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Preparation of four basic lead sulfate nano-rods additives and effect on the electrochemical performance of lead-acid battery

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ABSTRACT

As a type of commonly used active material additives, the grain size and structure of four basic lead sulfate (4BS) can seriously affect its performance. 4BS with smaller grain size and higher electrochemical activity can have a good additive effect. In this paper we prepare a type of 4BS nano-rods. By comparing the different sintering temperatures, it can be found that when the sintering is 400 °C, the 4BS can be prepared successfully and form nano-rod like crystal structure. The diameter can be controlled below 100 nm. CV and EIS results display that 4BS nano-rods has the higher electrochemical activity and active material conversion rate.

When the 4BS nano-rods are added to the active material, large crystal structure is not present and stable active material skeleton can be formed. That can make it have the higher active material specific capacity and long cycle life. The charge and discharge results show that when the discharge current rate was 0.1 C, 0.25 C, 0.5 C and 1 C, the specific capacity of the positive active material with 4BS nano-rods can reach 80.71 mAh g^{-1}, 75.67 mAh g^{-1}, 67.70 mAh g^{-1} and 62.96 mAh g^{-1}. With the increase of the current density, the specific capacity and the discharge voltage are not obviously decreased. After 100 cycles, the specific capacity was also only decreased by less than 20% of its initial capacity.

1. Introduction

Although a large number of innovative energy materials and systems constantly arise [1–10], lead-acid battery still attracts widespread attention of some researchers due to its low cost, mature technology and good security [11–14]. Some late-model lead-acid battery such as Pb-C Ultra-battery [15–18] and bipolar lead-acid battery [19–21] have the hope of responding to the electric power supply of hybrid electric vehicles (HEV). Despite lead-acid battery have some advantages, as an ideal power system remains limited by several inherent problems, including its low specific energy, specific power and cycle life. Among these problems, the main factors affecting cycle life are positive active material softening, negative irreversible sulfation, electrolyte decomposition (hydrogen evolution reaction during charging) and substrate corrosion [22]. In the past many years, numerous studies had been conducted to improve its cycle life. The main idea was the use of active material additives. Some researchers found that [23,24] adding a certain proportion of carbon material in the negative active material can effectively inhibit irreversible sulfation. Carbons particles can provide additional electronic conduction channels and isolate lead particles from each other, thereby blocking the growth condition of lead sulfate crystals. Adding some inhibiting hydrogen evolution additives in the active material or electrolyte can effectively improve electrodes' hydrogen evolution over potential and ensure the electrolyte concentration stability during the battery working process [25,26]. Improving the corrosion resistance of substrates usually involved more stable coating film on the surface or alloying treatment [27].

Positive active material softening is mainly due to the change in the crystal structure. It is believed that positive active material mainly includes α-PbO_2 and β-PbO_2. A-PbO_2 is the coarse and interwoven crystal structure. It can be used as the active material skeleton to maintain the stability of the active material [28]. B-PbO_2 is the small grain size and has high electrochemical activity. It is mainly used to provide electrode capacity. However, α-PbO_2 will gradually transform into β-PbO_2 along with the increase of the

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discharge depth. This causes the active material to soften and fall off. Pavlov D et al. [29] considered that the 4BS inside the positive material after curing can change to α-PbO_2 during the formation process. So the amount of 4BS in the cured active material directly affected the content of α-PbO_2 after formation. In order to increase the content of 4BS appropriately, some 4BS should be previously added in the electrode manufacturing process. During the curing, these 4BS as crystal seeds can promote the 4BS generation inside the active material. However, 4BS has lower electrochemical activity and a considerable portion is not converted to PbO_2 during the formation process. This will decrease the specific capacity. At present, it is generally recognized that if the 4BS has small grain size it has the high electrochemical activity and can improve its formation conversion rate. Therefore, many researchers have studied the preparation of 4BS additives [30–32].

Therefore, the study of 4BS mainly focuses on reducing its grain size. In this research, we prepared a type of 4BS nano-rods and added to the positive active material. It cannot only increase specific capacity, but also prolong the cycle life.

2. Experimental

2.1. Syntheses of 4BS nano-rods

First of all, weigh lead oxide(PbO)and lead sulfate ($PbSO_4$) in accordance with the mole ratio of 5:1 (PbO: $PbSO_4$) and put them into a beaker. Secondly, add a certain amount of deionized water and agitate. The amount of water can meet the PbO and $PbSO_4$ fully dispersed. Thirdly, add 5% PVA water solution of the same volume as deionized water slowly and heat to desiccation under the condition of 60 °C water baths. The PVA solution was utilized to increase the viscosity of the liquid with the increase of water bath time. Stop water bath heating when the dispersion and suspended state of PbO and $PbSO_4$ could be maintained. Finally, after drying 80 °C and grinding, the sample was sintered at different temperature for 6 h in the air environment to get high property 4BS nano-rods.

