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Recycling lead from spent lead pastes by oxalate and sodium oxalate and preparation of novel lead oxide for lead-acid battery

Cheng Ma ^a, Yuehong Shu ^{a,*}, Hongyu Chen ^{a,b,*}

^a School of Chemistry and Environment, South China Normal University, Guangzhou, Guangdong 510006, PR China

^b Production, Teaching & Research Demonstration Base of Guangdong University for Energy Storage and Power Battery, Guangzhou, Guangdong 510006, PR China.

*Corresponding author. Tel. /fax: 86-20-39310187.

E-mail addresses: hongersh@163.com (Y. Shu).

*Corresponding author. Tel. /fax: 86-20-39310187.

E-mail addresses: 994373678@qq.com (H. Chen).

Abstract: A sustainable way, with minimal pollution and low energy cost in comparison with the conventional smelting way, is proposed for treating components of spent lead acid battery by oxalate and sodium oxalate. Pure lead oxalate precursor of PbC_2O_4 is the only product crystallized in leaching experiment. Lead oxalate is readily crystallized from the solution due to its low solubility and can be combust to directly produce lead oxide as a precursor for making new battery pastes. Both lead oxalate and oxide products have been characterized by means of thermo-gravimetric (TG), and X-ray diffraction (XRD). The results show that lead oxides synthesized at different calcination temperatures are comprise of α -PbO and β -PbO. The assembled batteries using the novel lead oxide powder as positive active materials show good cyclic stability for 50 charge/discharge cycles. The cell used lead oxide powder containing 15wt.% β -PbO exhibits excellent initial capacity, cycling performance and high-rate discharge characteristics, and can deliver a discharge capacity of 180 mAh g^{-1} at 30 mA g^{-1} and more than 60 mAh g^{-1} at 240 mA g^{-1} . Within 50 cycles, its capacity loss is low (5%) with excellent cyclic stability.

Keyword: Spent lead pastes; Recycling; Hydrometallurgical process; Lead oxide; Lead acid battery

Introduction

A waste lead-acid battery comprises four components: electrolyte (11-30%), lead and lead alloy (20-30%), lead paste (30-40%), and organic matter and plastic material (22-30%). The lead paste, one of these fractions, has a particularly complex composition. It is an oxide-sulphate product with the following approximate composition: 60% of lead sulphate, 20-30% of lead dioxide, 5-15% of lead monoxide and 3% lead alloy. The sulphur content in the pastes is about 6%, which causes difficulties when direct pyrometallurgical processing is employed. In the traditional refining process, decomposition of lead sulphate requires a temperature at least 1180 °C or higher. The smelting process using coal or coke as fuel is associated with emissions of many gaseous and solid pollutants, such as SO₂ and lead fumes. Hence, it poses serious environmental and human health hazards.

High temperature (>1000 °C) is required for decomposing and reducing PbSO₄, which is associated with generation of dilute SO₂ gas streams in addition to the lead fumes. New developments in the pyrometallurgical processes have led to recycling in Isasmelt [1, 2] or short rotary furnaces [3] which use Fe or soda to remove the S in the furnace by forming FeS-PbS matte or Na₂SO₄ containing slag. However, disposal of the hazardous matte or the leachable slag is also expensive and harmful to the environment [4].

Thus, more and more attention is paid to the green recycling processes for spent lead-acid batteries, such as those involving hydrometallurgical routes. The most widely used hydrometallurgical method, which consists of pre-treatment, desulphurization, reduction and electro-winning process, can avoid the SO₂ and lead dust emission problems [4, 5]. However, the energy efficiency of the electro-winning process is low, with higher total energy consumption as compared to the traditional

pyrometallurgical routes. The suggested H_2SiF_6 or HBF_4 leaching solutions may lead to emission of fluorine in the environment which is also unacceptable.

