Journal of Power Sources 257 (2014) 27-36



Contents lists available at ScienceDirect

# Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

# A novel ultrafine leady oxide prepared from spent lead pastes for application as cathode of lead acid battery



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#### HIGHLIGHTS

• Novel leady oxide is prepared from  $Pb_3(C_6H_5O_7)_2 \cdot 3H_2O$ , recovered from spent lead pastes.

Properties of leady oxides, which affect battery performance, change with calcination temperature.

• Leady oxide prepared at 375 °C exhibits excellent initial capacity as PAM.

#### ARTICLE INFO

Article history: Received 7 September 2013 Received in revised form 10 January 2014 Accepted 20 January 2014 Available online 29 January 2014

Keywords: Lead acid battery Leady oxides Spent lead pastes Calcination temperature Electrochemical performance

# ABSTRACT

A novel ultrafine leady oxide has been prepared from a combustion–calcination process of lead citrate precursor ( $Pb_3(C_6H_5O_7)_2 \cdot 3H_2O$ ), by hydrometallurgical leaching of spent lead pastes firstly. The leady oxides are used to assemble lead acid battery which are subjected to cyclic voltammetry (CV) and battery testing. Various key properties of the new oxides, such as morphology, crystalline phases, degree of oxidation, apparent density and water and acid absorption value have been characterized by chemical analysis, X-ray diffraction (XRD) and scanning electron microscopy (SEM). The results show that leady oxides synthesized at different calcination temperatures mainly comprise  $\beta$ -PbO,  $\alpha$ -PbO and Pb. Unlike traditional leady oxide, the new oxide product prepared at 375 °C has a rod-like morphology with greater porous structure, and appears smaller density, lower value of acid absorption and larger propensity for water absorption. In battery testing, the 20 h rate and 1C rate discharge time have exceeded 26 h and 40 min, respectively. Results reveal that the leady oxide prepared at 375 °C exhibits excellent electrochemical performance and initial capacity as positive active material. While leady oxide obtained at 450 °C presents a relatively improved cycle life. Further work is to optimize the battery manufacturing process for better cycle performance.

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# 1. Introduction

The compositions of leady oxide mainly contain 70%–80% lead (II) oxide and 20%–30% metallic lead with a small amount of other lead oxides [1]. The two predominant methods used to produce leady oxides are the "ball-mill process" where lead is heated and oxidized by the tumbling action or the "Barton-pot" method where atomized liquid droplets are oxidized. The particle sizes of these traditional leady oxides are generally micron level [2,3]. In recent

years, nano-structured leady oxides have been attracting much interest because they are distinguished from the conventional materials by their small particle size and large specific area giving rise potential to remarkable electrochemical performance as active material [4,5]. Wang et al. [6] prepared nano-crystalline lead oxide through two-step chemical reactions using Pb(NO<sub>3</sub>)<sub>2</sub> as the starting material for application as the electrode active material for a valve-regulated lead acid (VRLA) battery. Karami et al. [7,8] synthesized uniform leady oxide nanostructures by the sono-chemical method. The electrochemical tests showed a high discharge capacity and excellent cycle characteristics.

However in these methods either expensive chemical reagents applied as raw material result in much difficult on industrialization, or the objective products of metallic lead need to be further

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<sup>0378-7753/\$ -</sup> see front matter © 2014 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.jpowsour.2014.01.091

processed into leady oxide as active materials of lead acid battery by oxidation [2,9–11]. Kumar [12] developed a novel technology for recovering lead from spent lead acid battery pastes via a hydro-metallurgical process. With this novel technology, ultrafine leady oxide with 200–500 nm can be obtained through leaching-calcination process. In our previous research [13,14], ultrafine leady oxides with various characteristics such as morphology can be synthesized by novel hydrometallurgical processes from spent battery pastes.

