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

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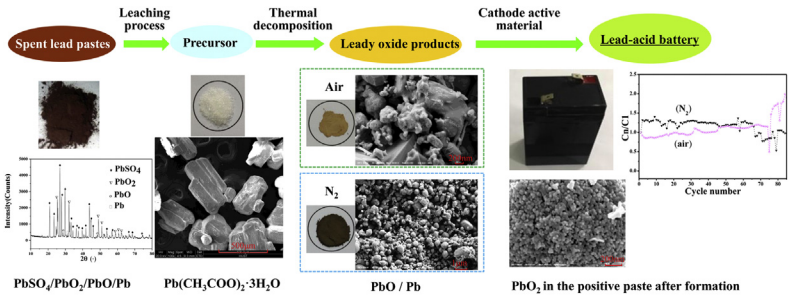
HIGHLIGHTS

- The $Pb(CH_3COO)_2{\cdot}3H_2O$ precursor was prepared from the spent lead battery pastes.
- Novel lead oxide products were prepared from the precursor in N_2 and air.
- The assembled batteries show a good cyclic stability in 80 charge/discharge cycles.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel green recycling process is investigated to prepare lead acetate trihydrate precursors and novel ultrafine lead oxide from spent lead acid battery pastes. The route contains the following four processes. (1) The spent lead pastes are desulphurized by $(NH_4)_2CO_3$. (2) The desulphurized pastes are converted into lead acetate solution by leaching with acetic acid solution and H_2O_2; (3) The $Pb(CH_3COO)_2{\cdot}3H_2O$ precursor is crystallized and purified from the lead acetate solution with the addition of glacial acetic acid; (4) The novel ultrafine lead oxide is prepared by the calcination of lead acetate trihydrate precursor in N_2 or air at 320–400 °C. Both the lead acetate trihydrate and lead oxide products are characterized by TG-DTA, XRD, and SEM techniques. The calcination products are mainly α-PbO, β-PbO, and a small amount of metallic Pb. The particle size of the calcination products in air is significantly larger than that in N_2. Cyclic voltammetry measurements of the novel ultrafine lead oxide products show good reversibility and cycle stability. The assembled batteries using the lead oxide products as cathode active materials show a good cyclic stability in 80 charge/discharge cycles with the depth of discharge (DOD) of 100%.

1. Introduction

Globally, lead-acid battery constitutes the largest volume among secondary batteries arising from the advantages of low cost, good

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

The traditional pyrometallurgical route, which is the most widely used in the recovery of secondary lead resource, can emit large quantities of SO_2 gas and lead dust, causing threat to the environment [12–14]. Moreover, the pyrometallurgical process requires a lot of energy for the decomposition of lead sulfate above 1000 °C, thus it will consume non-renewable resources of coal, coke, oil or natural gas.

More recently increasing attention has been paid to the recovery of spent lead-acid battery pastes through alternative hydrometallurgical process. The most used hydrometallurgy method, which consists of pretreatment, desulfurization, reduction and electrowinning process, can avoid SO_2 and lead dust emission problems [15,16]. However, the energy efficiency of electro-winning process is low, with a higher total energy consumption compared with traditional pyrometallurgical route. The suggested leaching solutions of H_2SiF_6 or HBF_4 can lead to emission of fluorine in the environment which is also unacceptable.

