



Nanocrosses of lead sulphate as the negative active material of lead acid batteries



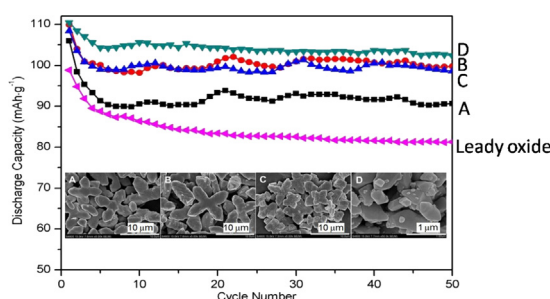
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HIGHLIGHTS

- PbSO_4 can be directly used as the negative active material in lead acid batteries.
- Nanocrosses morphologies PbSO_4 can be easily prepared.
- The prepared PbSO_4 discharges a capacity of 103 mA h g^{-1} at 120 mA g^{-1} and remains 80% of the capacity after 550 cycles.
- Products prepared were promising electrode candidates for lead acid batteries.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 31 December 2013

Received in revised form

26 February 2014

Accepted 26 March 2014

Available online 14 April 2014

Dedicated to Professor Xinquan Xin on the occasion of his 80th birthday.

Keywords:

Lead sulphate

Nanocrystal

Lead oxide

Active material for negative electrode

Lead acid battery

ABSTRACT

Lead sulphate transforms into PbO_2 and Pb in the positive and negative electrodes, respectively, when a lead acid battery is charged, thus, it is an active material. It is also generally acknowledged that sulphation results in the failure of lead acid batteries; therefore, it is very interesting to find out how to make lead sulphate more electrochemically active. Here, we demonstrate that nanocrystalline lead sulphate can be used as excellent negative active material in lead acid batteries. The lead sulphate nanocrystals, which are prepared by a facile chemical precipitation of aqueous lead acetate and sodium sulphate in a few minutes, look like crosses with diameter of each arm being 100 nm to $3 \mu\text{m}$. The electrode is effectively formed in much shorter time than traditional technique, yet it discharges a capacity of 103 mA h g^{-1} at the current density of 120 mA g^{-1} , which is 24% higher than that discharged by the electrode made from lead oxide under the same condition. During 100% DOD cycles, more than 80% of that capacity remains in 550 cycles. These results show that lead sulphate can be a nice negative active material in lead acid batteries.

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1. Introduction

Lead acid batteries occupy a half of the share in the rechargeable battery market owing to their high ratio of performance to cost [1,2]. In spite of this, there are still increasing concerns on improving of energy density [3–6], cycle life [7–9] and charge/discharge efficiency [10,11].

Currently, the materials used in lead acid battery manufacturing are lead oxide made from lead either via ball milling or by the Barton pot technique, which is typically a mixture of 20–30 wt.% metallic lead and 70–80 wt.% lead monoxide [12]. This lead oxide is heterogeneous and has grains of several micrometres big, consequently, it discharges only about 90 mA h g^{-1} , which is just about a half of the theoretical capacity of PbSO_4 (177 mA h g^{-1}).

Conventionally, pastes for positive and negative plates are formed by mixing lead oxide powder, small quantities of additives, water and sulphuric acid. In the processes of making pastes, both the amount of free lead oxidized and basic lead sulphate formed at

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each step (e.g. paste making, pasting, and curing) are very difficult to control accurately. This leads to variations of components in the finished plates, which, in turn, affects the physical, chemical and electrochemical properties of the plates and results in problem of uniformity in terms of electrochemical properties [13]. The pastes must go through the curing and drying processes, during which the temperature and humidity have to be carefully controlled. These processes consume long time (72–84 h), require considerable space and energy, and hence increase production cost [14].

PbSO₄, a well-known industrial product, has a wide range of applications [15]. It also plays a vital role in lead acid batteries, because it is formed during discharging process and consumed during charging process. However, few papers reported using PbSO₄ as the active material, which make it invisible to the community. Up to now, only two papers have reported about using PbSO₄ as positive active materials (PAM). In 2002, Yan et al. [16] prepared PbSO₄ from a reaction of leady powders with excessive sulphuric acid. They found that the specific energy by weight reached 37.19 and 35.47 W h kg⁻¹ at 5 h and 2 h rate, respectively, and the cycle life of 55% DOD attained 450 times in a 12 V, 10 A h battery. In 2012, Foudia et al. [17] reported that PbSO₄ could be served as a precursor for positive active material in the electrode. They combined the solutions of Pb(NO₃)₂ and Na₂SO₄ to prepare PbSO₄, which discharged a highest specific capacity of 92 mA h g⁻¹ in a positive electrode. Pitifully, both papers did not tell enough detailed information. What is more, to best of our knowledge, there have been no reports on PbSO₄ used directly as negative active material (NAM) in lead acid battery so far.

