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ORIGINAL PAPER

Pitch-based carbon foam electrodeposited with lead as positive current collectors for lead acid batteries

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Abstract Lead electrodeposited carbon foam (LCF), whose substrate was made from pitch by a template method, was investigated as possible positive current collectors for lead acid batteries. Scanning electron microscopy, cyclic voltammetry, and galvanostatic charge–discharge tests were employed to characterize the effect of the proposed collector on the structure and electrochemical properties of the positive active material (PAM). The LCF with uniform and dense lead coating shows the similar electrochemical characteristics to metallic lead in the voltage range where the positive electrodes of lead acid batteries operate. The LCF and lead slices were used as the positive current collectors to equip lead acid batteries, respectively. Comparative charge–discharge tests show that a battery equipped with a LCF collector exhibits higher PAM utilization efficiency and longer cycle life, for LCF can provide large specific surface area which is beneficial to electrochemical reactions and PAM adhesion. In addition, a light lead acid battery with a LCF positive current collector and a carbon foam negative current collector was made and tested for the first time. It deserves systematic industrial study in the future.

Keywords Carbon foam · Electrodeposition · Lead acid battery · Positive current collector

1 Introduction

Advanced lead acid batteries have many advantages such as reliability, economy and safety [1]. One of their biggest drawbacks is the low specific energy mainly due to the use of lead alloy grids as current collectors. A number of conductive materials including carbon, conductive ceramics and glass fibers coated with conductive tin oxide have been suggested as substitutes for lead alloy grids, with the purpose to reduce the weight of lead acid batteries, then to enhance their specific energy [2]. Carbon, one of these materials, is inert in sulfuric acid. Electrodeposition of lead and lead dioxide on carbon electrodes were evaluated, respectively [3, 4]. Their behaviors as lead acid battery electrodes indicated that carbon was suitable to act as current collectors for lead acid batteries theoretically, and so was reticulated vitreous carbon (RVC) [5]. Carbon foam, displaying its advantages of lightweight, three dimensional net structure, large specific surface area, good corrosion resistance and high electrical conductivity, is a promising candidate especially for the direct application as negative current collector [6, 7]. For employment as positive current collector, it still faces some problems. Yong-Il Jang et al. [6] used graphite foams and non-graphitized foams as positive current collectors for lead acid batteries, respectively. The batteries tests showed that because of the intercalation and deintercalation of bisulfate ions and sulfuric acid molecules between graphite layers in the positive voltage range, graphite foams could not be used as positive current collectors for lead acid batteries while the non-graphitized ones could. However, Ya Chen et al. [7] pointed out that due to the oxygen evolution, non-graphitized foams could not be used as positive current collectors either. Modification of the physical and/or chemical properties is therefore necessary to make carbon material

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suitable to serve as positive current collectors. A. Czerwinski et al. [8] found that the behavior of RVC covered with lead resembled the electrochemical behavior of metallic lead, which implied that RVC modified with lead might be used as current collectors for lead acid batteries like lead grids. But no data of battery tests were presented in his article. Elod Gyenge [9] electroplated a Pb–Sn (1 wt.%) alloy on RVC substrates and used them as current collectors for lead acid batteries. The battery completed 500 charge–discharge cycles and the positive active material (PAM) utilization efficiency was 21% under his testing conditions. The result was exciting except the relatively low PAM utilization efficiency. Furthermore B. Hariprakash et al. [10] prepared lightweight grids from flexible graphite sheets which were coated with lead followed by a corrosion-resistant polyaniline layer via electrodeposition. The specific energy of the lead acid battery with these lightweight grids was found to be ca. 40 Wh kg^{-1} at the C/5 rate, but the cycle life was not satisfying. Apart of these, there are few similar literatures referring to the study of using carbon material, especially carbon foam, as positive current collectors for lead acid batteries.