The physicochemical and microscopic properties of leady oxide such as particle size and shape, surface area, crystal structure, purity, and degree of oxidation, can potentially, individually or in combinations, affect the electrochemical performance [2]. CSIRO [15] has investigated the electrochemical properties of leady oxides with various morphologies prepared under different conditions in the recent past. Their lead oxides include such morphologies as sphere, column, flake, petal, et al. However their study has not demonstrated the positive connections between the different morphologies and electrochemical properties. Ferg [16] demonstrated that an electrode with a high porosity and a large pore volume distribution might give good results for high power discharge applications. Therefore, porous materials such as diatomites and silica gel were applied as positive electrode additives for rising porosity of the battery plates and enhancing discharge power of the battery [17,18]. But if the porosity is too high, a reduction in the life cycle ability of the electrode would occur because of poor adhesion between the particles, resulting in the shedding of the active materials [16]. Since the morphology of the active materials is subject to significant change with cycling [19]. Schrade [20] suggested that for deep-discharge batteries, leady oxide should have uniform, consistently reproducible characteristics. Additionally, Mayer [3] has investigated the influence of the oxide on battery performance. Their results indicate that both the oversized and the ultra-fine leady oxides do great harm to the battery cycle performance. It's speculated that porosity and efficiency of the active material in the leady oxide power are the determinate factors of initial capacity, while the cohesive strength between the particles affect definitely the cycle performance.

In this study, ultrafine leady oxide was prepared at different temperature in air from decomposition of lead citrate precursor (Pb<sub>3</sub>(C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>)<sub>2</sub>·3H<sub>2</sub>O). The precursor was synthesized firstly by leaching spent lead acid battery paste in a mixture solution containing sodium citrate and other reagents. The as-prepared leady oxide samples simultaneously varied complying with the calcination temperature. The morphology, structure and electrochemical performances of leady oxides were characterized, and batteries were made by the new leady oxides to examine its battery performance. 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 of China. Commercial negative plates were provided by Changguang Company of China. Sodium citrate (Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>·2H<sub>2</sub>O, >99% W/W), anhydrous acetic acid (CH<sub>3</sub>COOH, 99.5% W/W), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, 30% W/V) and concentrated sulfuric acid (98% W/W), were obtained from Sino-pharmaceutical company of China.

## 2.2. Preparation of leady oxides

Self-synthesized leady oxides were prepared by two chemical reaction steps. The first step is the process of leaching spent lead



Fig. 1. The flow sheet of experiments.

pastes, using sodium citrate and acetic acid as reagents, and using 30% hydrogen peroxide as the reductant for PbO<sub>2</sub> [14]. 1 kg of spent lead pastes was added to a solution made up of leaching agents with a solid/liquid mass ratio of 1/5. The pH of the solution was in a range of 5–6. In order to transform all lead compounds in spent lead pastes into lead citrate, the actual dosage of leaching agent was twice of the stoichiometry calculated dosage. The detailed reaction conditions are shown in Table 1. After leaching, the reaction vessel with lead citrate slurry was placed in homoeothermic water bath at 55 °C for 8 h for crystals growing up. Finally the lead citrates were washed with distilled water, vacuum filtrated and dried at 45 °C. In leaching process, the formula of leaching product is Pb<sub>3</sub>(C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>)<sub>2</sub>·3H<sub>2</sub>O and desulfurization efficiency of the lead pastes is over 99% with lead recovery ratio of about 97.5%.

The second step is combustion–calcination of lead citrate  $Pb_3(C_6H_5O_7)_2 \cdot 3H_2O$ . It has been found that the lead citrate can combust completely at a temperature higher than 350 °C in air and the morphologies of products convert from porous columnar to spherical structure with increasing temperature [21]. It means leady oxides obtained at different temperature will likely exhibit various electrochemical properties due to the different structure. Thus in order to find out the most suitable product for application of lead acid battery, leady oxide samples were prepared by calcining lead citrate in air at the temperatures of 350 °C, 375 °C, 400 °C, 425 °C and 450 °C for 1 h respectively, and the physicochemical and electrochemical properties were simultaneously examined.

#### 2.3. Characterization of leady oxides

The phase compositions of different leady oxides were determined by X-ray diffraction (XRD) by using D/MAX 2550 X-ray

 Table 1

 The detailed leaching reaction conditions

the detailed federing reaction (	conditions.	
Materials and reagents	$c/L/lra L^{-1}$	TIOC

Materials and reagents	ents S/L/kg L <sup>-1</sup> T/°C		T/°C	Stirring	Reaction	
Spent lead Sodium pastes/g citrate/g	Acetic acid/g				speed/r min <sup>-1</sup>	time/h
1000 1632	350	1/5	25	300	4	

Table 2		
The components of positive	e paste for the	battery assembly.