Given the disadvantages of the traditional pyrometallurgical and electro-winning methods, several new hydrometallurgical approaches have been developed [6-9]. The hydrometallurgical recovery process for the treatment of lead paste without electro-winning has not been practically employed so far. Hence, we need to develop an effective, low cost and environment-friendly process for recycling of spent lead paste. Attempts have been made to leach the components (PbSO_4 , PbO_2 and PbO) of spent lead pastes by citric acid and sodium citrate, as reported in previous studies [10-12]. D. Yang et al. [13] leached spent lead pastes using sodium citrate and acetic acid as reagents, and using 30% hydrogen peroxide as the reduction agent for PbO_2 . X. Zhu et al. [14] leached spent lead acid battery paste components by sodium citrate and acetic acid. In this leaching process, the lead citrate ($\text{Pb}_3(\text{C}_6\text{H}_5\text{C}_7)_2 \cdot 3\text{H}_2\text{O}$) 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, depending on the calcination temperatures. But the self-synthesized leady oxides comprised mainly β - PbO , it is the major phase contained in self-synthesized leady oxide instead of α - PbO which is the main component of conventional leady oxide [15].

In the present-day lead-acid battery industry, leady oxide is required for both negative and positive electrodes. Therefore, it would be of interest to synthesize PbO which would yield higher active material utilization and longer cycle-life. For example, J. Wang et al. [16] prepared crystalline α - PbO by calcination of PbCO_3 and used it as the positive electrode active material. The results showed that the α - PbO powder discharged a capacity 30% higher than that of the conventional ball-milled leady oxide. M. Cruz et al. [17] prepared a thin α - PbO film through chemical spray pyrolysis from an aqueous solution of $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ on a lead substrate. When the film

deposited on the substrate was used as a positive plate, it maintained a discharge capacity of 100 mAh g^{-1} upon extended cycling. H. Karami et al.[18, 19] synthesized a uniform structured lead oxide via a sonochemical method, which discharged a large capacity of 140 mAh g^{-1} and even 230 mAh g^{-1} as the cathode or anode of a lead acid battery. M. Salavati-Niasari et al. [20] also reported that the lead oxide powder could be prepared by decomposing lead oxalate at 500 °C, but no electrochemical results are reported. And, the performance of lead oxide powder included β -PbO has not been reported.

In this paper, as shown in Fig.1, spent lead paste was treated with an aqueous oxalate acid and sodium oxalate solution to generate a lead oxalate precursor, which was then separated from the solution. Lead could be recovered as lead oxide powder after the calcination of lead oxalate precursor. Furthermore, the two polymorphism of PbO can be easily prepared. Control of the content of β -PbO in lead oxide powder, and new batteries assembled with the novel lead oxide. The results will be used to recovery lead in Secondary lead industry and produce high-performance lead oxide.

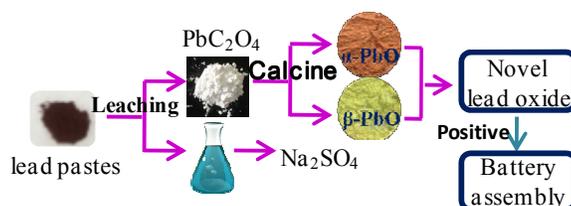


Fig.1. The flow sheet of experiments.

Experimental

Materials and Methods

Spent lead paste was provided by a secondary lead smelting plant in Hunan Zhuzhou, China. Sodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$, AR \geq 99.5%), oxalic acid ($\text{H}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$, AR \geq 99.5%) and concentrated sulphuric acid (98%) were obtained from Aladdin of Shanghai, China.

