



# Leaching of lead slag component by sodium chloride and diluted nitric acid and synthesis of ultrafine lead oxide powders



Yuehong Shu <sup>a</sup>, Cheng Ma <sup>a</sup>, Longguan Zhu <sup>c</sup>, Hongyu Chen <sup>a, b, \*</sup>

<sup>a</sup> School of Chemistry and Environment, South China Normal University, Guangzhou, Guangdong 510006, PR China

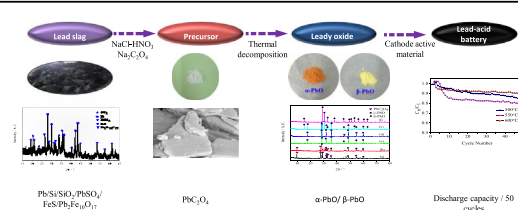
<sup>b</sup> Production, Teaching & Research Demonstration Base of Guangdong University for Energy Storage and Powder Battery, Guangzhou, Guangdong 510006, PR China

<sup>c</sup> Zhuzhou Jinding High-level Equipment Co. Ltd., Zhuzhou Hunan 412000, PR China

## HIGHLIGHTS

- HNO<sub>3</sub>–NaCl solution is used as the lead slag leaching solution.
- α-PbO and β-PbO nano-structures can be easily prepared.
- The prepared α-PbO can discharge a capacity of 150 mAh g<sup>-1</sup> at 25 mA g<sup>-1</sup>.
- α-PbO and β-PbO in different ratios have different battery performance.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 12 November 2014

Received in revised form

22 January 2015

Accepted 27 January 2015

Available online 30 January 2015

### Keywords:

Lead slag

Lead oxalate

Calcination temperature

Lead oxides

Lead-acid battery

## ABSTRACT

The compounds in lead slag are transformed into [PbCl<sub>4</sub>]<sup>2-</sup> in a mixed solution of HNO<sub>3</sub> and NaCl, which is converted into PbC<sub>2</sub>O<sub>4</sub> by the addition of sodium oxalate and polyethylene glycol dispersant. Novel lead oxides are prepared via a combustion-calcination process from lead oxalate precursor. Key properties of the new oxides, such as crystalline phases and morphology, have been characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The results show that lead oxides synthesized at different calcination temperatures comprise mainly α-PbO and β-PbO phases. In battery testing, the results reveal that the α-PbO phase exhibits higher initial capacity as positive active material, discharging about 150 mAh g<sup>-1</sup> at 20 mA g<sup>-1</sup>. While β-PbO yields a relatively improved cycle life, in 50 cycles, its capacity loss is 5%. Further work is being carried out with the aim to optimize the battery manufacturing process or to find out the optimum ratio of α-PbO to β-PbO in order to sustain high discharge capacity and acceptable cycle life.

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## 1. Introduction

Recently, the secondary lead industry has stepped into a boom period as the main source of raw material for lead-acid battery production. The process of secondary lead production comprises several main stages, including crashing and separation of the waste

lead-acid batteries, desulphurization of the waste diachylon, smelting, etc. Production of lead results in considerable amounts of waste slags, called lead smelting slag. The lead smelting slag originated from the manufacturing of lead from both lead concentrates and recycled car batteries to produce new car batteries. For each ton of metallic lead produced, 100–350 kg of slag is generated that contains approximately 5% of lead compounds [1,2]. Apart from Pb, these slags may contain quantities of minor and trace elements [1,3–5], that, if the slag is not constrained, can contaminate the environment through leaching. Recycling of car batteries currently

\* Corresponding author. School of Chemistry and Environment, South China Normal University, Guangzhou, Guangdong 510006, PR China

E-mail address: [hychen@scnu.edu.cn](mailto:hychen@scnu.edu.cn) (H. Chen).

generated 200,000 t/a of slags in Europe [6]. This means that there is a significant quantity of lead-contaminated waste that has to find its way to designated landfill sites.

The traditional pyrometallurgical route, which is the most widely used in the recovery of secondary lead resource, can emit large quantities of  $\text{SO}_2$  gas and lead dust, causing threat to the environment [7–9]. Moreover, the pyrometallurgical process requires a lot of energy for the decomposition of lead compounds above 1000 °C, thus it will consume non-renewable resources of coal, coke, oil or natural gas.

Due to the increasingly stringent legislations for these emissions, there has been a large research effort to find a hydrometallurgical route to replace lead-acid battery recycling operations. More recently increasing attention has been paid to the recovery of lead slag through alternative hydrometallurgical process [10–17], whose effect, energy consumption and environmental pollution could be dealt with validly [7]. That is to say, first, the lead and its compounds are leached from the lead slag by chloride or alkali. Then, the leaching dynamics of lead slag is studied and the effects of various factors on the process of leaching are evaluated, and finally the leaching elements are transferred into materials, which have application value. For example, M. Volpe [18] recovered metallic lead from lead-acid battery paste by urea acetate dissolution and cementation on iron. Gabriel Meneghetti Faé Gomes [19] investigated the reduction in toxicity and generation of slag in secondary lead process. So we can conclude that the hydrometallurgical process has made a certain progress. However, those researches mostly focus on slag or sulfuric acid burn, while seldom study the lead slag, coming from the reduction smelting converter, whose composition is more complicated.