No.	Compound	wt%
1	Leady oxide powder	81.63
2	Sulfur acid ( $d = 1.4$ )	7.35
3	Distilled water	11.01
4	Fibers	0.01

diffraction analyzer (Japan) using Cu  $K_{\alpha}$  radiation ( $\lambda=$  1.54 Å) at 300 mA and 40 kV.

The morphologies of different leady oxides were examined by ESEM Quanta-200FEG FEI (Holland) scanning electron microscopy (SEM) technique.

The residual quantities of element carbon and sulfur in the leady oxides were measured by HCS140 (China) Infrared carbon–sulfur analyzer.

The basic physicochemical characteristics of different leady oxides included the density, oxidizability, water-absorption and acid-absorption value. Density of leady oxide mainly referred to apparent density, which is equal to the specific value of its mass or weight to its volume. Oxidizability of leady oxide refers to the mass percentage of lead monoxide in the leady oxide products. The water-absorption value of leady oxide refers to the volume of water absorbed by 1 kg of the leady oxide product. The acid-absorption value reflects the degree of reaction between leady oxide and sulfuric acid (1.055 g cm<sup>-3</sup>) absorbed by each kg of the leady oxide product.

## 2.4. Electrochemical testing

Electrochemical tests were performed at room temperature using VMP-2 electrochemical workstation from USA. The Cyclic Voltammetry (CV) curves were tested by a three electrode system. The working electrode was a self-made micro-porous electrode filled with the samples of different leady oxides. The counter electrode was double platinum electrode, and the reference electrode was an Hg/Hg<sub>2</sub>SO<sub>4</sub>/K<sub>2</sub>SO<sub>4</sub> (sat.) electrode. The electrolyte was sulfuric acid solution with concentration of 1.175 g cm<sup>-3</sup>. The CV curves were applied to observe the electrochemical behavior of



Fig. 3. XRD patterns of leady oxides prepared at different temperatures: (a) 350 °C; (b) 375 °C; (c) 400 °C; (d) 425 °C; (e) 450 °C.

different leady oxides over a certain voltage range. A scanning speed of 20 mV  $\cdot$  s<sup>-1</sup> was used within a potential range of 0 to +1.5 V.

# 2.5. Battery assembling and testing

Self-synthesized leady oxides were used as positive active material (PAM) in the lead acid battery assembly. In order to measure the performance of the positive active mass, negative plates from a commercial source were used. Positive pastes were prepared with the components listed in Table 2.

The grids used in battery assembly were low antimony alloys of Sn–Al–Ca–Pb. The size of the plate was 35 mm  $\times$  60 mm  $\times$  1.2 mm. Fig. 2 shows the schematic diagram of the assembly process for making lead acid battery. After mixing and pasting, the positive plates were cured in a curing vessel at a relative humidity of 95% and a temperature of 80 °C. The cured pasted plates were dried at 70 °C for 20 h. The formation process of plates was carried out in a



**Ripe plate** 

Fig. 2. Schematic diagram of the assembly of lead acid battery.



Fig. 4. SEM images of leady oxides prepared at different calcination temperatures: (a) 350  $^{\circ}$ C; (b) 375  $^{\circ}$ C; (c) 400  $^{\circ}$ C; (d) 425  $^{\circ}$ C; (e) 450  $^{\circ}$ C.

sulfuric acid solution with a specific gravity of 1.05 g cm<sup>-3</sup>, including two processes. In the first process, the cured plate was soaking in sulfuric acid solution on open circuit for 2 h, resulting in formation of  $3PbO \cdot PbSO_4 \cdot H_2O$ ,  $PbO \cdot PbSO_4$  and small amounts of  $PbSO_4$ . In the second process, the formation of positive plate was carried out under a constant current for 48 h (sextuple theory capacity). Each dried positive plate was coupled with two commercial negative plates soaking in sulfur acid solution (1.335 g cm<sup>-3</sup>) electrolyte so that testing batteries under 2 V/2 Ah could be made.

