

Short communication

## Effects of lead-foam grids on performance of VRLA battery

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### Abstract

Lead-foam grids have been prepared by electrodepositing lead on a copper-foam substrate that has good conductivity and a symmetrically three-dimensional reticulated structure. VRLA batteries with lead foam as the negative electrode current collector material have been fabricated; the effects of the lead foam on the specific capacity, the active material utilization efficiency and the negative active material transformation process of the VRLA batteries have been studied. The results show that a lead-foam grid has a bigger specific surface area than a cast grid. The charge voltage of a VRLA battery with a lead-foam negative electrode is significantly lower than that of a VRLA battery with a cast grid electrode during a charge process. The discharge capacity, the mass specific capacity, and the active material utilization efficiency of a VRLA battery with a lead-foam electrode can be greatly improved at different states of discharge. The EIS research revealed that a lead-foam negative electrode has higher electrochemical reactivity. Observed by means of a scanning electron microscope, it was found that the spongy Pb crystals at a lead-foam grid negative electrode are smaller than that of a cast grid negative electrode at a state of charge; while the PbSO<sub>4</sub> crystals are smaller than that of a cast grid negative electrode at a state of discharge.

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### 1. Introduction

The competition of automobile power source became more vehement with the development of 36/42 V auto power systems, but at present lead-acid batteries are still the most practical choice for electric vehicles [1]. However, conventional lead-acid batteries have many drawbacks such as low specific capacities, low specific powers, short cycle lives and poor charge acceptances [2]. Meanwhile, as an auto power, lead-acid batteries also suffer from the serious sulfation at negative electrodes at a partial state of charge (PSOC). Recently, lead foam has attracted much attention because of its excellent properties such as its low density, high specific surface area and high porosity [3]. It has been reported in the literature that cast reticulated, open-cell current collectors possessed a specific surface area of 14 cm<sup>2</sup> cm<sup>-3</sup> and positive active material (PAM) utilization efficiencies up to a value 50% higher than typical book-mould grids [4]. The lead foam obtained by electrodeposition may have a better potential application because of its lower density, better uniformity and higher specific area [4,5]. Lead foam obtained by electrodeposition based on reticulated vitreous carbon (RVC) can significantly

enhance the specific energy and the active material utilization efficiency of a lead-acid battery [5] and can prevent the negative electrode from sulfation when it is used as the negative electrode current collector material. In order to improve the conductivity and specific area of lead foam, consequently, to improve the specific energy of VRLA batteries, in the present paper, lead was electrodeposited on copper foam to prepare lead foam which was then employed to be the negative electrode current collector material of VRLA batteries. The effects of lead foam on the battery performance and the transformation process of the NAM were also studied.

### 2. Experimental

#### 2.1. Preparation of lead foam

Copper foam (20 PPI; surface density: 600–700 g m<sup>-2</sup>; thickness: 2.0 mm) was firstly rinsed with tap water, then with distilled water. Next it was dipped into diluted boratofluoric acid to be activated. Then, it was washed again, sequentially, with tap water and distilled water. After the washing, lead was electrodeposited on it. After the electrodeposition, it was washed for the third time as described above. Then, it was dipped into distilled water for about 5 min. After it was blown to dryness, lead foam on a

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copper-foam substrate was obtained, and its surface density was about  $2200 \pm 150 \text{ g m}^{-2}$ .

## 2.2. Preparation of experimental VRLA batteries

To ensure the capacity of a battery to be limited by the negative electrode, VRLABs of two positive electrodes and one negative electrode were assembled with the positive electrodes being made of common cast grids and the negative electrodes of lead-foam grids and common cast grids, respectively. The common paste was used in experimental batteries and sulfuric acid ( $0.78 \text{ mol L}^{-1}$ ) was used as the dipping acid. Curing was performed at a temperature ranging from  $70$  to  $75^\circ\text{C}$  and under  $95$ – $100\%$  relative humidity using an outside formation process.

## 2.3. The measurement of specific surface areas of lead-foam grid and negative electrode

A chronoamperometer in a CHI630 electrochemistry work-place was applied for measuring the specific surface area of the lead foam. Pt was used as the counter electrode and an  $\text{Hg}/\text{Hg}_2\text{SO}_4$  (the concentration of the sulfuric acid was  $4.80 \text{ mol L}^{-1}$ ) electrode served as the reference electrode with a standard potential of  $0.6210 \text{ V}$  (versus SHE,  $25^\circ\text{C}$ ). The measurement was carried out with  $4.80 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$  as the electrolyte at  $20 \pm 0.5^\circ\text{C}$  in a pure glass electrolytic bath, which was prewashed with DI water and concentrated sulfuric acid. A potential in the vicinity of the open circuit potential was selected for the experiment. The initial potential = the open circuit potential  $\pm 11 \text{ mV}$ ; the highest potential = the open potential +  $11 \text{ mV}$ ; the lowest potential = the open potential, and the impulse width was  $0.25 \text{ s}$ . Each result from the three independent triplicate experiments was integrated by the Origin software to obtain the average result. The double layer capacitance of an Hg electrode of unit area was adopted as the standard capacitance, namely  $C_N$  was equal to  $20 \mu\text{F cm}^{-2}$ .

