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ORIGINAL PAPER

Influence of pitch-based carbon foam current collectors on the electrochemical properties of lead acid battery negative electrodes

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Abstract Pitch-based carbon foams prepared by a template method were used as negative current collectors to assemble flooded lead acid batteries, and the effect of the current collectors on the performance of the negative electrodes was investigated. Comparative galvanostatic charge–discharge tests show that the utilization efficiencies of the active material on the carbon foam negative current collector are 14% and 30% higher than those of the material on a lead grid one at 20 and 10 h discharge rates, respectively. Further EIS tests imply that there are also significant differences in the impedance spectra between the two electrodes. SEM images reveal that at the fully charged state, the particle size of the active material formed on the carbon foam current collector is much more uniform than that on the lead grid.

Keywords Carbon foam · Current collector · Lead acid battery · Negative electrode · Active mass utilization efficiency

1 Introduction

Lead acid batteries have been in widespread use for many years. The applications include starting–lighting–ignition (SLI) batteries for cars, small-capacity consumer batteries, and large-capacity stationary batteries. Recently, this rechargeable electrochemical storage system has also attracted public attention as an electric source for an electric car from the point of views of environmental problems [1–3]. This is due to the main advantages of this system: availability, low cost, satisfactory power density, safety. However, Conventional lead acid batteries are relatively heavy and thus have a low specific energy. The heavy weight is a direct result of the use of large amounts of lead in the electrodes, both in the grids and in the active materials [4]. To improve the specific energy, lightweight, electronically conductive materials have been proposed as potential substitutes for lead alloy grids [4–14].

Various carbon foams have also been widely investigated as current collectors for lead acid batteries due to their specific properties, such as lightweight, large specific surface, good corrosion resistance, and high electrical conductivity. Czerwinski and Zelazowska [10, 11] firstly investigated the electrochemical behavior of Pb and PbO_2 deposited on reticulated vitreous carbon. Based on cyclic voltammetry studies, it was concluded that the reticulated carbon substrate had no negative influence on the performance of the active materials. But no experimental data were presented detailing the behavior of the deposited reticulated electrodes in lead-acid batteries. Gyenge et al. [12] employed reticulated vitreous carbon coated with a lead alloy as a current collector material for lead-acid batteries, and good battery cyclibility was obtained. Virtually, this material was similar to lead alloy foams since the lead coating was so thick (about 200–400 μm). Recently, Jang et al. [13] evaluated the electrochemical stability of graphite foams as current collectors for lead acid batteries. But the assembled batteries exhibited bad cyclibilities and low active material utilization efficiencies. In addition, it seemed difficult to uniformly apply battery pastes on the foam due to the small pores in the cell walls of the foam material. In our previous work, a new pitch-based carbon foam with large pores in the cell walls was developed and investigated as current collectors for lead

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acid batteries [14]. Cyclic voltammetry studies showed that the carbon foam was suitable for use as negative current collectors for lead acid batteries. In the present research, flooded lead acid batteries were prepared by using the carbon foam as the negative current collectors, and the influence of the carbon foam current collectors on the electrochemical properties of the negative electrodes was further investigated by galvanostatic charge–discharge tests, electrochemical impedance spectroscopy (EIS), and scanning electron microscope (SEM).

2 Experimental

The carbon foam slabs used in this study were fabricated by a template method described in our previous work. The pore size was ca. 1 mm (shown in Fig. 1), and the slab size was ca. 42 mm × 25 mm × 5 mm. The bulk density and surface area of the carbon foams was 0.3 g cm^{-3} and 89 cm^{-2} cm^{-3}, respectively. The battery pastes were prepared according to Ref. [15]. The negative paste was physically forced into the pores of the carbon foam slabs with a plastic spatula, and excess paste was scraped off of the surface. For preparation of the positive electrodes, lead grids with punched pores were used as the positive current collectors. The pore diameter and space between the pores were ca. 2 mm and ca. 3 mm, respectively. The positive paste was coated on the lead grids with another plastic spatula. Subsequently, the electrodes were immersed in a 14.5% H_2SO_4 solution for about 5 s, and then cured at 70 °C and a relatively humidity 90% for 36 h, and dried at 80 °C for 12 h.