The performance of constructed batteries was tested on a battery tester. Initial capacity and large current discharge performance of the battery were tested at 20 h discharge rate and 1C discharge rate, respectively. 20 h discharge rate was carried out with a constant discharge current of 100 mA until terminal voltage 1.75 V reached. 1C discharge rate was carried out with a discharge current of 2000 mA with a cut-off voltage of 1.60 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%).

### 3. Results and discussion

## 3.1. Characterization of leady oxides

As shown in Fig. 3, the XRD patterns of the self-synthesized leady oxides mainly comprise  $\beta$ -PbO, and  $\alpha$ -PbO with a little amount of Pb. Differently,  $\beta$ -PbO is the major phase existed in self-synthesized leady oxide instead of  $\alpha$ -PbO which is the main component of conventional leady oxide [1]. Fig. 3(a) shows that there is a small amount of incomplete combustion product at 350 °C, which may detrimentally affect the electrochemical performance.

The SEM images of the self-synthesized leady oxides are shown in Fig. 4. The micro-morphology of the leady oxides can be perceived as a granular structure, which is more similar to the traditional Barton-pot oxide rather than the ball-mill oxide [11]. And the primary particles of self-synthesized leady oxides are loose granules with particle size of 100–500 nm, much smaller than the Barton-pot leady oxide.

When temperature is at 350 °C, the decomposition products containing element C and H begin to combust violently. As a result of decomposition gas emission, leady oxide presents porous rodlike morphology with a larger size, shown in Fig. 4(a). However, lead citrate precursor has not decomposed completely, and then a small amount of incomplete combustion product containing element C has existed in the product at 350 °C, which is consistent with the XRD pattern in Fig. 3(a). Therefore, incomplete combustion products connect leady oxide particles together, and then the products show larger rod-like morphology. When the calcination temperature increases up to 375 °C, lead citrate precursor decomposes completely with the emission of more gases. And then, the products at 375 °C show smaller particles with more porous morphology, as shown in Fig. 4(b). The porous morphology can provide more contact area for electrochemical reaction of the active materials, which is beneficial for capacity enhancement.

When temperature is higher up to 400 °C, leady oxide particles begin to agglomerate rapidly, as shown in Fig. 4(c). The products at 425 and 450 °C show larger agglomerated particles significantly, as shown in Fig. 4(d) and (e).

#### 3.2. Physicochemical characteristics of leady oxides

Results characterizing key properties are shown in Table 3. It can be seen that the apparent density of the combustion product at  $350 \degree$ C and  $375 \degree$ C are much lower than the traditional leady oxide.

Tab	le 3
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he chemical characteristics of different leady oxid
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Calcination temperature/°C	Apparent density/g cm <sup>-3</sup>	Oxidizability/%	Water- absorption value/ml kg <sup>-1</sup>	Acid- absorption value/g kg <sup>-1</sup>
350	1.46	87.7%	300.0	377.0
375	1.51	82.9%	239.8	440.3
400	1.87	75.2%	219.9	352.8
425	1.90	71.2%	180.0	376.9
450	2.05	67.6%	140.0	380.0
Traditional	1.93	83.2	110.0	381.3

The oxidizability ranges from about 70% to 85%. Due to ultradispersed structure of the primary particles, it is easy to demonstrate that the specific surface area of self-synthesized leady oxides is much larger. Therefore, the self-synthesized leady oxides present much higher water absorption value than traditional leady oxide.

Both thermodynamically and kinetically, the degree of oxidation is expected to decrease with the increasing temperatures. As the calcination temperature rises, particle size of self-synthesized leady oxide increases so that the agglomeration has the effect of restraining the oxidation of lead resulting in lower degree of oxidation with increasing ratio of Pb/PbO. Effects of agglomeration can be further enhanced as the operating temperature is increased further away from the melting point of Pb at 320 °C. Accordingly as the specific surface area is decreased, the apparent density is increased, and the absorption values for water-absorption are correspondingly decreased.