In our previous work, pitch-based carbon foam was successfully made by a template method. The manufacturing process is simple and economical. It was proved that our non-graphitized carbon foam was agreeable as negative current collectors for lead acid batteries, but not favorable to positive use. In this paper, carbon foam electrodeposited with lead is studied as positive current collectors for lead acid batteries by means of scanning electron microscope (SEM), cyclic voltammetry and galvanostatic charge–discharge tests. A light lead acid battery employing lead electrodeposited carbon foam (LCF) as positive current collector and carbon foam as negative current collector is also studied for the first time.

2 Experimental

The physical characteristics of pitch-based carbon foam slabs (25 mm × 5 mm × 40 mm) in our study are presented in Table 1. The carbon foam slabs were then electrodeposited with a lead coating in thickness of ca. 50 μm, using a fluoroborate bath [11]. The morphology of the lead deposit was observed under a JSM-6360 LV scanning electron microscope.

Table 1 The physical characteristics data of the pitch-based carbon foam from Ref. [7]

Property	Number of pores per inch (ppi)	Specific surface area ($\mathrm{cm}^2\ \mathrm{cm}^{-3}$)	Bulk density ($\mathrm{g\ cm}^{-3}$)	Porosity	Electronic conductivity ($\mathrm{S\ cm}^{-1}$)
Value	30	89	0.3	0.85	20

A lead electrodeposited carbon foam (LCF) slab with dimensions of 25 mm × 5 mm × 5 mm exposed (the rest part was covered with epoxy resin) underwent cyclic voltammetry as a working electrode at a scan rate of 5 mV s^{-1} using a ChI660B electrochemical workstation. The reference electrode was $\mathrm{Hg/Hg_2SO_4}$ in saturated $\mathrm{K_2SO_4}$ solution (MSE) and the counter electrode was a large piece of platinum. A $\mathrm{H_2SO_4}$ solution (50 ml of 1.75 M) was used as the electrolyte. For comparison, the cyclic voltammetry was also performed on a piece of metallic lead with a geometric area of ca. 56 cm^2 immersed in the electrolyte.

The battery pastes were prepared by a common method described in Ref. [12]. The paste was manually forced into the pores of the LCF slabs with a plastic spatula. The amount of the positive paste applying on one LCF slab was 0.5 g, while the size of the pasted part was 25 mm × 5 mm × 2 mm. Then the LCF positive electrodes were prepared. Some lead slices were also manually pasted with the negative paste of 1.0 g or positive paste of 0.5 g each to make negative electrodes or positive electrodes, respectively. A carbon foam slab was treated according to LCF slabs, but using the negative paste of 0.5 g to make a carbon foam negative electrode. Subsequently, the electrodes were all cured at 80°C for 48 h at a relative humidity of 90% and dried at 80°C for 12 h. Forming was performed in a 1.75 M $\mathrm{H_2SO_4}$ solution with a charge of 600 Ah $\mathrm{kg}_{\mathrm{PAM}}^{-1}$.

Two kinds of flooded lead acid cells were made. One called LCF cell was equipped with a LCF positive electrode and a lead slice negative electrode; the other called lead cell was assembled with both lead slice electrodes. Galvanostatic charge–discharge tests were performed on them using a Newware battery test system. The charge–discharge capacity was limited by positive electrodes for all cells. The cells were charged to its 200% initial discharge capacity at C/10 and then discharged at the same rate with the cut-off voltage of 1.7 V. A $\mathrm{H_2SO_4}$ solution (50 ml of 4.5 M) was used as the electrolyte for the tests. Besides, another cell called foam cell employing a LCF positive electrode and a carbon foam negative electrode also underwent the charge–discharge experiment following the similar algorithm, but its charge–discharge rate was C/5.

3 Results and discussion

3.1 Structure parameters of the electrodes

The current collector structure characterized by α and γ factors has an important role with regard to the active material utilization efficiency and the cycle life of lead acid batteries. The α factor is the ratio of collector to electrode weight $\left(\mathrm{g_{COL}\ g_{ELECTRO}^{-1}}\right)$ and its tipical value varies between 0.35 and 0.60. The tendency is to reduce this value as much as possible. The γ factor is the ratio of active mass to collector surface area $\left(g_{AM}\ cm_{COL}^{-2}\right)$, and the value of γ typically ranges between 1.6 and 1.8 for tubular and 2–2.5 for book-mould starting-lighting-ignition (SLI) plates, respectively. In order to increase the active material utilization efficiency, an effectual way is to design electrodes with low γ factors $\left(\text{e.g. } \gamma < 1 g_{AM}\ cm_{COL}^{-2}\right)$ [13]. A low γ factor guarantees large electrode surface area and low current density over the collector, thus ensures high active material utilization efficiency and large discharge capacity.