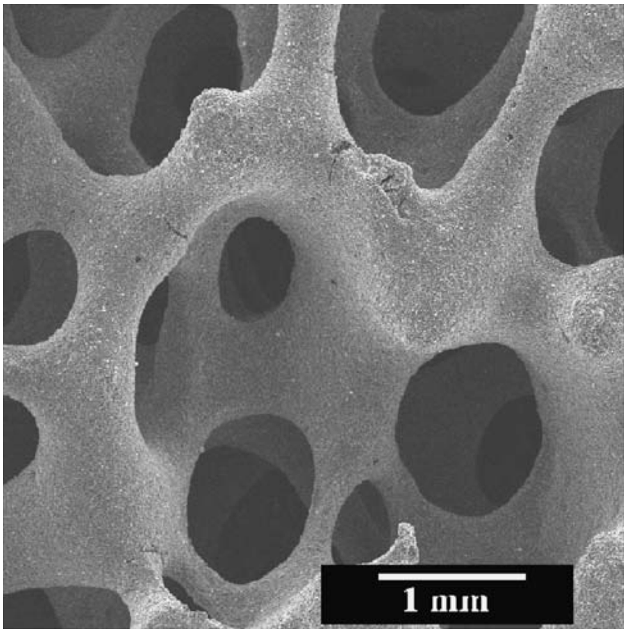

Fig. 1 SEM image of the carbon foam

The amount of the negative paste coated on the carbon foam slab was ca. 0.6 g, and the electrode size (the size of the coated part of the foam slab) was ca. 25 mm × 6 mm × 2 mm. For the positive electrode, the amount of the paste and the electrode size were ca. 1.2 g and ca. 25 mm × 12 mm × 3 mm, respectively. For comparison, negative electrodes with lead grids as the current collectors were also prepared by the same method. The electrode size and amount of the paste were ca. 25 mm × 5 mm × 3 mm and ca. 0.6 g, respectively. The electrodes were connected with conductive wires by soldering and then, the joints and the uncoated parts of the carbon foam slabs were covered by epoxy resin. Flooded lead acid batteries were assembled with one positive electrode and one negative electrode, thus the charge–discharge capacity was limited by the negative electrode.

Formation and galvanostatic charge–discharge tests were carried out using a Neware battery test system. Prior to the charge–discharge tests, the batteries were formed in a 14.5% H_2SO_4 solution. The formation algorithm included two steps as following:

1. 10 h rate 2.4 V
2. 20 h rate 2.57 V

During charge–discharge testing, a 4.5 M H_2SO_4 solution was used as the electrolyte and the batteries were initially discharged at a 20 h rate. The galvanostatic charge–discharge tests were performed by charging them to 75 mA h at a 20 h rate followed by their discharge at various hour rates. In all cases, the discharge cut-off voltage was 1.7 V.

EIS tests were carried out in a frequency range of 0.01 Hz–10 kHz using a ChI660B electrochemical workstation and a three-electrode beaker cell. The lead grid and carbon foam negative electrodes were used as the work electrodes. The reference electrode was Hg/Hg_2SO_4 in saturated K_2SO_4 solution (MSE), and 50 mL of 4.5 M H_2SO_4 solution was used as the electrolyte. The counter electrode was a large piece of lead (40 mm × 30 mm). The surface morphologies of the negative electrodes were observed under a JSM-6360 LV scanning electron microscope.

3 Results and discussion

For comparison, the negative electrodes with carbon foam and lead grid current collectors were used to assembled flooded lead acid batteries, respectively. During galvanostatic charge–discharge testing, the batteries were all charged at a 20 h rate and then discharged at a 10 or 20 h rate. The typical charge curves for the batteries with different negative current collectors are presented in Fig. 2. As can be seen, although the voltages of the batteries are closed to each other at the initial stage of charge, they are significantly different at the last stage of charge. In addition, it can be clearly seen that each charge curve has a clear 'turning point' which divides the curve into two parts. According to Lam et al. [16], the first part below the turning point can be attributed to the reactions of the electrode active materials, while the last part above the turning point is mainly due to the evolution of hydrogen and oxygen. Thus, the time or capacity related to the first part can be used to assess the charging ability of the battery. The longer time taken for the voltage of the carbon foam battery to the turning point implies that the battery has better charging ability.