In general, acid-absorption value is affected by oxidizability of leady oxides and particle size of leady oxides simultaneously. Higher oxidizability and smaller particle size of leady oxides are contributed to higher acid-absorption value. As discussed in Fig. 4, the particle size of leady oxide product at 375 °C is the smallest. As shown in Table 3, acid-absorption value of leady oxides at 375 °C is maximum, which is decided by both oxidizability value and particle size of leady oxides combinationally. Therefore, acid-absorption values change nonlinearly with increasing calcination temperature. The testing results from infrared carbon—sulfur analyzer show that there exist nearly no sulfur element in self-synthesized lead citrate and leady oxides, and thus desulfurization in the aqueous phase is very effective. Carbon element concentration in leady oxide prepared at 350 °C is about 0.36% while those at other temperatures have not been detected.

# 3.3. Electrochemical performance

Fig. 5 shows the 10th CV curve results of leady oxides, while the explanations of 3 peaks are shown in Table 4. The discharge capacities of the positive electrode at different CV curves are listed in Fig. 6.

From Table 4, there may occur two reactions when potential (vs.  $Hg_2SO_4$ ) is lower than 1.1 V. When there exists enough  $SO_4^{-}$  and potential is high enough, PbO<sub>2</sub> is converted into PbSO<sub>4</sub>(s) directly, or it will be converted into Pb<sup>2+</sup> (aq) firstly and then PbSO<sub>4</sub> through chemical reaction. Leady oxide powders prepared at 375 °C are smaller particles and they are more fully contacted to the electrolyte, so the formation of Pb<sup>2+</sup> (aq) are more violent, resulting the twin peaks in the curve.

Leady oxide prepared at 350 °C indicates no significant electrochemical activity. It's inferred that the incomplete combustion product resulting in the presence of plumbonacrite distributed in leady oxide may adversely affect the redox activity of the product.



Fig. 5. The 10th CV curves of electrode made from leady oxides prepared at different temperatures.

Meanwhile, in the 10th curve, leady oxide prepared at 375 °C shows good discharge capacity, resulting from its porous morphology. As calcination temperature is increased to 400 °C, the cathodic discharge current starts to decline. In Fig. 5, the reduction peaks for leady oxides prepared at 425 °C and 450 °C are much smaller than that at 375 °C. It indicates that higher calcination temperature of 425 °C and 450 °C deteriorates electrochemical properties of leady oxide powder.

From Fig. 6, the electrochemical activities of all leady oxides improved as cycle count increased. At the beginning of the 13th cycle, the capacity of leady oxides prepared at 400–450 °C rise relatively slowly, while the growth of discharge capacity of the 375 °C product is much higher and relatively stable. However, after the 10th cycle CV test, the capacity of 450 °C product increased rapidly and showed remarkable capacity even after 20 cycles.

# 3.4. Battery performance

In this experiment, batteries with a calculated capacity of 2 Ah were assembled by different leady oxides. Fig. 7 shows the XRD patterns of ripe plates made from different leady oxides after formation. The pastes in the ripe plates mainly comprise  $\beta$ -PbO<sub>2</sub> and small amount of PbSO<sub>4</sub> and PbO. It's speculated that the crystal phase  $\beta$ -PbO<sub>2</sub> is beneficial for the initial performance of battery [22].

After curing and formation, the main composition of positive active material turned into PbO<sub>2</sub>, whose morphology is fundamentally different from the initial oxides. From the SEM images of the ripe plates and their two-dimensional results after Image-Pro software processing shown in Fig. 8, the fine PbO<sub>2</sub> granules in the pastes showed spherical and needle-like morphology with particle sizes ranging from 10 to 100 nm.

Table 4			
The corresponding half-cell reaction of	peaks in	the cu	irve.

Peak	Half-cell reaction	<i>E</i> (V)
1	$PbSO_4+2H_2O \rightarrow PbO_2+H_2SO_4+2H^++2e^-$	>1.1
2	$2H_2O\rightarrow O_2+4H^++2e^-$	>1.4
3	$PbO_2 + SO_4^{2-} + 4H^+ + 2e^- \rightarrow PbSO_4 + 2H_2O$	<1.1
	$PbO_2 + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2H_2O$	



Fig. 6. The discharge capacities of the positive electrode at different CV curves.