The reduction treatment of spent lead paste (the quantity of the spent lead paste was 10.00 g) was carried out as follows: 50 mL of 10 wt.% $\text{H}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ were added to the spent lead paste in a conical-flask as the reduction agent to convert lead (IV) to lead (II) [21]. Desulphurization of the samples was carried out as follows: the sample obtained above was added to 150 mL of sodium oxalate saturated solution. The conical-flask was heated under continuous stirring at 200 r min^{-1} . In order to transform all lead compounds in the spent lead pastes into lead oxalate, the actual dosage of the leaching agent was twice the stoichiometrically calculated amount. After reduction and desulphurization, the conical-flask with lead oxalate slurry was placed in a homoeothermic water bath at $60 \text{ }^\circ\text{C}$ overnight to allow the crystals to grow. Finally, the lead oxalate was washed with distilled water, vacuum filtered and dried at $110 \text{ }^\circ\text{C}$ overnight.

The main reactions involved in the process are as follows:



In Eq. (1), oxalic acid which is known with strong reduction and acidity, in previous reported, as the reduction agent. The Eq. (3) is based on the difference between the ionic products of lead sulphate and lead oxalate: $K_{\text{sp}}(\text{PbC}_2\text{O}_4) < K_{\text{sp}}(\text{PbSO}_4)$

The recovery efficiency of lead from spent lead paste was calculated by Eq. (4):

$$\text{Lead recovery (\%)} = \frac{m_1}{m_2} \times 100\% \quad (4)$$

In Eq. (4), m_1 (g) is the actual mass of PbC_2O_4 that can obtained from XRD results, m_2 (g) is the theoretical weight of PbC_2O_4 . By using the software Jade, the contents of PbC_2O_4 are calculated.

In air, the lead oxalate powders were calcined at $450 \text{ }^\circ\text{C}$, $500 \text{ }^\circ\text{C}$, $550 \text{ }^\circ\text{C}$ and $600 \text{ }^\circ\text{C}$ for 1 h,

respectively. Calcination temperature was determined based on TG data and the transition point of α -PbO to β -PbO which is 488.5 °C.

Characterization of materials

The phase composition of the different lead oxides was determined by X-ray diffraction (XRD) analysis using D/MAX 2550 X-ray diffraction analyzer (Japan) with Cu K_{α} radiation ($\lambda=1.54$ nm) at 80 mA and 5.0 kV. The crystal morphology of the different lead oxides was examined by scanning electron microscopy (SEM) technique using an environmental scanning electron microscope ESEM Quanta-200FEG FEI (Holland)

Plate preparation

Self-synthesized lead oxide powders were used as positive active material in lead acid batteries. In order to measure the performances of the positive active mass, the negative pastes from a commercial source were used. Positive pastes were prepared with the components listed in Table 1. We referenced the formula of diachylon of valve regulated lead-acid battery.

Table 1 Composition of the positive paste for the test batteries.

No.	Compound	wt%
1	Lead oxide powder	79.03
2	Aquadag	0.158
3	Fibers	0.158
4	Distilled water	10.54
5	Sulfur acid ($d=1.40$ g·mL ⁻¹)	10.12

The grids used for the test batteries were made of low antimony alloy, Sn-Al-Ca-Pb. The size of the positive plate was 20×15×1.5 mm and the negative plate was sized 20×30×1.5 mm. The pasted

plates were immersed in sulphuric acid solution for 5 s (the solution density was 1.15 g mL^{-1} for the positive plates and 1.06 g mL^{-1} for the negatives, respectively). The plates were put in an oven with sustained temperature of $100 \text{ }^\circ\text{C}$ for 5 min, then the temperature of the oven was lowered to $55 \text{ }^\circ\text{C}$ and the relative humidity was $>95\%$. The curing process was conducted for 24 h. After that, the plates were dried at $60 \text{ }^\circ\text{C}$ for 5 h.

Battery performance tests

All formation and cycling tests were performed by using a NEWARE Cycler (BTS-5V3A Shenzhen NEWARE Electronics Co., Ltd., China). Test batteries were assembled with one experimental positive plate and two negative plates, the cell capacity was restricted by the positive plate, separated by absorptive glass-mat (AGM) separator. The electrolyte used was H_2SO_4 solution with a relative density of 1.28 g mL^{-1} .

