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Investigation of lead dendrite growth in the formation of valve-regulated lead-acid batteries for electric bicycle applications

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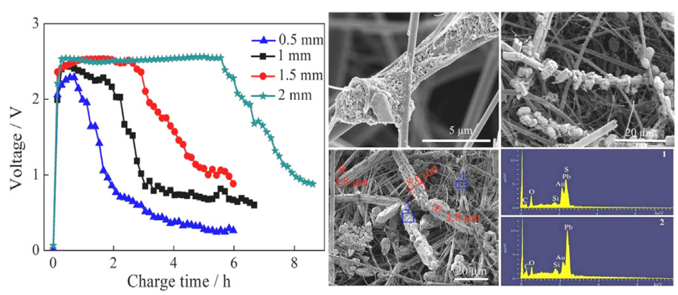
HIGHLIGHTS

- Low acidity, high temperature and small $PbSO_4$ particles increase Pb^{2+} concentration greatly.
- The middle of separators becomes neutral due to difficult diffusion of H_2SO_4 into plate group.
- Higher Pb^{2+} concentration makes more $PbSO_4$ tend to deposit on the coarse glass fibers and even enwrap entire fiber.
- The $PbSO_4$ on coarse fibers is reduced to lead dendrites in the charge and leads to battery short circuit.

GRAPHICAL ABSTRACT



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ABSTRACT

The battery temperature, H_2SO_4 distribution, Pb^{2+} ion concentration and composition of the plates during the plate soaking of the 12 V 12 Ah valve-regulated lead-acid (VRLA) battery are studied. A simulated cell composed by two pure Pb plates and the absorptive glass mat (AGM) separator is used to investigate the growth of the lead dendrite in the separator, which is verified by analyzing the faulty batteries after the formation and the failure batteries after the usage. It is found that the H_2SO_4 is exhausted very quickly after filling and the separator near the plates can become neutral during soaking. Low acidity, high temperature and small PbSO4 particle size will increase the Pb^{2+} ion concentration. Higher Pb^{2+} ion concentration makes more $PbSO_4$ tend to deposit on the coarse glass fibers, develop along them and even enwrap the entire fiber. And the fine $PbSO_4$ crystals are continually transformed into large $PbSO_4$ crystals via dissolution-deposition. In the subsequent charge, these $PbSO_4$ crystals will be reduced to the club-shaped lead dendrites and may lead to short circuit of the battery.

1. Introduction

In the last two decades, much effort has been done to investigate valve-regulated lead–acid (VRLA) batteries in various applications such as electric vehicles (EVs), telecommunications and energy storage devices for renewable energy, uninterruptible power supplies (UPS) and solar traffic lights, and the market demand for VRLA batteries was steadily increasing [1]. Recently, the excessive carbon emission becomes a global concern which makes the electric vehicle attract global attention due to its major advantage of low energy consumption and zero tailpipe emissions [2]. China has a

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population of more than 1.3 billion, which leads to traffic jams and crowded and slow public transport in many big cities. Electric bicycles (EBs) as a popular travel mode provide an inexpensive, flexible and convenient form for short-distance trips [3]. More and more people in China choose EBs as an alternative travel mode for public transit or regular cycling. According to incomplete statistics, the held amount of EBs in China was beyond 200 million up to 2014. At present, most vehicles use the 36 or 48 V VRLA battery packs to drive 250 or 350 W electromotor, respectively [4,5]. The capacity of the battery chosen depends on the power of the electromotor. The battery types used in over 80% markets are 6-DZM-12 (12 V 12 Ah) and 6-DZM-20 (12 V 20 Ah) batteries. With the increasing awareness of environmental protection and the rapid development of Chinese or Asian economy, more and more EBs will be needed, which will also promote the development of battery market in the coming years.

The formation processes for VRLA batteries contain the plate soaking and then the charge. The charge procedure is normally composed of several charge–discharge cycles in a container formation of VRLA batteries. Since the plate group of most VRLA batteries is under high assemble pressure, filling H_2SO_4 solution into cells becomes a complex process, especially filling the electrolyte containing a little gel. The soaking process depends on the diffusion of H_2SO_4 into the interior of the plate group, which is closely related to the pore system in AGM separators and plates, the size of plates and the assemble pressure of the plate group [6]. After filling H_2SO_4, H_2SO_4 reacts with PbO to form $PbSO_4$, basic lead sulfates and H_2O, and the gradient of H_2SO_4 concentration appears in the plate group [6–10]. The sulfation on the surface of the plates also makes it difficult for H_2SO_4 to penetrate into the interior of the plate [11]. Since $PbSO_4$ and basic lead sulfates are transformed into α- and β-PbO_2 in the subsequent charge, respectively, the composition of the soaked plates determines the ratio of α-/β-PbO_2, which affects the initial capacity and cycle life of the batteries [7,12–14]. Normally, the soaking period ranges from 1 to 3 h. Since the chemical reactions are very fast and exothermic, the battery temperature rises quickly and it is necessary to cool the battery in the water tank in the formation to avoid excessive battery temperature [6,15]. The longer the soaking time, the more $PbSO_4$ is formed and the lower the acidity in the AGM separator becomes [11,15]. This can accelerate the $PbSO_4$ dissolution into the AGM separator and the Pb^{2+} ions near the negative plate can be reduced into lead dendrite, which increases the risk of short circuit of the separator [15]. In order to prevent the growth of lead dendrites, the 'dendrite prevention additives' such as Na_2SO_4, $(NH_4)_2SO_4$, K_2SO_4 and $MgSO_4$ [16–19] are used as additives in the electrolyte in the VRLA battery manufacturers and Na_2SO_4 is preferred from the economic standpoint [20].