In the last 5 years, we have developed a novel route for recycling of spent lead acid batteries, in which all the active materials both in positive and negative electrodes are separated separately from their grids, and then converted into electrochemically active PbO. We have found the PbO is more active than the commercial leady oxide, and the process saves much energy and releases much less environmental hazards [18,19]. As we know, the materials in the negative electrodes are a mixture of PbSO₄ and Pb; those in the positive electrodes are PbSO₄ and PbO₂, we are wondering if the PbSO₄ itself can be more electrochemically active, which could make the recycle process further simpler and save more energy and consumption. That initiates our investigation on PbSO₄.

As it is generally known, both the particle size and morphology of active materials have great effect on their electrochemical properties (for example, in lead acid battery chemistry, sulphation that leads to failure of the batteries is actually the formation of big PbSO₄ crystals). It is important to know how they affect the electrochemical properties. PbSO₄ with different morphologies have been prepared through various methods, such as cube-like PbSO₄ precipitated in a solution of polyethyleneimine using a double jet crystallizer [20], plate-like PbSO₄ nanocrystal produced in micro-emulsion system [21], rod-like PbSO₄ obtained from a mixture of Pb(CH₃COO)₂·3H₂O and sodium-*p*-styrene sulphonate (PSS) with constant stirring [22], highly ordered stabilized lamellar PbSO₄ nanocrystal with well-crystallized walls synthesized through hydrothermal treatment method [15], PbSO₄ crystals with almost entirely of micrometre-scale structures and branch-type can also be prepared [23].

According to the traditional technique, leady oxide needs curing to form PbSO₄ and 3PbO·PbSO₄ (3BS) or 4PbO·PbSO₄ (4BS). Using lead sulphate as the active material do not need that process, consequently, time, energy, human resources and machinery can be saved. Also, lead sulphate has the smallest density of all the lead compounds, which may bring out higher porosity. Table 1 lists the densities and molar volumes of some compounds, which shows that lead sulphate has the highest molar-volume. Increasing the

porosity facilitates the diffusion of the electrolyte inside the plate and thus may improve its discharge capacity.

This paper reports what we have found on PbSO₄ precipitated from lead acetate and sodium sulphate, and electrical performance of the as-prepared PbSO₄ as the negative electrode active material.

2. Experimental

2.1. Material preparation

The nanocrystalline PbSO₄ was obtained as follows: 0.01 mol of Pb(CH₃COO)₂·3H₂O together with 0.3 wt.% different surfactant: (A) none; (B) poly(sodium-*p*-styrenesulphonate) (PSS); (C) sodium dodecyl sulphonate (SDS); (D) poly(vinyl pyrrolidone) (PVP) were dissolved in 200 mL of distilled water at 70 °C, then poured into 100 mL of 0.1 mol L⁻¹ Na₂SO₄ solution with stirring. The mixture was kept at 70 °C for another 10 min, and then the solid was filtered out, washed several times with distilled water, and dried overnight at 70 °C.

2.2. Characterization

Powder X-ray diffraction (XRD) patterns of the samples were conducted using a Bruker D8 Discover instrument operating at 40 kV and 20 mA, by using CuK α radiation ($\lambda = 0.15406$ nm). Scanning electron micrographs (SEM) of samples were carried out on a Hitachi S-4800 microscope.

2.3. Electrode preparation

The conventional leady oxide paste was prepared by mixing 1.0 g leady oxide (obtained from Huafu Holding Group), 0.003 g of graphite, 0.02 g of BaSO₄, 0.12 mL of distilled water and 0.12 mL of sulphuric acid (36 wt.%) were added to it slowly. The procedure included placing the required amount of leady oxide and additives in a container, and grinding for about 5 min to make a good dispersion. Then, sulphuric acid was added slowly with grinding; finally, the water was added to the mixture, and grinded for another 5 min.

Pastes based on the PbSO₄ were prepared by mixing 1.0 g of an as-prepared sample (A, B, C, or D) and 0.03 g of conducted graphite and acetylene black, respectively, 0.02 g of BaSO₄, 0.006 g of lignosulfonate together with 0.14 mL of distilled water. The other procedures were the same as the conventional ways. Because lead sulphate has low electrical conductivity, more conductive additives were added to make pastes.

The plates were obtained by applying the paste evenly onto a Pb–Ca alloy grid with dimensions of 10 × 8 × 2 mm³. After pasting, the conventional leady oxide-based plate was put into an oven maintained at 50 °C with relative humidity >95%. The curing was conducted for 36 h. After that, the plate was dried at 70 °C for 48 h; while the PbSO₄ based plates were only need 24 h for drying at 70 °C. The mass of the active material for the calculation of the densities was the mass of the dried plate minus that of the blank grid.

Table 1
Densities and molar volumes of some lead compounds.

Lead compounds	Density (g cm ⁻³)	Molar volume (cm ³ mol ⁻¹)
PbSO ₄	6.32	48.2
PbO·PbSO ₄	7.02	38.0
3PbO·PbSO ₄ ·H ₂ O	6.50	38.0
Pb	11.34	18.27

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