After immersing the plates in the electrolyte for 2 h, the formation of the test batteries was carried out in three steps. Firstly, the plate was charged at a current density of 15 mA g^{-1} to 100 mAh g^{-1} ; then it is charged at 25 mA g^{-1} for another 150 mAh g^{-1} ; and finally, it was charged at 8 mA g^{-1} for another 100 mAh g^{-1} .

After formation, the initial capacity test was carried out with a constant discharge current of 30 mA g^{-1} until a terminal voltage of 1.75 V was reached. The charge/discharge cycling tests were performed repeatedly at a constant discharge current of 30 mA g^{-1} with a cut-off terminal voltage of 1.75 V (depth of discharge DOD = 100%).

Results and discussion

Leaching of spent lead paste by $\text{Na}_2\text{C}_2\text{O}_4\text{-H}_2\text{C}_2\text{O}_4$ solution

After a high ball mill, the dried reddish powder sample of lead paste was separated by a sieving process. And then the battery plate grid (oversize) was separated from the fine lead paste (undersize). In our laboratory, the powders were washed with distilled water to remove sulphuric acid until the pH was about 6.5. The cleaning process of spent lead paste was shown in Fig.2. The cleaning process would continue until the number of the first pH-meter was about 6.5, and through the waste water treatment units and the control of the second pH-meter, that can achieved zero-emission of waste water. This process may also be useful in factory as it is efficient and environment friendly. It is also includes waste water to maximize the conservation of fresh water which can be recycled.

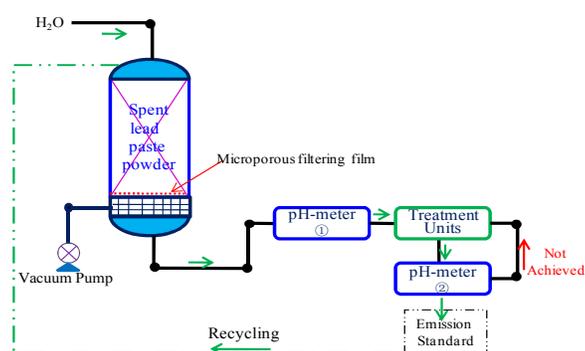


Fig.2. The flow sheet of cleaning process of spent lead paste powder.

In this work, only fine lead paste (less than 150 mesh size) was used in the leaching tests in order to eliminate the negative effect of particle size non-homogeneity. The percentage of PbSO₄, PbO₂, PbO and others are about 67.0%, 27.5%, 5.0%, and 0.5%, respectively. The chemical composition of the paste sample was analyzed by the chemical titration method.

The reactions are described in Eqs. (1)~ (3). In Eq. (1), H₂C₂O₄ acts as a reductant, and Pb (IV) turns into Pb (II) in the acidic condition. In Eq. (3), Na₂C₂O₄ acts as a desulfating agent, and oxalate acid provides an acid leaching condition which benefits for the desulfuration reaction of lead sulfate

leaching. The effects of temperature and time on lead recovery rate of Pb from the spent lead paste are presented in Fig.3. When leaching time under 0.75 h, the reaction was incomplete, and the recovery rate nearly 90% at 90 °C. Therefore, if we want to improve the recovery rate, we must extend the reaction time. The lead recovery rate increased with the increasing of leaching temperature, when the leaching time at 2 h, the lead recovery rate could increase up to over 97% for a leaching temperature of 70 °C. When the leaching temperature was over 70 °C, the rate keeps mostly unchangeable. Thus, it is reasonable to settle at 70 °C as the optimal leaching temperature. While 2 h is sufficient as an increase in leaching time to 3 h does not significantly increase the leaching efficiency of spent lead paste. The activation time 2 h is, therefore, appropriate for leaching reaction when economy and practicality are taken into consideration.

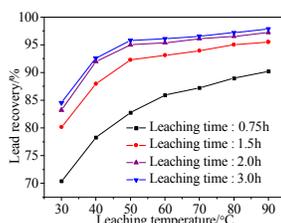


Fig.3. Effects of temperature and time on lead recovery rate of Pb from the spent lead paste.