Although the manufacture technology and product design of VRLA batteries for the electric bicycle application are increasingly improved, there still exist some unsolved problems for the typical products of 6-DZM-12 and 6-DZM-20 batteries with high volume specific energy design. The discharge time of both batteries in the first three cycles can reach 130 min at the C_2 rate. The weights of 6-DZM-12 and 6-DZM-20 batteries produced by Chaowei Power Co. Ltd., China are about 4.3 and 6.9 kg and their volume specific energies reach 36.3 and 37.7 Wh/kg, respectively. The separator thickness at 100 kPa is only 1.1–1.2 mm. Especially, the manufacturers used a lot of coarse fiber in the AGM separator production because of the market competition and cost limitation. This leads to the enlargement of the pores in the separator and the bigger risk of short circuit of the lead dendrite. At present, the short circuit caused by lead dendrites and crack of the separators are responsible for about 20–30% of the failure 6-DZM-12 batteries in guarantee period.

The purpose of this work is to do researches in detail on the soaking process and its effects on the lead dendrite growth in the separator between positive and negative plates in the formation, which may provide the basis for the later work such as choosing AGM separator and optimizing the content of sodium sulfate used as additive in the electrolyte to prevent the formation of lead dendrites.

2. Experimental

2.1. Batteries and temperature measurement

The test batteries in this study were 6-DZM-12 VRLA batteries (12 V 12 Ah) used for electric bike, produced by Chaowei Power Co. Ltd. China. They have the dimensions of 151(L) × 99(W) × 97(H) mm. Each cell was assembled with eight negative plates and seven positive plates which were wrapped by the double layer absorptive glass mat (AGM) separators. The Pb–Ca–Sn–Al alloy was used as the positive grid with the dimensions of 44.3 (W) × 72(H) × 2.4 (T) mm and the Pb–Ca–Al alloy as the negative grid with the dimensions of 44.3 (W) × 73(H) × 1.4 (T) mm. The positive and negative plates have 30 and 22 g pastes containing 42 and 37 g H_2SO_4 per 1 kg lead powder, respectively. Six cell were put into a battery case with 2 × 3 arrangement. The assemble pressure of plate groups reaches about 80 kPa. The batteries were filled by 148 ml 34.8% H_2SO_4 electrolyte containing 1.5% Na_2SO_4 at 20 °C and then placed in a water pool.

In order to measure the battery temperature, a temperature probe was embedded into the pasted positive plate which was placed in the interior of the plate group. Then we assemble the 12 V 12 Ah battery, fill the H_2SO_4 electrolyte, form the battery according to the charge profile at the ambient temperature of about 23 °C. In Fig. 1, the soaking time before the charge is 2 h and two discharges were carried out in the formation. The data of temperature, voltage and current were acquired by HP34970A Data Acquisition/Switch

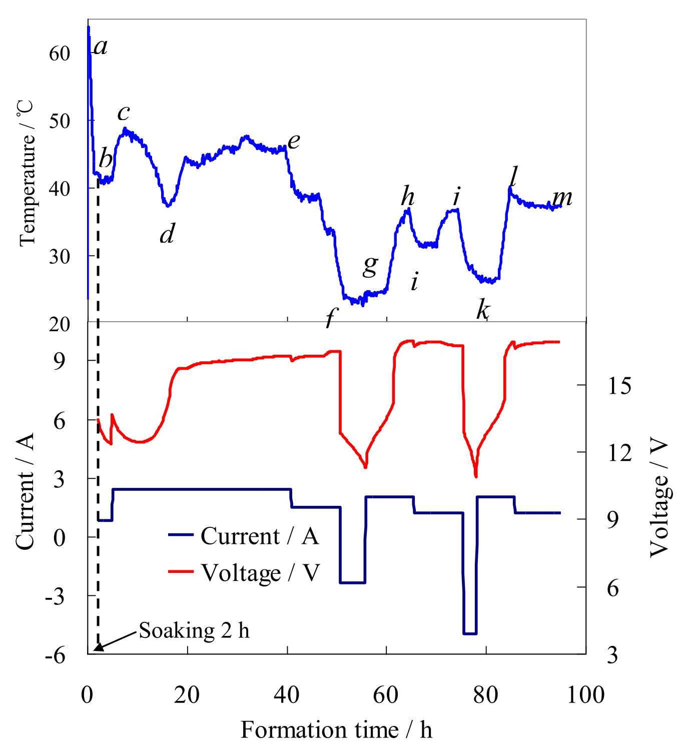

Fig. 1. Changes of battery temperature, current and voltage in the formation of the battery.