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Short communication

The use of nanometer tetrabasic lead sulfate as positive active material additive for valve regulated lead-acid battery

Xiaoshi Lang, Dianlong Wang*, Chiyu Hu, Shenzhi Tang, Junsheng Zhu, Chenfeng Guo

School of Chemical Engineering and Technology, Harbin Institute of Technology, Harbin 150001, PR China

HIGHLIGHTS

- The study on a kind of nanometer 4BS with high purity and small grain size.
- The nanometer 4BS has the very high effective lead dioxide conversion rate.
- Adding nanometer 4BS doesn't effect positive active material's specific capacity.
- Adding 4% nanometer 4BS can effectively improve the cycle life of the battery.

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ABSTRACT

Conventional tetrabasic lead sulfate used as positive active material additive shows the results of the low effective lead dioxide conversion rate due to the large grain size and crossed the crystal structure. In this paper, we study on a type of nanometer tetrabasic lead sulfate. Through the XRD and SEM test and Material Studio software calculation, the purity of tetrabasic lead sulfate is very high, the grain size of the nanometer 4BS is almost unanimous, and can be controlled below 200 nm. When charged and discharged in 1.75 V–2.42 V with the current density of 40 mA g^{-1}, 80 mA g^{-1} and 160 mA g^{-1}, the effective lead dioxide conversion rate of nanometer 4BS after formation can achieve to 83.48%, 71.42%, and 66.96%.

Subsequently, the nanometer 4BS as additive is added to positive paste of lead-acid battery. When the batteries are tested galvanostatically between 1.75 V and 2.42 V at 0.25 C charge and 0.5 C discharge rates at room temperature. The ratio of adding nanometer 4BS is 0%, 1% and 4% and the initial discharge specific capacities are 60 mAh g^{-1}, 65 mAh g^{-1} and 68 mAh g^{-1}. After 80 cycles, the initial discharge capacity of positive active material with 1% nanometer 4BS decreased less than 10%, while adding 4% nanometer 4BS, the initial discharge capacity doesn't decrease obviously.

1. Introduction

Over the last few years, the lead-acid battery has been extensively applied in automobile, energy storage and many other fields. It accounts for more than fifty percent of the battery market [1,2]. This is due to the simple structure, ripest craft and non-expensive technology [3]. But at present the development of battery needs it has the higher specific capacity, higher specific power and longer cycling life for hybrid electrical vehicle (HEV) or electrical vehicle (EV) industry. In the past few years, there were a number of studies which are on the cycle life of lead-acid battery. The most common damage mechanisms for a valve regulated lead-acid (VRLA) battery include positive electrode corrosion, irreversible sulfation, water loss, positive electrode softening and shedding, electrolyte stratification, internal short circuit and so on [4–9]. They are not generated individually, but common effect of the same piece of the battery. Usually, research of VRLA battery's cycle life is mainly to reduce these effects.

In these damage-mechanisms, it is believed that the positive electrode softening and shedding is one of the essential factors. It is mainly reason for the failure of the positive plate. The positive plates of the VRLA battery are assembled from a mixture of PbO and Pb_3O_4. During the curing and formation processes, the transformation of the material is responsible for the structural integrity and electrical contact among the active material particles. In the process of curing, positive electrode material is transformed into tribasic lead sulfate (3BS) and tetrabasic lead sulfate (4BS) lead sulfate. On the basis of "crystal-gel" theory [10], the structure of

* Corresponding author.
E-mail address: wangdianlonghit@163.com (D. Wang).

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positive active material transforms into two kinds of lead dioxide in the process of formation. Tribasic lead sulfate converts to β-PbO_2 and the tetrabasic lead sulfate converts to α-PbO_2. The crystal structure of these two kinds of pbO_2 is significantly different. β-PbO_2 has higher discharge capacity due to its better electrochemical activity than α-PbO_2. However, α-PbO_2 has the larger crystal size and harder particles, so it can be the positive active material skeleton in order to increase the cycle life of the lead-acid battery. Therefore, 3BS decides the positive active material's capacity and 4BS decides its cycle life. Changing the ratio of 3BS and 4BS can directly affect the capacity and cycle life of positive plate (lead dioxide). Through the studies of D. Pavlov and M. Cruz-Yusta et al. [11–14], they considered that the mixing lead paste temperature can determine the proportion of 3BS and 4BS in the positive lead paste. And they all found that the proportion of 4BS in the lead paste was increased with the rising of temperature.