## 2.4. The charge–discharge equipment and system of the experiment batteries

The charge and discharge tests were carried out using a BTS 5 V/10 A battery testing system (made by Neware Technology Company Shenzhen, China) according to the Mechanism Industry Standard of the People's Republic of China (JB/T 10262-2001) for sealed lead-acid batteries used for electrical mopeds.

## 2.5. SEM observation of the surface morphology of the lead foam

The surface morphologies of the NAMs of the lead foam and the cast grids were observed using a Hitachi Japan S-4700 scanning electronic microscope.

## 2.6. Measurement and resolution of EIS

The EIS tests were carried out under different conditions at  $20 \pm 0.5^\circ\text{C}$  using a Model 273 potentiostat (made by EG&G

Princeton Applied Research), a 5210 phase-lock amplifier, a NEC Powermate ITX computer system, and EG&G M 398 EIS testing system in a range of  $0.1 \text{ Hz}$ – $10 \text{ kHz}$ . The cast grid negative electrode and the lead-foam negative electrodes were adopted as the work electrode, respectively, the counter electrode, reference electrode and electrolyte were the same as those in Section 2.3. The results of the measurements were analyzed by using the EG&G EQUIVCRT software.

## 3. Results and discussion

### 3.1. The measurement of specific surface area of lead foam

The specific surface area is an important parameter for the lead-foam material. The bigger the specific surface area of lead foam and the better the connection between it and the active mass, the higher the utilization efficiency of the active mass. Usually, a smaller value of  $\alpha$  indicates a bigger amount of the active material and a higher capacity of the electrode, resulting in a greater  $\gamma$  value that can cause a decrease in the active material utilization efficiency. In contrast to, a smaller  $\gamma$  value can lead to a higher energy output and active material utilization, which, however, will increase the corrosion rate of the positive grid [6]. Table 1 gives the test results of the two different electrodes with lead-foam grids and cast grids as the current collectors, respectively.

From the experimental results in Table 1, by comparing the lead-foam grid negative electrode with the cast grid one, we can see that the former not only showed a smaller mass but also had a greater contact surface area between the grid and the NAM. The enhancement in the contact area will result in a much lower current density at the interface of the active material and the lead-foam grid, which will further result in a lower degree of the electrochemical polarization of the experimental battery. All the properties discussed above of the new lead-foam material make the improvement in the charge–discharge performance of the corresponding VRLA batteries possible.

The specific surface area of the lead foam was measured by means of chronoamperometry to be about  $5700 \text{ m}^2 \text{ m}^{-3}$ . The results show that the specific surface area of this lead foam is

Table 1  
Parameters of the two different electrodes

	Parameter of different electrodes values	
	Lead-foam grid	Cast grid
Electrode mass before coating active material (g)	8.50	13.61
Electrode mass after coating active material (g)	40.52	45.63
Apparent surface area of grid ( $\text{cm}^2$ )	31.54	31.52
Specific surface area ( $\text{cm}^2 \text{ cm}^{-2}$ )	17.34	0.99
$\alpha$	0.20	0.34
$\gamma$ ( $\text{g cm}^{-2}$ )	0.048	0.84

$\alpha = M_{\text{collector}} / (M_{\text{NAM}} + M_{\text{collector}})$ ,  $\gamma = M_{\text{NAM}} / S_{\text{collector}}$ .  $M_{\text{collector}}$  is the mass of collector,  $M_{\text{NAM}}$  the mass of negative active material and  $S_{\text{collector}}$  is the specific surface area of collector.

17 times as big as its apparent area and much bigger than that of the lead foam obtained on a substrate of RVC ( $1800 \text{ m}^2 \text{ m}^{-3}$ ) [5].