Following charging, the batteries were discharged at 10 or 20 h rate. Fig. 3a shows the discharge curves of the batteries at the 20 h rate. The capacity of the carbon foam battery is ca. 62 mA h, corresponding to the negative active mass utilization efficiency of ca. 57%. Under similar conditions, the capacity of the lead grid battery is ca. 54 mA h and the utilization efficiency is ca. 50%. The utilization efficiency for the carbon foam electrode is ca. 14% higher than that for the lead grid one. The difference in the active mass utilization efficiency is more pronounced at 10 h discharge rate. As can be seen in Fig. 3b, the utilization efficiency for the carbon foam electrode is ca. 30% higher than that for the lead grid one. Furthermore, it is noteworthy that the voltages of the both batteries are uniform over the entire 20 h or 10 h rate. This implies that the three-dimensional nature of the carbon foam current collector has less negative impact on the potential distribution in the negative electrode, when compared to a lead foam current collector. The latter was reported to result in a non-uniform potential distribution in the collector-active material assembly [17]. Considering the results in Fig. 3 and the low bulk density of the carbon foam material (ca. 0.3 g cm^{-3}), it can be supposed that the lead acid battery with the carbon foam negative current collector must provide a higher specific energy density as compared to the conventional one. Nevertheless, further evaluation based on a commercial lead acid battery with the carbon foam material as the negative current collector is still needed to determine the exact figures of merit, such as specific energy and power.

Although the increase in the active mass utilization efficiency can be attributed to factors, such as the specific BET areas of the active materials, it is postulated that the lead acid batteries with carbon foam current collectors may benefit from the specific structure of the collectors. The reticulated, open-cell structure characterized by a high specific surface area provides a large effective contact area

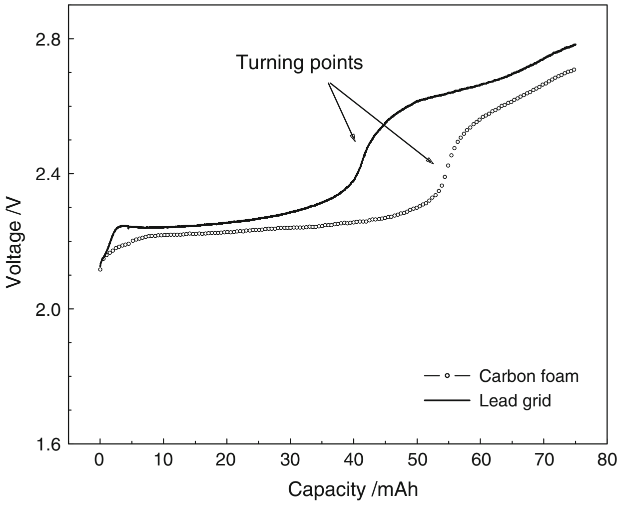

Fig. 2 Charge curves for the batteries with different negative current collectors at 1/20 h rate

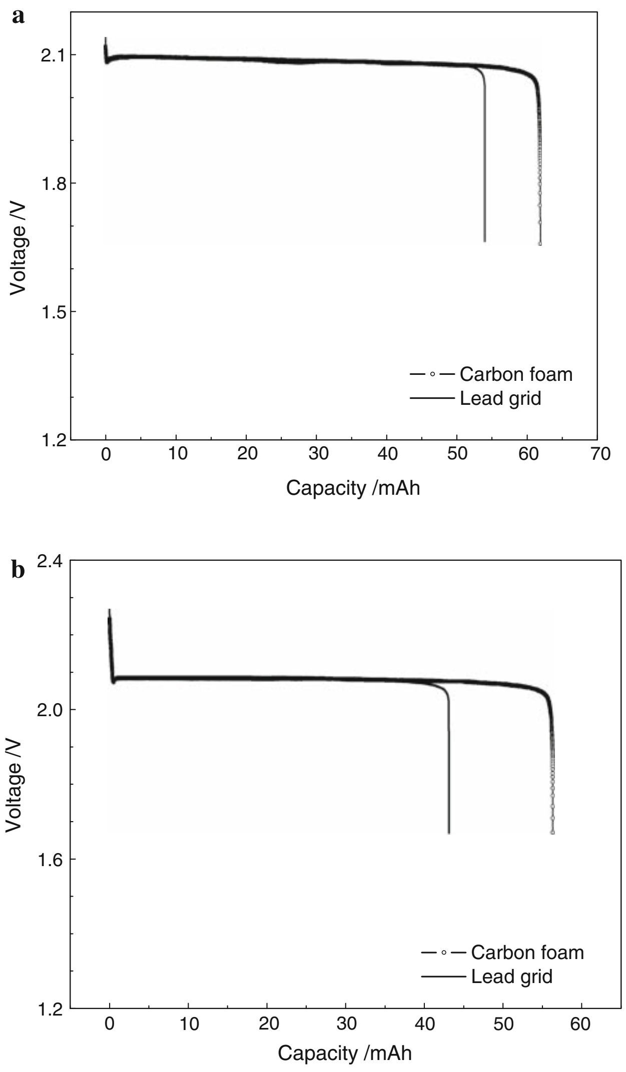

Fig. 3 Discharge curves for the batteries with different negative current collectors at: (**a**) 1/20 h and (**b**) 1/10 h rates