Given the disadvantages in the traditional pyrometallurgical and electro-winning methods, several new hydrometallurgy approaches have been developed. Attempts have been tried to leach the components ($PbSO_4$, PbO_2 and PbO) of spent lead pastes by citric acid and sodium citrate as reported in our previous studies [10,11,17]. In this leaching process, the lead citrate precursor is separated from the leaching solution by simple crystallization. The ultra-fine lead oxide powder can be obtained through calcination of lead citrate at a temperatures less than 400 °C. In order to improve the desulphurization efficiency of spent lead pastes, spent lead pastes were firstly converted into the desulphurized pastes with desulphurizing agents, then the desulphurized pastes were leached with citric acid solution to generate lead citrate [18]. In order to improve the speed of leaching reaction and decrease the consumption of citric acid, a modified version using acetic acid and sodium citrate leaching system was developed for the recovery of spent lead pastes [19]. However, in these previous researches, the impurities in spent lead pastes can easily join and contaminate the lead citrate precursor, leading sometimes to an unacceptably high content of the impurities in the final leady oxide. And then, the capacity retention ratio of the batteries manufactured with the leady oxide as the active material of the cathode decreases rapidly after 20–30 cycles. The impurities in the leady oxides could lead to the deterioration of the cycle life performance of the batteries [20]. Moreover, the leaching agents of citric acid and sodium citrate are relative more expensive than other organic or inorganic acids.

The objective of this work was to seek a more efficient method to obtain high-performance leady oxide with lower content of impurities by applying high-purity lead acetate trihydrate as a precursor. Flow sheet of this process was schematically shown in Fig. 1. The suggested method can be described as “paste to paste” recycling. In this novel approach, the high-cost leaching reagents of citric acid and sodium citrate were substituted by the cheaper acetic acid. Furthermore, the impurities in spent pastes could be effectively separated by the three filtering-separating procedures. The morphology, mineral phases and electrochemical performances of lead oxide products prepared in N_2 or air were characterized, and batteries were fabricated by the new lead oxide products to examine the battery performance.

2. Experimental

2.1. Reactants and raw materials

The samples of spent lead acid battery pastes were provided by Hubei Jinyang Metallurgical Co. Ltd., China, where typically spent lead battery pastes are pyrometallurgically treated to recover lead as a metal using a conventional smelting process. Lead pastes from the spent lead-acid batteries were made available for this work after a separation process using Engitec Technologies Company CX

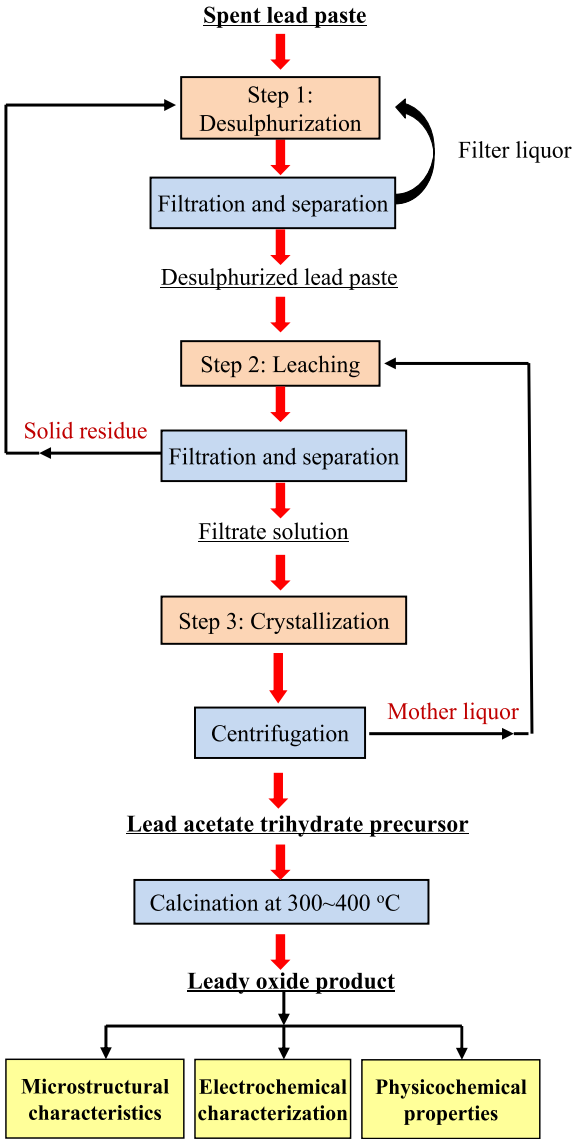

Fig. 1. Flow-sheet of the new hydrometallurgical process for recovery of lead pastes.