SEM images of plate with leady oxides at 375 °C after different soaking time are shown in *Fig. 1S*. The smaller sulfate particles could be obtained for the soaking time of 1 h, as shown in *Fig. 1S*(c). Larger particles generate for the soaking time of 2 h and 4 h, as shown in *Fig. 1S*(d) and (e), respectively. SEM images of plate with leady oxides at 450 °C after different soaking time are shown in *Fig. 2S*. Smaller particles could be obtained for the soaking time of 2 h and 4 h, as shown in *Fig. 2S*(d) and (e), respectively. Since the initial particles in the plate with leady oxides at 450 °C are larger, longer soaking time is needed.

Formation process has a significant effect on the morphology of ripe electrodes paste. Therefore, the morphology of ripe electrodes paste is not only decided by initial leady oxides at different calcination temperature. But in this manuscript, the same soaking condition was investigated for different plates with different leady oxides prepared at different temperatures. Thus further work is being carried out with optimizing the battery manufacturing process. How do the soaking and formation process of plates affect the morphology of PbO<sub>2</sub> product in ripe electrodes paste? The reason will be investigated in the further studies.





After the secondary formation process, the morphology of PbO<sub>2</sub>, synthesized through electrochemical reaction, continues to change into different morphology (shown in Fig. 8). The particles grow along with the PbO<sub>2</sub> crystal nucleus whose crystal size is much smaller than lead monoxide, so particle sizes of all pastes are much smaller and similar.

The results of the battery performance are shown in Fig. 9. The average 20 h rate capacities after 6 tests have exceeded the theoretical capacity 2 Ah. And battery with a nominal capacity of 2 Ah made from the 375 °C product is found to have discharge time of 32 h, representing 60% excess initial capacity. The 450 °C product while exhibiting a lower utilization of active material in comparison with leady oxides made at the other calcinations temperatures, also shows 30% excess capacity of 2.6 Ah.

The discharge performances of different leady oxides are also tested at 1C discharge rate, by using a large discharge current of 2000 mA. The calculated time of discharge in these tests is 27 min. From Fig. 10 it can be seen that the 1C discharge times also follow the same trend as the 20 h rate behavior, such that the 1C discharge time of battery made from the 375 °C product is the highest in our study. All the samples in this study (made at the temperature range 350–450 °C) show excess capacity ranging from 55% excess (for the 450 °C sample) to 120% excess (for the 375 °C sample) with the 1C rate discharge times varying from 42 to 60 min, much higher than the calculated discharge time of 27 min.

The results of both the 20 h rate and the 1C rate are consistent with the electrochemical results in Section 3.3. The utilization of



Fig. 8. SEM images of ripe plates made from leady oxides at different temperatures after formation: (a) 350 °C; (b) 375 °C; (c) 400 °C; (d) 425 °C; (e) 450 °C.



Fig. 9. The initial capacity (20 h rate testing at 100 mA) of batteries made by leady oxides synthesized at different temperatures (nominal capacity is 2 Ah).

PAM is speculated to be determined by plate porosity which is influenced by properties of leady oxides at different temperatures. Therefore, as calcination temperature increases, the initial capacity of battery is decreased because of lower specific surface area as shown in Fig. 8.

Cycle performance of batteries manufactured by different leady oxides is shown in Fig. 11. The capacity retention ratio of battery made from 350 °C decreases rapidly at the beginning, which may result from the residual incomplete combustion products. It is thus confirmed that 350 °C is not sufficient as the calcination temperature. The results indicate that the capacity of battery made from 375 °C is maintained stably in the first 15 cycles, but it does drop sharply subsequently. This phenomenon is supposed to be result from the loose inner structure on the one hand. On the other hand, conventional battery manufacturing methods and high concentration of electrolyte are not fit for novel ultrafine leady oxides [22]. In future work we will report on optimization of battery manufacturing parameters and the use of additives to improve the cycle life performance of the samples calcined at the lower temperatures.



**Fig. 10.** The initial capacity (1C rate) of battery made by leady oxides synthesized at different temperatures (nominal capacity is 2 Ah).



Fig. 11. The capacity retention ratio of battery made from leady oxides synthesized at different temperatures.