Table 2 shows the apparent collector density ρ, and the electrode design factors α and γ for the LCF positive and the carbon foam negative electrodes. For comparison, typical values for conventional book-mould plates reported in [10] are also given as a reference.

In Table 2, the apparent collector density ρ and design factor α of LCF positive electrode are parallel to those of book-mould plate, whereas its γ is reduced by more than order of magnitude as compared to the reference. This means that if LCF were used instead of lead alloy grids in industrial lead acid battery, though it would not reduce the weight of the positive electrodes greatly, it could highly increase the PAM/collector interface area for electrochemical reactions and then enhance the PAM utilization efficiency and the cycle life. As for the carbon foam negative electrode, ρ, α and γ are all much lower than book-mould plate, which indicates the carbon foam can cut down the weight of the negtive electrode significantly, and greatly help improve the specific energy if used in industrial lead acid battery. Our previous work has already proved carbon foam a possible negative current collector for lead acid battery. Now we are trying to study the possibility and advantages of LCF as positive current collector.

3.2 Morphology of the lead coating

Lead electrodeposition from different systems and on different substrates has been widely studied [14–19], but the ready-made process of lead electroplating on carbon foam is unavailable. The rough surface of the carbon foam makes it difficult to eliminate any exposed substrate surface during electroplating. If the carbon foam substrate is exposed to the electrolyte, the oxygen evolution will occur before the electrochemical reactions of PAM. The battery then fails to charge and discharge. To make sure the carbon foam is covered completely, a uniform and dense lead coating is necessary. Figure 1 (a) and (b) show SEM images of LCF in different magnifications. It is seen from the images that the carbon foam substrate is entirely covered by the lead coating which is uniform and dense. The lead coating is supposed to well protect the carbon foam substrate against the electrolyte penetration. Figure 2 presents the SEM image of a representative cross-section for LCF. The image demonstrates that the electrodeposited lead has good contact with the carbon foam substrate. The thickness of the lead coating is about 50 μm. A certain thickness of lead coating for LCF is essential because positive current collectors are likely to be corroded during charge–discharge cycles. Literature [9] has reported a sort of reticulated vitreous carbon current collector electroplated with Pb–Sn alloy. As the Pb–Sn alloy coating had a few pinholes with diameters between approximately 0.5 and 5 μm, it needed a coating thickness as of 200–300 μm to avoid positive corrosion, which is much thicker than this LCF.

Table 2 The apparent collector density and design factors of LCF positive electrode and carbon foam negative electrode

Electrode	$\rho\left(g_{COL}\ cm_{COL}^{-3}\right)$	$\alpha\left(g_{COL}\ g_{ELECTRO}^{-1}\right)$	$\gamma\left(g_{AM}\ cm_{COL}^{-2}\right)$
LCF positive electrode	3.54	0.64	0.02
Carbon foam negative electrode	0.34	0.15	0.02
Book-mould plate	3.1–5	0.47–0.60	0.66–1.23