2.2. Characterization and electrochemical analysis of 4BS nano-rods

The physical properties of 4BS nano-rods were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). XRD test was carried out with a D Max-RD12 Kw diffractometer with Cu Kα radiation using Rigaku Ultima IV. The scan data were collected in the 2θ range 10–90° at scan rate 2° min^{-1}. Trough XRD diffraction peak analysis, the chemical composition of the sample could be achieved. The micro morphology of 4BS nano-rods sintered at different temperature was observed by means of SEM using S-4800 FESEM. The grain size and morphology of the sample could be achieved successfully.

Electrochemical properties of 4BS nano-rods were analyzed by cyclic voltammetry(CV)and AC impedance (EIS) with LK2005A. These two tests were made using the three electrode system (platinum wire as auxiliary electrode, Hg/Hg_2SO_4 as a reference electrode and the sulfuric acid solution (ρ = 1.26 g cm^{-3}) as the electrolyte). The work electrode is a microelectrode that loads a small amount of sample onto a platinum wire enclosed in a glass tube. The potential range of CV measures was from 0.3–1.5 V. Sweep speeds were respectively 5 mV/s, 10 mV/s and 20 mV/s. The frequency range of the EIS measures was from 100 KHz to 10 mHz with the 5 mV amplitude.

2.3. 4BS nano-rods as positive active material additive for lead-acid batteries

In this research, the preparation method of the positive and negative electrode and battery assembly was the same as the previous studies [33]. The positive active material is composed of lead powder, Pb_3O_4, $SnSO_4$, graphite, 4BS and short fiber. The negative active material is composed of lead powder, lignin, humic acid, short fiber and $BaSO_4$. Firstly, lead powder with positive or negative additives fully mixed according to certain proportion. And then add a certain amount of water and sulfuric acid solution. The sulfuric acid solution requires to be slowly dropped to prevent a large amount of heat. Finally, the positive and negative active material was coated on the Pb-Sn alloy grid. The electrodes were cured at the specific temperature and humidity. The thicknesses of positive electrodes were about 2.3 mm and the negative electrodes were about 1.6 mm. Quantity of positive active material on the electrodes was about 24–26 g and the negative active material was about 17–19 g. In this experiment the proportion of 4BS addition was selected as 1%. This was mainly because according to the results of previous studies on numerous 4BS, it was found that the electrochemical properties of the active materials were optimum when adding 1%. The micromorphology of the lead paste with 1% 4BS nano-rods after curing was observed by SEM test.

2.4. Experimental battery assembly

One positive electrode and two negative electrodes after curing were used to assemble the 2 V experimental battery. The separator was absorptive glass mat (AGM) and the electrolyte was the sulfuric acid solution (ρ = 1.26 g cm^{-3}). PTFE plates were used for ensuring a certain assembly pressure. The experimental battery was tested after the container formation.

The charge and discharge performances were tested by multi-channel battery testers (BTS 5 V, 10 A, Neware, Shenzhen in China) at the setting current density under room temperature. The current rates were obtained under different charging and discharging conditions and calculated by Peukert equation. The specific capacities were calculated on the basis of the weight of positive active material.

3. Results and discussion

3.1. Physical property characterization of 4BS nano-rods

XRD diffraction peaks for the samples sintered at different temperature were shown in Fig. 1. Compared with the 4BS standard PDF card (PDF 23-0333), it can be found that the main diffraction peaks are all 4BS diffraction peaks at the sintering temperature of 400 °C, 500 °C and 600 °C. This implies that the 4BS can be

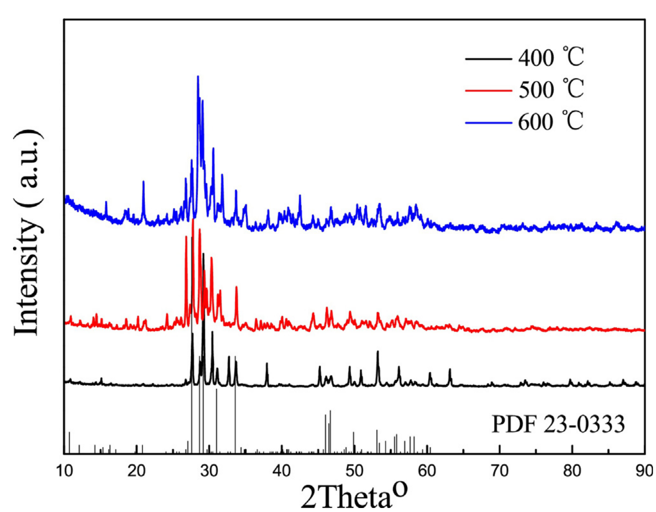

Fig. 1. XRD diffraction peaks for the samples sintered at different temperature.