At present, some researchers also found that tetrabasic lead sulfate can be a type of ideal positive active material additive to promote the generation of 4BS in the lead paste during the curing process and this can improve the cycle life of lead-acid battery. Nonetheless, E. Bashtavelova et al. [15] showed that the grain size of conventional 4BS is very large. And it as additive adding to the positive lead paste will make the 4BS generated in the lead paste during the curing process has large needles. In the lead-acid battery manufacturing process, the formation of this kind of positive plate is very difficult to achieve. In order to resolve this problem it needs a very long and expensive formation process. Thus, it needs to change the grain structure of tetrabasic lead sulfate. L. Torcheux et al. [16] studied on the improvement of the formation efficiency of the tetrabasic lead sulfate for lead-acid batteries. They presented a calculation model to forecast the formation efficiency of 4BS plates. They concluded that the most effective method is reducing the 4BS crystal size (especially the needle section). They also suggested that long crystal 4BS presenting a small section is also a kind of ideal material. This material could give positive active material with a very high interconnection degree combined with high porosity and high specific surface. This could be another step in allowing sensible reduction of starting raw material without affecting battery quality. Thus, decreasing the grain size of 4BS has become the focus of the research. D. Pavlov et al. [13] prepared tetrabasic lead sulfate paste for lead-acid battery by means of semi-suspension technology. Through this method, the dimensions of 4BS crystals can be controlled between 20 μm and 25 μm. The 4BS paste preparation facilitates the formation of stable positive active material structure that ensures high capacity and long cycle life of the positive plates (lead dioxide) of lead-acid batteries. S. Grugeon-Dewaele et al. [17] synthesized a kind of small crystal size 4BS by means of mechanical grinding method. They researched the structure of 4BS through the regulation of $PbO/PbSO_4$ mass ratio, moisture content of raw materials and ball milling time. Grain size of 4BS prepared by this method is less than 1 μm and it has very high electrochemical activity. David P. Boden et al. [18] added 4BS to the paste of lead-acid battery and used lead monoxide to produce the paste instead of conventional leady oxides with residual free lead. Using this technology the positive plate of the lead-acid battery could contain a high concentration of tetrabasic lead sulfate and a low concentration of free lead. The positive plate could eliminate conventional curing process. It could reduce the cost of lead-acid battery due to it's a time-consuming and expensive process. They also found that the 4BS crystal in the positive plate was small and uniformly.

Nanometer material is a kind of very promising material. Its activity is much greater than traditional material. So in this paper, we used a kind of nanometer tetrabasic lead sulfate as the positive active material additive for lead-acid battery. The nanometer 4BS is synthesized by means of mechanical grinding method by our team and the cooperative enterprise. Because the enterprise needs to secure some synthetic process, the manuscript doesn't describe the synthesized process of nanometer 4BS in order to guarantee its authenticity. Firstly, through XRD and SEM, study on the nanometer tetrabasic lead sulfate's microstructure and morphology and calculate its purity. Secondly, its effective lead dioxide conversion rate was investigated by means of charge–discharge test. Effective lead dioxide refers that it can participate in the electrochemical reaction in the charging and discharging process. Through charge and discharge test we obtained the discharge capacity of nanometer 4BS positive plate after formation, and it could calculate the effective lead dioxide conversion rate of 4BS compared with the theoretical capacity of lead dioxide (224 mAh g^{-1}). At last, we described the electrochemical properties of the positive active material of lead-acid battery with nanometer 4BS as additive.

2. Experimental

2.1. Investigations of the properties of 4BS

In this paper, the properties of nanometer 4BS were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM). XRD analysis was carried out with a D Max-RD12Kw diffractometer with Cu Kα radiation. The scan data were collected in the 2θ range 10°–90° at scan rate 2° min^{-1}. Purity of nanometer 4BS was also briefly calculated with the XRD data and Materials Studio software. SEM was performed using a Quanta 200 instrument. The critical size and micro-morphology of nanometer 4BS were described.

In order to research effective lead dioxide conversion rate of nanometer 4BS, we made electrodes with nanometer 4BS.The thickness of nanometer 4BS electrodes was 1 mm. The nanometer 4BS electrode as the working electrode with the negative plate of traditional lead-acid battery as auxiliary and reference electrode was checked galvanostatically between 1.75 V and 2.42 V on multichannel battery testers (Neware, Shenzhen in China) at various current densities at room temperature. The current densities and specific capacity were measured by the weight of nanometer 4BS.

2.2. Nanometer 4BS as positive active material additive

2.2.1. Lead paste preparation

Negative and positive pastes were prepared in the conventional manner. Raw materials of positive paste were lead powder, red lead (Pb_3O_4), graphite, polypropylene fiber, $SnSO_4$ and different ratio nanometer 4BS. In this paper, the ratio of nanometer 4BS added to the positive paste was 1% and 4%. Following consideration of the cost of the battery, the amount of nanometer 4BS cannot exceed 4%. Raw materials of negative paste were lead powder, barium sulfate, lignosulphonate and humic acid.

The raw materials of the positive and negative pastes were mixed in a plastic container for 10 min. Distilled water was added to above mixture and mixed for 15 min. And then, sulfuric acid (1.4 g cm^{-3}) needed to be added slowly. In the process of adding sulfuric acid, the lead paste needs to hold the temperature lower than 60 °C with a water cooling system. At last, lead paste was mixed for a time period so that water, sulfuric acid and lead paste could be mixed adequately.

2.2.2. The electrochemistry performance of lead-acid battery with nanometer 4BS as additive

After preparation of positive and negative paste, the lead paste was pasted on the Pb–Ca alloy grids respectively. The thickness of