* Data of conventional book-mould plate from [10] are for references

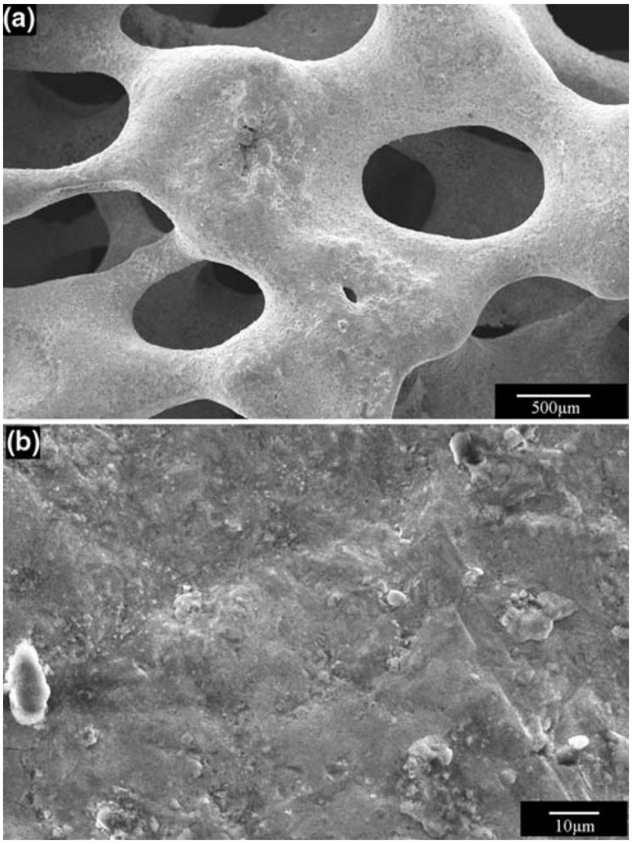

Fig. 1 Scanning electron microscopy images for LCF: (**a**) ×30, (**b**) ×1,000

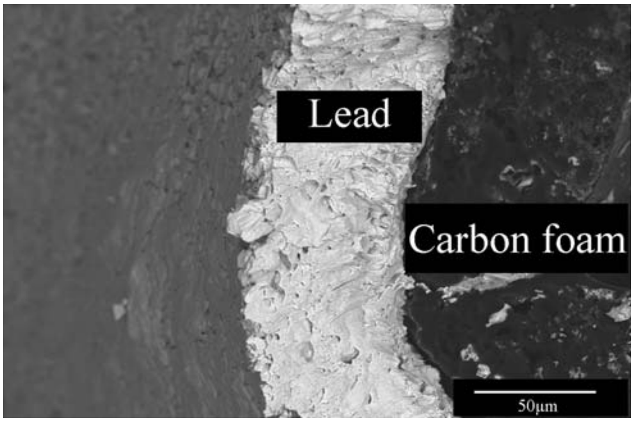

Fig. 2 Scanning electron microscopy image of a representative cross-section for LCF × 500

3.3 Cyclic voltammetry of LCF

The cyclic voltammetry can provide wide range of electrochemical information on LCF when it works as an electrode. Figure 3 (a) and (b) show the typical cyclic votammograms of 5 cycles for LCF and metallic lead in the voltage range from their open circuit potentials to 1.8 V at a sweep rate of 5 mV s^{-1}, respectively. It is seen obviously that the cyclic votammograms of LCF and metallic lead have the same profile, which means they have similar electrochemical characteristics. It implies that the lead coating covers the carbon foam substrate thoroughly. This result is consistent with that of SEM. In either Fig. 3 (a) or (b), there are three distinct peaks marked A, B and C. The peak A corresponds to the evolution of oxygen; peak B represents the oxidation of $PbSO_4 \rightarrow PbO_2$; and peak C the reduction of $PbO_2 \rightarrow PbSO_4$. With the cycle numbers increasing, for both Fig. 3 (a) and (b), the peak currents climb due to the accumulated reactants on the electrodes. Especially for the peak B, it is not seen untill the third cycle because no enough $PbSO_4$ formed on the electrode surface. The peaks potentials almost keep the same: the peak A above 1.5 V, peak B at ca. 1.4 V and peak C at ca. 0.9 V. For carbon foam, oxygen evolution occurs at ca. 0.6 V [7], which is lower than the potential of $PbSO_4 \rightarrow PbO_2$ and leads to poor charge acceptance of the battery. Contrastively for LCF, its oxygen evolution potential is higher than that of $PbSO_4 \rightarrow PbO_2$. So it can avoid the shortcoming of premature oxygen evolution on carbon foam when used as positive current collectors for lead acid batteries.