Crystallization of lead oxalate

In $\text{Na}_2\text{C}_2\text{O}_4\text{-H}_2\text{C}_2\text{O}_4$ leaching system, the product of the leaching process was PbC_2O_4 and the lead recovering rate can reach 98.6% under the optimal leaching conditions, so it can greatly reduce lead pollution to the environment. The XRD patterns of lead oxalate precursor is shown in Fig.4 (a) and the photograph and SEM of the lead oxalate product are shown in Fig.4 (c) and (d), which preliminarily indicate that the leaching product is pure lead oxalate. Therefore, the desulfurization rate in the leaching process was approximately 100%.

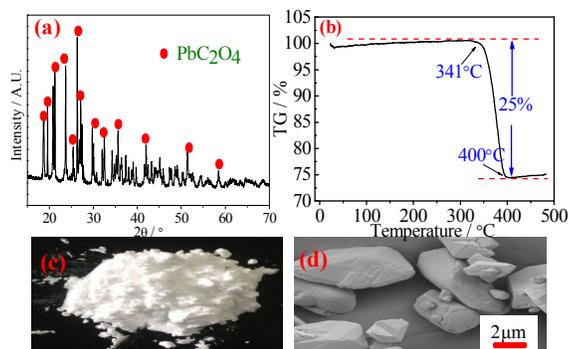


Fig.4. The XRD pattern (a), TG curve for the decomposition (b), photograph (c) and SEM image (d) of the lead oxalate.

Characterization of lead oxide

Fig.4 (b) shows the TG curves in static air for the precursor obtained from the solvothermal reaction and the desulphurization of spent lead pastes in $\text{H}_2\text{C}_2\text{O}_4\text{-Na}_2\text{C}_2\text{O}_4$ solution. There is only one weight loss step in the temperature range 341~400 °C. The weight loss at 341~400 °C may be ascribed to the decomposition of the oxalate. The weight loss is about 25.00%, which is close to the theoretical value (24.39 wt.%) in Eq. (5).



According to the reaction equation, the calcination products obtained from lead oxalate precursor at different temperatures are only lead oxide in air. This is consistent with the change of the TG curve in the paper.

This weight loss is due to the decomposition of lead oxalate to lead oxide because the oxidation number of the lead ions is constant during the thermal decomposition process.

Fig.5 shows the XRD patterns of the products after calcination of the precursor at 450 °C, 500 °C, 550 °C and 600 °C for 1 h, respectively. There is no doubt that high purity lead oxide can be obtained by this method. Moreover, $\alpha\text{-PbO}$ is the major phase at low temperatures, which also is the main

component of conventional lead oxide [15]. Additionally, the amount of β -PbO increases as the temperature goes up. The XRD patterns of the calcination-combustion products obtained at 450 °C and 500 °C indicate that they are mostly α -PbO (Fig.5 (a) and Fig.5 (b)), and at 550 °C, the lead oxalate precursors had transformed to α -PbO and β -PbO phases. At the higher temperature of 600 °C, the lead oxalate have completely transformed to β -PbO. As for the lead-acid battery industry, α -PbO is the preferred phase. If the proposed process was used in the battery industry, the lower temperature range would be selected for the calcination process. Although, the theory transition point of α -PbO to β -PbO is 488.5 °C, in the process of our experiment, the calcinations product are still α -PbO at 500 °C.

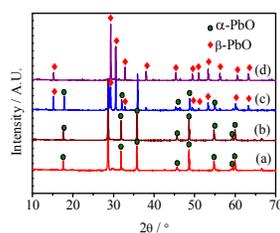


Fig.5. XRD patterns of the calcination products obtained from lead oxalate precursor at different temperatures for 1 h: (a) 450 °C, (b) 500 °C, (c) 550 °C and (d) 600 °C.