The present article chooses lead slag that comes from waste diachylon smelted by reduction smelting converter as the study object. We propose a wet leaching technology for lead slag.  $\text{HNO}_3\text{--NaCl}$  solution was used as the leaching liquid, and make the lead exists in the form of  $[\text{PbCl}_4]^{2-}$ . So at this point, add appropriate amount of hot sodium oxalate saturated solution, heat it and stir to speed up the reaction rate, and the lead ions in the filtrate are converted to  $\text{PbC}_2\text{O}_4$ . Then, precipitate and filter the filtrate to get

lead oxalate crystals. And finally, decompose it at high temperature, roast at different temperatures to obtain lead oxide powders [20]. Thus produced lead oxide powder could be applied in the lead-acid battery industry for the manufacture of leady oxide powder to be used eventually as the positive active material for lead-acid batteries. Batteries produced with such active material will have high discharge capacity and good cycling performance.

This paper studies the effect of crystal type on battery performance by using different crystalline polymorphs of lead oxide. Pure  $\alpha\text{-PbO}$ , mixed  $\alpha\text{-PbO}$  and  $\beta\text{-PbO}$ , or pure  $\beta\text{-PbO}$  crystals can be obtained when calcined at 500 °C, 550 °C and 600 °C, respectively. The initial discharge capacity of these oxides is 150  $\text{mAh g}^{-1}$ , 96  $\text{mAh g}^{-1}$  and 113  $\text{mAh g}^{-1}$ . When  $\alpha\text{-PbO}$  is used, the discharge capacity of the battery decreases quickly, and the battery exhibits a stable performance within 50 cycles when the leady oxides powder is of the  $\beta\text{-PbO}$  crystal type.

The flow sheet of experiments is presented in Fig. 1.

## 2. Experimental

### 2.1. Material preparation

Some secondary lead plants in China adopt reducing smelting by converter to smelt spent lead pastes, and defined amount of iron powder has been added in the manufacturing operation by the factory as reductant and slagging agent. During smelting process, different compounds of iron will be formed. Spent lead slag was provided by a secondary lead smelting plant in Zhejiang Changxin, China. After crushing, the spent lead slag was put into a vacuum drying oven for 24 h at 120 °C and then it was milled until 300 mesh, the desired sample particle size.

The solvent  $\text{HNO}_3\text{--HCl--HClO}_3\text{--HF}$  was used for the four acid digestion of the lead slag. After digestion, it was cooled to room temperature and then 0.2  $\text{mol L}^{-1}$  3 mL of ammonium hydrogen phosphate was added. The solution was transferred into a volumetric flask and shake mixture well for measurement.

The sample of lead slag was disposed as follows: a  $\text{HNO}_3\text{--NaCl}$  solution was used as the leaching liquid: 250  $\text{g L}^{-1}$  of sodium chloride, pH = 1, and stirred at 70 °C for 2 h.

Add  $\text{H}_2\text{O}_2$  to convert all the iron from the filtrate to  $\text{Fe}^{3+}$  and then add 1  $\text{mol L}^{-1}$   $\text{NaOH}$  solution to adjust the filtrate pH to 4–4.5. Since  $\text{Fe}^{3+}$  ions can be completely precipitated in aqueous solution with pH = 3.7,  $\text{Fe}^{3+}$  can be completely transferred to the  $\text{Fe}(\text{OH})_3$  precipitate and ensure that the lead still exists in the form of  $[\text{PbCl}_4]^{2-}$ .

Hot sodium oxalate solution and polyethyleneglycol (PEG 400) were added to the leaching solution. Through heating and stirring the solution we obtained lead oxalate, which is because of the different solubility in water of lead chloride and lead oxalate (the solubility product constants of lead chloride and lead oxalate at 25 °C are  $2.0 \times 10^{-5}$  and  $4.8 \times 10^{-10}$ , respectively), the precursors were dried at 110 °C for 8 h and then calcined the lead oxalate in air at different temperatures of 350 °C, 400 °C, 450 °C, 500 °C, 550 °C and 600 °C for 2 h respectively. Then, the crystalline phases, morphology and battery properties of the obtained lead oxides were simultaneously examined by XRD, SEM and battery test in the following.

### 2.2. Characterization

The phase composition of the different lead oxides were determined by X-ray diffraction (XRD) analysis using a D/MAX 2550 X-ray diffraction analyzer (Japan) with  $\text{Cu K}\alpha$  radiation ( $\lambda = 0.15406 \text{ nm}$ ) at 300 mA and 5.0 kV.

The crystal morphology of the different leady oxides were

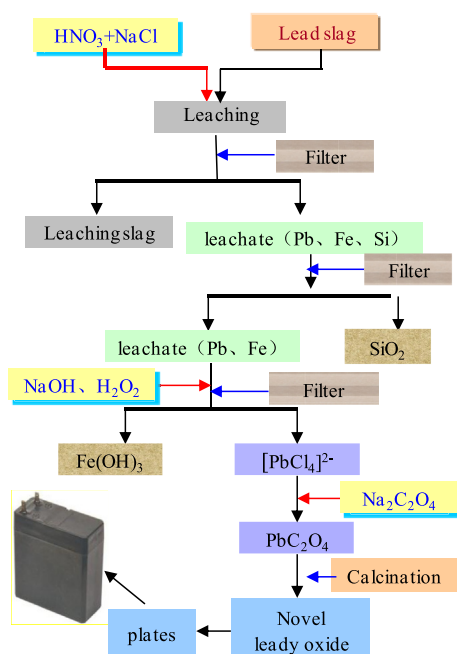


Fig. 1. The flow sheet of experiments.

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