3.4 Charge–discharge tests on LCF cell and lead cell

Figure 4 shows the first discharge curves of a LCF cell and a lead cell. It is notable that there is a "voltage lip" at the beginning of discharge for both LCF cell and lead cell,

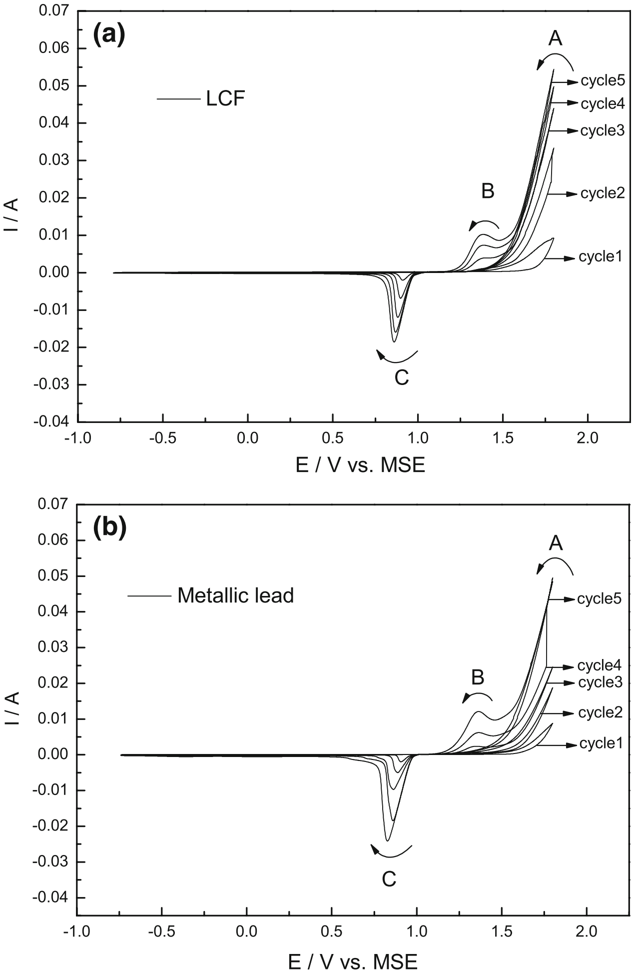

Fig. 3 Cyclic voltammograms of **a** LCF and **b** metallic lead in the positive voltage range Electrolyte: 1.75 M H_2SO_4. Scan rate: 5 mV s^{-1}

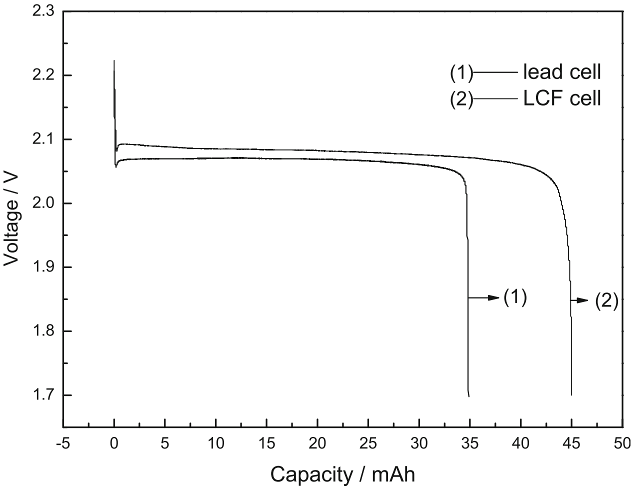

Fig. 4 The first discharge curves of different cells: (*1*) lead cell, (*2*) LCF cell Charge–discharge rate: C/10