Preparation of novel lead oxide powders and their formation in positive electrodes of a lead-acid battery

The main component of every battery paste is basic lead sulphate. In the curing process of lead-acid battery, $3\text{PbO}\cdot\text{PbSO}_4\cdot\text{H}_2\text{O}$ and $4\text{PbO}\cdot\text{PbSO}_4$ are produced by mixing lead oxide, sulphuric acid and water. The relative proportions of the two polymorphs of PbO are important in the production of battery pastes, and as we have reported previously [6]. The result indicated that the α -PbO delivers higher initial capacity and the β -PbO yields a relatively improved cycle life. This is due to the α -PbO favours formation of tribasic lead sulphate ($3\text{PbO}\cdot\text{PbSO}_4\cdot\text{H}_2\text{O}$), while β -PbO promotes tetrabasic lead sulphate ($4\text{PbO}\cdot\text{PbSO}_4$) [22]. It is well known that the improvement of

capacities is related to the 3BS content which would give the battery a high discharge capacity. And, cured plates containing a mounts of 4BS exhibit good mechanical strength and a long cycle life. [23]. 3BS and 4BS are mixed together can form fibroblastic reticular structure. Therefore, it is very important for the performance of the lead-acid battery to find the optimum ratio of α -PbO and β -PbO in the lead oxide powder. And X. Sun [24] reported that the oxidizability of leady oxide products prepared from lead acetate ($\text{Pb}(\text{CH}_3\text{COO})_2$) was about 99.10%. So, we attempted to use pure lead oxide as positive materials and had been successfully. In our study, the novel lead oxide powder is a mixture of α -PbO and β -PbO (Table 2). The content of α -PbO is higher than that of β -PbO, which is based on the fact that α -PbO is the main component of conventional leady oxide [14].

Table 2 Content of β -PbO and α -PbO phases in novel lead oxide powders.

Sample	β -PbO(wt.%)	α -PbO(wt.%)
A	5	95
B	10	90
C	15	85
D	20	80

According to the XRD patterns of the samples after formation (Fig.6 (a)), four samples all have similar composition, including β -PbO₂ and small amount of PbSO₄. The content of β -PbO₂ for the four samples are calculated by the software Jade and the amount of β -PbO₂ obtained in sample C is higher than that of other samples. PbO₂ is the active material in the positive plates of lead-acid battery.

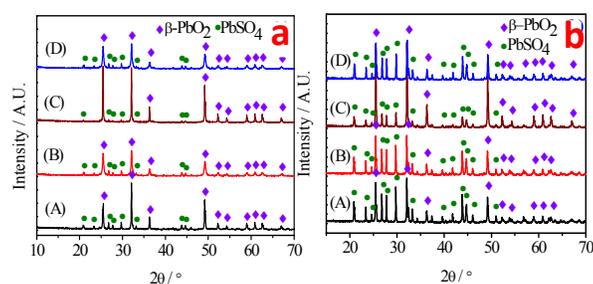


Fig.6. XRD patterns of the four samples: (a) after formation; (b) after charge and discharge test.

The morphology of the positive active material has a vital impact on battery performance. To observe the morphology of the samples after formation, the active materials were stripped from the positive plate after formation. The SEM images of the four samples after the formation process are shown in Fig.7 (A~D). The smallest building element of the positive active material structure is the PbO_2 particle. These particles interconnect in different ways. The SEM data show that sample A has polyhedral structure with particle size of 100~300 nm. Several small particles feature heterogeneous structures in sample A. The particles in sample B are irregular sphericity morphology with a size of ~200 nm, i.e. they are much smaller and stacked together. However, the particles in sample C are rod-like and smallest than other samples. It can provide more contact area for electrochemical reaction, so the positive active material morphology of sample C is beneficial for the initial discharge capacity and cycle life performance of the battery. In sample D, the PbO_2 particles have coalesced into small agglomerates.