The capacity retention of batteries made by leady oxides prepared at 425 °C and 450 °C has retained 70% of the initial values after 50 charge—discharge cycles. And these batteries demonstrate a tendency that the capacity decreased slowly at beginning and then rise after several cycles. Thus leady oxides prepared at the higher calcinations temperatures with loosely agglomerated granular morphology with uniform porous structure show better cycle performance.

After 50 charge and discharge cycles, batteries prepared from leady oxides produced at 375 °C and 450 °C were dissembled after a final charging. The positive lead plates were dried at 50 °C for 5 h. Both microscopic and SEM images (with EDX data) of the positive plates are shown in Fig. 12. The XRD patterns shown in Fig. 13 indicate that the pastes on the plates mainly comprise PbO<sub>2</sub> and PbSO<sub>4</sub> with a higher degree of sulfation for the lower temperature sample as listed in Table 5.

From Fig. 12, in the macroscopic image it can be noted that some of active materials were lost and grids were exposed in the positive plate I made from the active mass prepared at 375 °C, while the plate II made from leady oxide at 450 °C is still intact.

It's speculated that small particles inside plate I lack good binding contact points. Thus after several cycles, reactions to form irreversible lead sulfate is more readily promoted. As listed in Table 5, the degree of the sulfation reaction in plate I is deeper than that in plate II. The results indicate that due to high porosity and large specific surface area, particles in plate I react with sulfuric acid more severely. Generally cycle performance depends largely on excellent connectivity between the active particles and the availability of uniform porous structure which acts as reservoir for the liquid electrolyte. The results in Section 3.4 are consistent with this analysis.

#### 4. Conclusions

In this paper, leady oxides of different microscopic characteristics are prepared by a hydrometallurgical leaching of spent lead pastes to crystallize lead citrate, followed by a relatively lowtemperature calcinations—combustion process.

 The properties of leady oxide product synthesized from lead citrate [Pb<sub>3</sub>(C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>)<sub>2</sub>·3H<sub>2</sub>O] crystals are dependent upon the



Fig. 12. The macroscopic and SEM images (+EDX results) of the scrapped positive plates after 30 cycles made from leady oxide produced at different temperatures: (I) 375 °C; (II) 450 °C; (III) SEM/EDX (450 °C).

calcination temperature. As temperature rises from 350 to 450 °C, leady oxide particles agglomerate and the morphology progressively change from porous rod-like micro-structure to a less porous but more uniform globular



Fig. 13. The XRD patterns of the pastes on the scrapped plates.

structure, accompanied by a small increase in the average particle size.

- (2) Self-synthesized leady oxides mainly comprise  $\alpha$ -PbO,  $\beta$ -PbO and Pb with a degree of oxidation in the range of 70–85%. Compared to traditional leady oxide, the current samples show smaller apparent density, lower acid absorption and larger water absorption values.
- (3) Battery testing results reveal that initial capacity and highcurrent discharge capacity of lead acid battery manufactured by self-synthesized leady oxides, especially at lower temperatures, are better than those of traditional lead acid battery and exceed the nominally calculated capacity for all the samples at low and high discharge rates.
- (4) Further work is being carried out with optimizing the battery manufacturing process or importing additives in order to capitalize on the advantages of high initial capacity with acceptable cycle life.

Table 5			
The compositions	of the	scrapped	pastes.

Calcination temperature/°C	Percentage composition/%	
	PbO <sub>2</sub>	PbSO <sub>4</sub>
375	69.6	30.4
450	81.0	19.0

#### Acknowledgments

The authors thank for the financial supports from the National Science Council of China (NSC 50804017), New Century Excellent Talents Project of Ministry of Education (NCET-09-0392), the international technology cooperation plan of innovation fund, HUST (2013ZZGH015), the Wuhan Planning Project of Science and Technology, China (2013060501010168), the National Key technology R&D Program, China (2014BAC03B02) and National Postdoctoral Science Foundation of China (No: 20110491157). The authors would like to thank the Analytical and Testing Center of Huazhong University of Science and Technology for providing the facilities to fulfill the experimental measurements. The technical supports from Wuhan Changguang Power Sources. Co. Ltd., are also gratefully acknowledged.

## Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jpowsour.2014.01.091.

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