which can be explained by a dissolution–precipitation mechanism. The dissolution–precipitation mechanism is based on the idea that PbO_2 is reduced on its surface to Pb^{2+} during discharge, and then goes into solution [20]. In the solution Pb^{2+} increases in concentration, arriving at a super-saturation state and giving rise to the precipitation of $PbSO_4$ crystals. At the beginning of the $PbSO_4$ crystals formation, the super-saturation reaches the maximum while the polarization is in the highest degree and the voltage of the cell drops to the bottom. As the $PbSO_4$ crystals start to grow, the polarization decreases and the voltage of the cell climbs gradually. Thus a "voltage lip" is observed. A charge–discharge voltage plateau appears subsequently when the electrochemical process reaches equilibrium, then the voltage of a cell is determined. The voltage of the LCF cell is higher than that of the lead cell for the first discharge as well as for the subsequent discharges. This means the LCF cell has lower internal resistance. It has been reported that an electrode with low γ factor can discharge at higher voltage than the one with high γ factor [13]. The LCF featuring low γ factor is supposed to contribute the high discharge voltage of the LCF cell. Also from Fig. 4 the LCF cell exhibits an initial discharge capacity of 45 mA h while the lead cell initially releases only 35 mA h. The probable reason is that the LCF can provide larger reaction area and make the conversion of PAM more adequate. The two cells experienced 15 cycles and the discharge capacities data including PAM utilization efficiencies related to each cycle are shown in Fig. 5. The LCF cell presents much higher capacities than the lead cell, and there is no obvious trend of capacity loss within the 15 cycles. By contrary, the capacity of the lead cell decreases gradually in 15 cycles. The changes over PAM utilization efficiencies for the LCF cell and the lead cell are the same to those of the discharge capacities, respectively. The PAM utilization efficiency of LCF cell is much higher than that of lead cell with its highest value of 78%, larger by nearly 100% than the highest value 39.5% for lead cell. During charge–discharge cycles, the transformation of $PbO_2 \leftrightarrow PbSO_4$ leads to looseness of PAM particles due to the different molar volume of PbO_2 and $PbSO_4$. In addition, a quantity of oxygen evolution accelerates the PAM softening and shedding. As active materials shedding from the positive electrodes is one of the main reasons for the failure of a lead acid battery [21], the better cycling stability for the LCF cell implies that the three dimensional net structure of LCF could hold the PAM more tightly and slow down the shedding rate. This can be confirmed from the less shedding PAM at the bottom of the LCF cell. After 15 cycles, the lead cell failed as it could never give a capacity higher than 20 mA h, which was too much lower than its rated capacity, whereas the LCF cell could still charge and discharge for another 30 cycles even at a higher rate, with the capacity declining gradually due to the active material shedding (seen in the inset of Fig. 5).

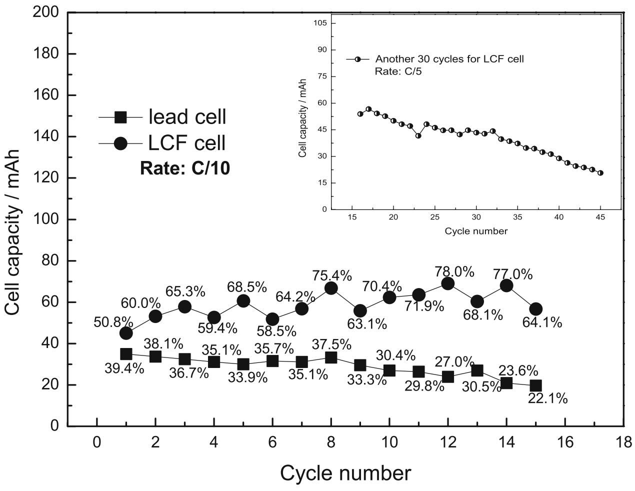

Fig. 5 Cycling property and PAM utilization efficiency data of 15 cycles for different cells: (*square*) lead cell, (*dot*) LCF cell Charge–discharge rate: C/10; Another 30 cycles for the LCF cell (*the inset*) Charge–discharge rate: C/5