for the active material, which leads to decrease in the density of the current passing through the contact surface and the polarization resistance of the electrode [9, 17]. In addition, the three-dimensional, interconnected ligaments of the carbon foam current collector may also have the same effect as carbon fibers which are usually added in the active material. For many years, carbon (including fibers and particulates) has been favored as an additive to the negative active-material in lead acid batteries, despite the fact that there has never been universal agreement on the reasons for its use. It was commonly accepted that the primary function of the carbon material was to clear the negative electrodes during formation [18]. It was also described that the carbon additive could influence the porosity of the negative electrodes [19].

After several charge–discharge cycles, the batteries at fully charged or discharged states were disassembled, and the carbon foam and lead grid negative electrodes were used to assemble beaker cells to investigate the electrochemical behavior by means of electrochemical impedance spectroscopy. Fig. 4 shows the Nyquist plots of the cells. The different high-frequency resistance (R_{HF}) values can be due to the lower electron conductivity of the carbon material compared to metallic lead. When the electrodes at fully charged states were used as the working electrodes, each impedance spectrum exhibits a high frequency loop and a low frequency curve, as shown in Fig. 4a. This is consistent with an impedance curve for the limited diffusion with an ideal reservoir at the boundary [20], which indicates that the limited diffusion in the pores of the electrodes is the rate-determining step in both cases. The difference in the impedance spectrum may imply that the two electrodes have different pore structure parameters [21, 22]. When the electrodes at fully discharged states were used as the working electrodes, the shapes of the Nyquist plots are semicircle, as shown in Fig. 4b. Difference in the impedance spectrum can also be seen in this case. The diameter of the semicircle for the cell with the carbon foam electrode is about two-part lower compared to the cell with the lead grid negative electrode. In addition, for the cell with the discharged carbon electrode, the impedance spectrum exhibits a clear loop at the high frequency part as shown in the inset of Fig. 4b. This needs further investigation and discussion in the future.

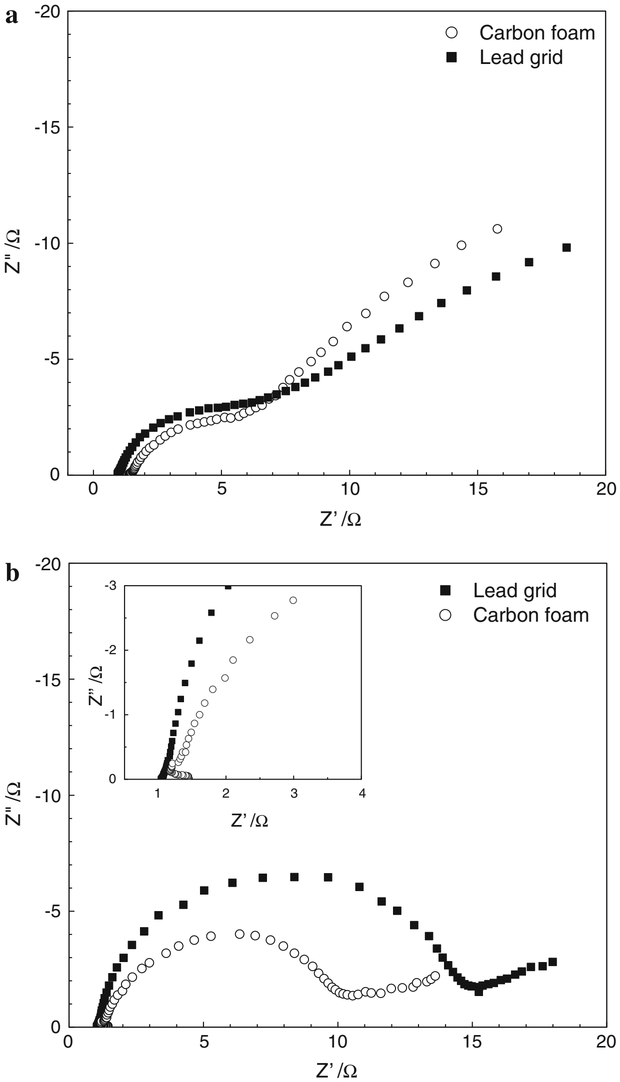

Fig. 4 EIS of the cells with carbon foam or lead grid negative electrodes at: (**a**) fully charged and (**b**) fully discharged states

