially at the higher oxygen concentration in the gas.



Fig. 5. SEM images of the porous carbon specimens of (a) and (b) C370, (c) and (d) C450, (e) and (f) C600, (g) and (h) EDX spectra of C600 specimen.



Fig. 6. The XRD patterns of porous carbon specimens of C370, C450 and C600.

The above discussion is illustrated using a pictorial model for the calcination of lead citrate, shown as Fig. 8.

#### 4. Conclusions

Preparation of leady oxides has been investigated by decomposition of lead citrate in a mixture of  $O_2/N_2$  with various  $O_2$  volumetric proportions at 370 °C, 450 °C and 600 °C. Molar ratio of Pb metal to total Pb in leady oxides increases with increasing  $O_2$  proportion in calcination atmosphere at 370 °C and 450 °C. Pb metal in leady oxides declines slightly at 600 °C. Mesoporous carbon is formed as the structural skeleton in the leady oxide carbon composite of calcination products. The leady oxide particles are formed on the surface



**Fig. 7.** The change of  $\Delta G^0$  versus different reaction temperatures for Reactions (1) to (6).

of the carbon skeleton. The content of mesoporous carbon decreases from about 8 wt % to about 0.3 wt % when increasing the proportion of O<sub>2</sub> in the calcination atmosphere and cannot be eliminated completely even in 100 v/v% O<sub>2</sub>. With increasing the proportion of O<sub>2</sub>, particle size became bigger from 50 nm to 1  $\mu$ m and the mesoporous carbon skeleton is gradually destroyed.

A model is proposed to analyze the mechanism of lead citrate thermal decomposition: porous structure and generated gas can form oxygen-deficient environment and reducing atmosphere can generate in reaction system. Exothermic oxidation of CO, C and other



Fig. 8. Sketches of calcination theory model.

oxidizing substance are affected by calcination atmosphere leading to the increase of local temperature, which affects the chemical equilibrium of the mixture system. The proposed work can help to generate suitable combination of carbon and leady oxide to form a paste precursor as active materials for anode and cathode for a new lead-acid 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.2015.11.030.

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