3.5 Morphology of positive active material on different electrodes

In view of dissolution–precipitation mechanism, the solubility of PbO_2 and $PbSO_4$ which is related to the crystal size is a critical factor for electrochemical activity of PAM. Small-sized PbO_2 and $PbSO_4$ have large surface area and high reaction activity, which will enhance the PAM utilization efficiency. It was reported that the percentage of utilization higher than 45% was obtained from nanosized PbO_2, and its cycling stability was excellent [22]. In this context, forming small-sized PbO_2 on electrodes is effective to improve the performance of lead acid battery. Figure 6 (a) and (b) are the SEM images of the LCF and the lead slice positive electrodes which were fully charged (at 100% state of charge (SoC)). In Fig. 6 (a), the PbO_2 on LCF is fine, compact and uniform; while in Fig. 6 (b), the PbO_2 on lead slice is lumpish, loose and inhomogeneous. This indicates that the PAM on LCF has been oxidized more completely. The fine compact and uniform PbO_2 particles have larger surface area, better adhesion and electronic connections. They may be reduced more adequately during the subsequent discharge and give a larger capacity. This viewpoint is confirmed by Fig. 6 (c) and (d). Figure 6 (c) and (d) are the SEM images of the LCF electrode and the lead slice positive electrode that were fully discharged (at 0% state of charge (SoC)). In Fig. 6 (c), the crystals of $PbSO_4$ on LCF are small and uniform, indicating the reaction of $PbO_2 \rightarrow PbSO_4$ complete. On the other hand, in Fig. 6 (d) the $PbSO_4$ on lead slice is lumpish

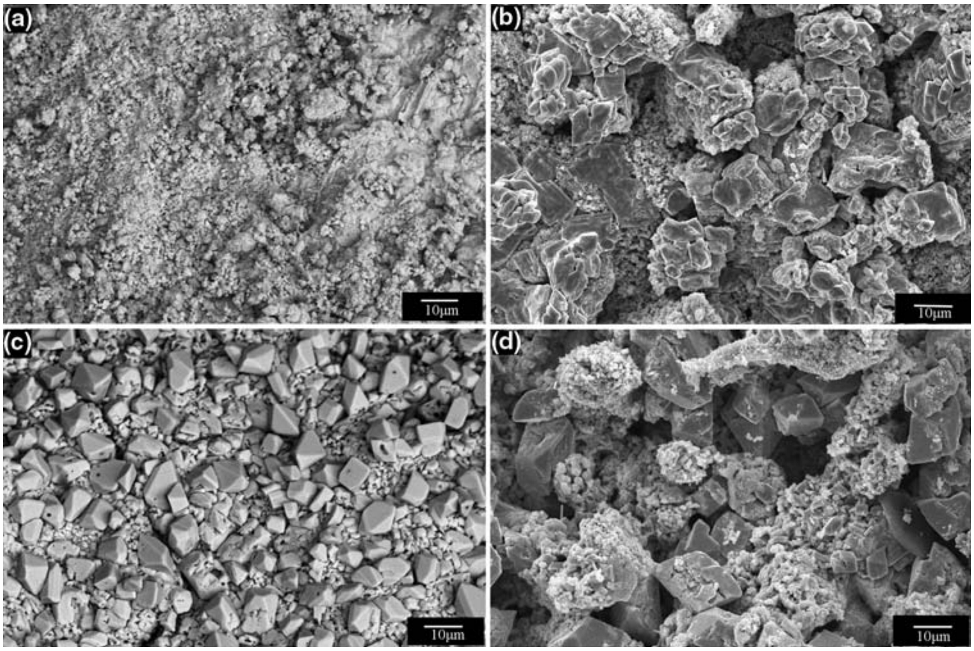

Fig. 6 SEM images of PAM on different positive electrodes at different states of charge: (**a**) LCF positive electrode at 100% SoC (**b**) lead slice positive electrode at 100% SoC (**c**) LCF positive electrode at 0% SoC (**d**) lead slice positive electrode at 0% SoC

and loose. There even remains some PbO_2 unreduced among the $PbSO_4$ particles due to the poor electronic connection. The looseness of PAM can also contribute to the PAM shedding.

Current collectors have been thought to influence the active material morphology [23]. From the above SEM information, the formation of the uniform small-sized PAM is probably due to the LCF current collector because of its large surface area and three dimensional net structure. The analysis on PAM morphology is consistent with the results of charge–discharge tests.