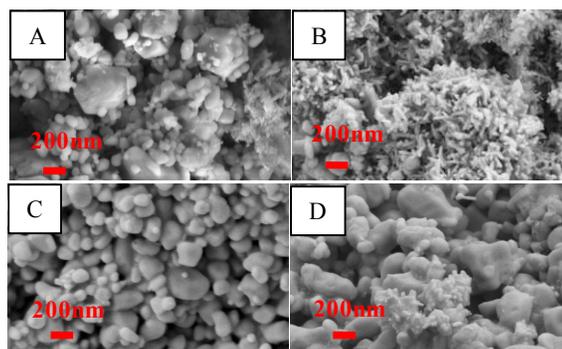


Fig.7. SEM images of the positive active materials formed from the novel lead oxide powders after the formation process (A-Sample A, B-Sample B, C-Sample C, D-Sample D).

Battery performance of novel lead oxide powders

Fig.8 (a) presents the initial discharge curves (at a current density of 30 mA g^{-1}) for batteries

prepared with the four types of lead oxide samples. As evident from the data in the figure, the initial discharge capacity of the battery made with sample C is about 180 mAh g⁻¹. If the utilization of active material is defined as the ratio of the discharged capacity to the corresponding theoretical capacity, and the theoretical capacity of pure PbO is 240 mAh g⁻¹, the utilization of sample C is about 75% at the discharge current density of 30 mA g⁻¹. The other samples yield capacities less than 180 mAh g⁻¹. According to Fig.5 (a), the content of β -PbO₂ in sample C is higher than that of in the other samples. Therefore, the initial discharge capacity is the highest. It has been found that the content of β -PbO₂ determines the performance of the plate [22, 25].

Fig.8 (b) shows the cycling performance of batteries made with the four types of lead oxide samples. Cycling was conducted at discharge current density of 50 mA g⁻¹. It can be seen that powder sample C sustains quite stable capacity within the 50 cycles, and the capacity retention of battery has retained 95% of the initial discharge capacity. Battery C shows a better cycle performance, and the other samples exhibit gradual decline in capacity on cycling. The discharge capacity of the battery made with powder samples A and B decreases rapidly, which may be related to the lower content of β -PbO in these samples. The data in Fig.6 (b) give us grounds to conclude that higher amounts of β -PbO phase in the lead oxide powder may enhance the cycle life of the battery. But, when the content of β -PbO is about 20 wt.%, the battery exhibits poor performance.

To evaluate the high-rate discharge performance of batteries made with the novel lead oxide powders, their discharge capacities were measured and plotted versus discharge current densities in Fig.8 (c). As expected, the discharge capacity decreases as the current density increases. Fig.8 (d) shows the battery voltage versus discharge capacity. The tests were conducted at different discharge current densities while at the same charge current density. The charge current density was fixed at 0.5 C (1C = 120 mA g⁻¹) and the discharge current density was varied from 0.25 C to 3 C, with a cut-off

potential of 1.75. The discharge performance of the battery with powder sample C is better than the others, i.e. its discharge capacity is about 180 mAh g⁻¹ at 30 mA g⁻¹, 130 mAh g⁻¹ at 60 mA g⁻¹, 93 mAh g⁻¹ at 120 mA g⁻¹, 60 mAh g⁻¹ at 240 mA g⁻¹ and 40 mAh g⁻¹ at 360 mA g⁻¹.

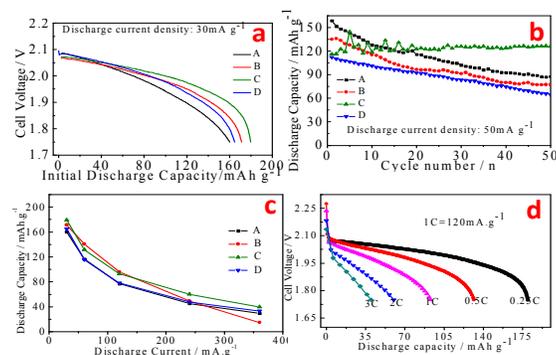


Fig.8. Battery performance of the four samples: (a) the initial discharge capacities; (b) the discharge capacity versus cycle number; (c) discharge capacity versus the current density of the four samples; (d) the curves of potential versus discharge capacity of sample C at different discharge current density.