The SEM images of the surface morphologies of the carbon foam and the lead grid electrodes at the fully charged state are presented in Fig. 5. It can be clearly seen that the particles of the active material formed on the carbon foam current collector are uniform and the particle size is ca. 2 μm as shown in Fig 5a and b. On the other hand, in the case of the lead grid, the particle size ranges from ca. 10 μm to several hundred nanometers as shown in Fig. 5c and d. The results indicate that the current collector has an influence on the active material morphology. According to a charge mechanism of the negative electrodes in lead acid batteries [23], the conversion of lead sulfate to sponge lead proceeds via two reactions, namely, dissolution and deposition. Dissolution is the chemical reaction, while the subsequent deposition is the electrochemical reaction. In the case of the carbon foam current collector, the three-dimensional structural nature of the current collector must lead to a three-dimensional current distribution in the discharged electrode, which may make the electrochemical deposition develop evenly throughout the electrode.

4 Conclusion

The effect of the carbon foam current collector on the electrochemical properties of lead acid battery negative

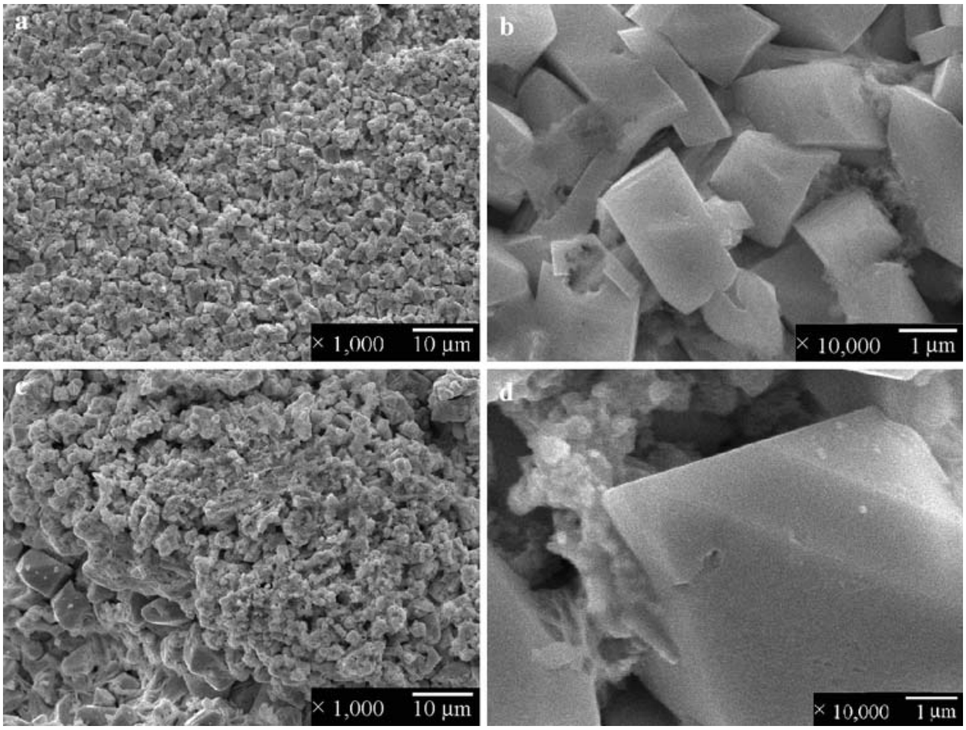

Fig. 5 SEM images of the charged negative active material on: (**a**–**b**) carbon foam current collector and (**c**–**d**) lead grid current collector

electrodes was investigated. The results indicate that the carbon foam current collector can improve the charging ability and active mass utilization efficiency of the negative electrode. At 10 h discharge rate, the active mass utilization efficiency of the carbon foam electrode is 30% higher than that of the lead grid one. It is postulated that the above improvement is partially due to the high specific surface area and three-dimensional ligament structure of the carbon foam material. Electrochemical impedance spectroscopy results imply that there are significant differences in the impedance spectra between the carbon foam and lead grid electrodes. SEM images reveal that the particle size of the active material on the carbon foam current collector is much more uniform than that on the lead grid at the fully charged state. To complement the present research, further experimental studies based on a commercial lead acid battery using the carbon foam as the current collector are still needed to determine the exact figures of merit, such as charge ability, specific energy, and power.

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