3.6 A charge–discharge experiment on foam cell

In our previous study, pitch-based carbon foam was used as negative current collector for lead acid battery successfully. Since the LCF has been successful in usage of a positive current collector and better than lead slice according to the above experiments, a light foam cell employing LCF as a positive current collector and carbon foam as a negative current collector should be tested and the data of this kind of foam cell have not been reported yet. Galvanostatic charge–discharge experiment was performed on the foam cell. Figure 7 shows its changes in capacity with time of cycling during 15 cycles and the inset is the picture of its second charge–discharge curves. It is seen from Fig. 7 that the foam cell performs well with a good cycling stability, but its PAM utilization efficiency was not as high as that of the LCF cell. The largest discharge capacity of the foam cell was 46.5 mA h and the corresponding PAM utilization efficiency was 52.8%. The probable reason is a higher charge–discharge rate for the foam cell. According to the inset, the charge process of the foam cell experiences two voltage plateaus: A–B and C–D. They represent two electrochemical equilibrium processes respectively: active material transformation and water decomposition. The voltage of the water decomposition is depended on the overvoltage of hydrogen and oxygen on the electrodes. If the hydrogen and the oxygen overvltages on the electrodes are too low during charge, the active material will not transform adequately before water decomposition and the capacity of the cell will be limited. For this foam cell, the water decomposition voltage is as high as 2.8 V, which is good for active material transformation. Thus the subsequent discharge process of the cell

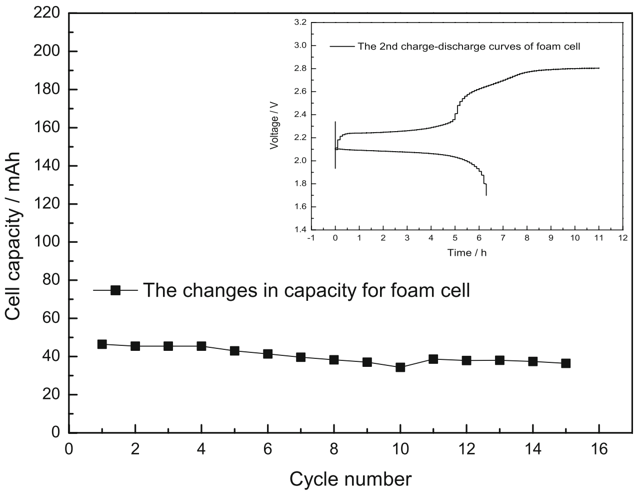

Fig. 7 Cycling property and second charge–discharge curves (*the inset*) for foam cell Charge–discharge rate: C/5

reaches a plateau (O–E) with a voltage of 2.0 V and gives a capacity of 45.5 mA h.

Considering the apparent density ρ of carbon foam negative collector is about one tenth the value of conventional book-mould collector, if the foam cell can be applied successfully into the lead acid battery industry, it is expected to enhance the specific capacity significantly.

4 Conclusions

(1) Through the information from scanning electron microscopy and cyclic voltammetry, it is known that the carbon foam substrate can be thoroughly electrodeposited with a dense lead coating of ca. 50 μm in thickness, making its electrochemical behavior resemble that of metallic lead. The LCF can be used as positive current collectors for lead acid batteries.

(2) The galvanostatic charge–discharge tests show that a LCF cell can give higher discharge capacity and longer cycle life than a lead cell. The high specific surface area of LCF is believed to provide more active reaction spots for PAM. Therefore, the PAM can be transformed completely into small particles during redox reactions, which benefits the improvement of PAM utilization efficiency. Meanwhile, the three dimensional net structure of LCF can prevent the shedding of PAM, thus the cycle life of the battery is enhanced.

(3) A foam cell featuring its lightweight property is tested. Systematic studies and evaluation on this kind of cell are needed in our future industrial experiments, including optimization of the coating thickness and content, amelioration of paste formulation, improvement of the pasting and curing techniques, adjustment of the charge–discharge algorithm and so on.

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