After 50 charge/discharge cycles, batteries prepared with the novel lead oxides (containing 5 wt.%, 10 wt.%, 15 wt.% and 20 wt.% β -PbO, respectively) were disassembled after a final charge cycle. The positive lead plates were dried at 60 °C for 8 h and samples of active materials were examined by X-ray diffraction analysis and scanning electron microscopy. The XRD patterns in Fig.6 (b) indicate that the active materials scraped from the positive plates mainly comprise PbO₂ and PbSO₄, in which sample C has a lower degree of sulphation.

The SEM images of the four active material samples after the cycling test are shown in Fig.9 (A~D). It can be seen that sample C comprises much smaller particles. Generally, the good cycling performance mostly depends on the excellent connectivity of the active material particles and their large specific surface area, which will enhance their reactivity with the sulphuric acid (electrolyte) more readily. As evidenced from the SEM images of samples A, B and C in Fig.9, the particle size

decreases with the increase of the content of β -PbO in the powder samples. However, in sample D the particles are much bigger than in the other samples, it can be seen that the crystal particles are less consolidated. This kind of scattered granular crystal structure facilitates expansion of the plate and reduces the stability of the plate structure.

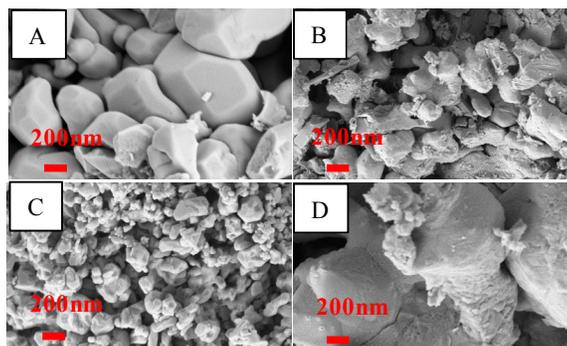


Fig.9. SEM images of the positive active materials formed from the novel lead oxide powders after discharge and charge cycles test (A-Sample A, B-Sample B, C-Sample C, D-Sample D).

Conclusions

A hydrometallurgical method is employed in the secondary lead industry. Leaching of spent lead pastes by $\text{H}_2\text{C}_2\text{O}_4\text{-Na}_2\text{C}_2\text{O}_4$ solution can avoid smelting and electro-winning, and can greatly reduce lead pollution to the environment.

Highly purified lead oxalate can be obtained, which can be useful as the precursor where α -PbO and β -PbO can be generated, by a process of combustion-calcination at different temperatures, and directly use in the preparation of lead pastes for new batteries. And different polymorphs of PbO have different properties.

The obtained test results of batteries made by lead oxides synthesized at different temperatures indicate that different polymorphs of PbO have significant effect on battery performances. Thus, the control of the α -PbO : β -PbO ratio is of fundamental importance for the production of lead oxide.

Novel lead oxide powders, comprising a mixture of α -PbO and β -PbO in different proportions, are synthesized and test batteries with these oxides are assembled and set to tests. The obtained results show that the lead oxide sample C (with 15 wt.% β -PbO content) yields the highest initial discharge capacity, which is 180 mAh g⁻¹ at 30 mA g⁻¹ and 60 mAh g⁻¹ at 240 mA g⁻¹, respectively, and behaves excellently in terms of cyclic stability, the capacity loss being less than 5% for 50 cycles.

The content of impurities (such as, Sb, Fe and BaSO₄) in real lead paste about 0.5%, these are probably the most difficult to deal with. But, impurities in the recovered lead oxide have a greatly influences on the performances of the new battery, we will investigate the typical impurities in the spent lead paste in a further study.

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