### 3.2. Effect of the lead foam on charge acceptance of VRLAB

In order to compare the performance of the lead-foam VRLAB with that of the cast grid VRLAB, their charge acceptance was researched. Fig. 1 displays the charge curves of both the batteries charged at 10 h and 2 h rates, respectively. From Fig. 1, it can be seen that the initial charge voltages of both kinds of the batteries at both charge rates were very close to each other. However, after being charged for about 200 min, compared with the cast grid battery, the lead-foam one showed a much lower charge voltage and this trend became more significant with the prolongation of charge time at 10 h charge rate, and the lead-foam grid battery all along showed a much lower charge voltage at 2 h charge rate. In addition, the hydrogen evolution reaction in the cast lead battery appeared earlier than in the lead-foam one. The lead-foam VRLAB could be charged a larger quantity of electricity than the other one at the same charge voltage, which shows that the charge acceptance of the former is better than the latter.

### 3.3. Effect of lead foam on discharge performance of VRLAB

In order to research the difference in discharge performance between the VRLAB of lead foam and the VRLAB of cast grids, the discharge capacities of the two different batteries were tested. Fig. 2 shows the discharge curves of both the experimental batteries at different discharge rates.

At 20 h and 10 h discharge rates, there were improvements of 10% and 23% in the negative active material utilization efficiencies with the negative electrode of the lead-foam VRLAB compared with the cast grid one, respectively, and the mass specific capacities were 26–31% higher than those of the cast grid one, respectively, at 5 h and 2 h discharge rates and a high current discharge rate, there were improvements of 24%, 23% and 18% in the negative active material utilization efficiencies with

the lead-foam VRLAB compared with the cast grid one and the mass specific capacities of the lead-foam negative electrode were 36%, 41% and 31% higher than those of the cast grid one. The electrode of the lead foam can reduce the density of the current passing through the contact surface, the polarization resistance, and the ohmic resistance of the electrode because the lead foam has a bigger contact area with the active material. As a result, the corresponding battery has higher discharge voltages. Therefore, the lead foam can obviously improve the discharge performance of batteries.

### 3.4. Effect of lead foam on charge and discharge state of NAM

Fig. 3 shows the SEM images of the lead-foam grid and the cast grid negative electrodes at states of charge after several charge–discharge cycles. The results show that the spongy Pb crystals of the cast grid negative electrode agglomerated to form non-uniform granules, while the spongy Pb crystals of lead-foam negative electrode were smaller and uniform, thus the latter had a higher specific surface area. The performance of a lead-acid battery is controlled by the negative electrode at high current discharge rates and the decrease in the negative electrode performance results from the passivation of the negative electrode, which bears a relationship with the current density and the temperature of discharge. The higher the current density of discharge and the lower the discharge temperature, the more the negative electrode will be inclined to be passivated. Both the current collector of the lead foam and lead-foam grid negative electrode have high specific surface area values, which results in a decrease in the current density of reaction, and thus the passivation of the negative electrode is prevented. As a result, the high rate discharge performance of battery is improved, and the corresponding experimental battery shows a higher NAM utilization efficiency.

Fig. 4 displays the SEM images of the lead-foam negative electrode and the cast grid negative electrode at states of discharge after several charge–discharge cycles.

The results show that the  $\text{PbSO}_4$  crystal grains of the lead-foam negative electrode were small and loose, while the most of those of the cast grid negative electrode were big and compact,

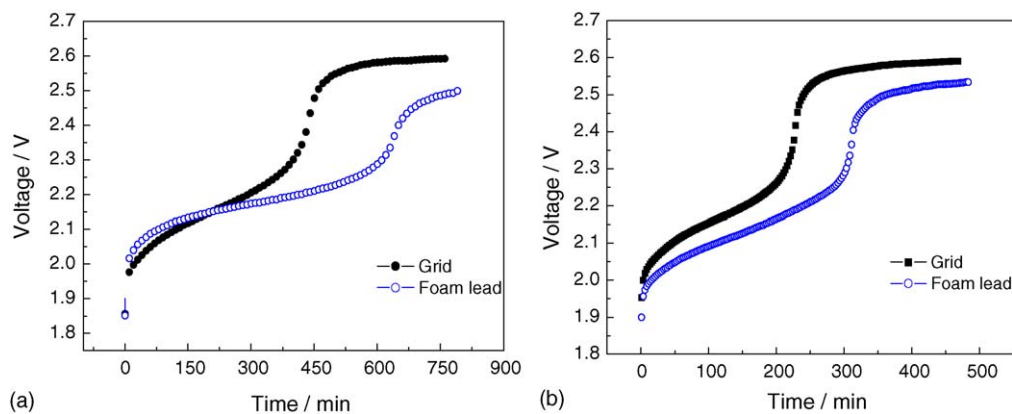


Fig. 1. Charge curves of the two different batteries at: (a) 10 h and (b) 2 h rates.

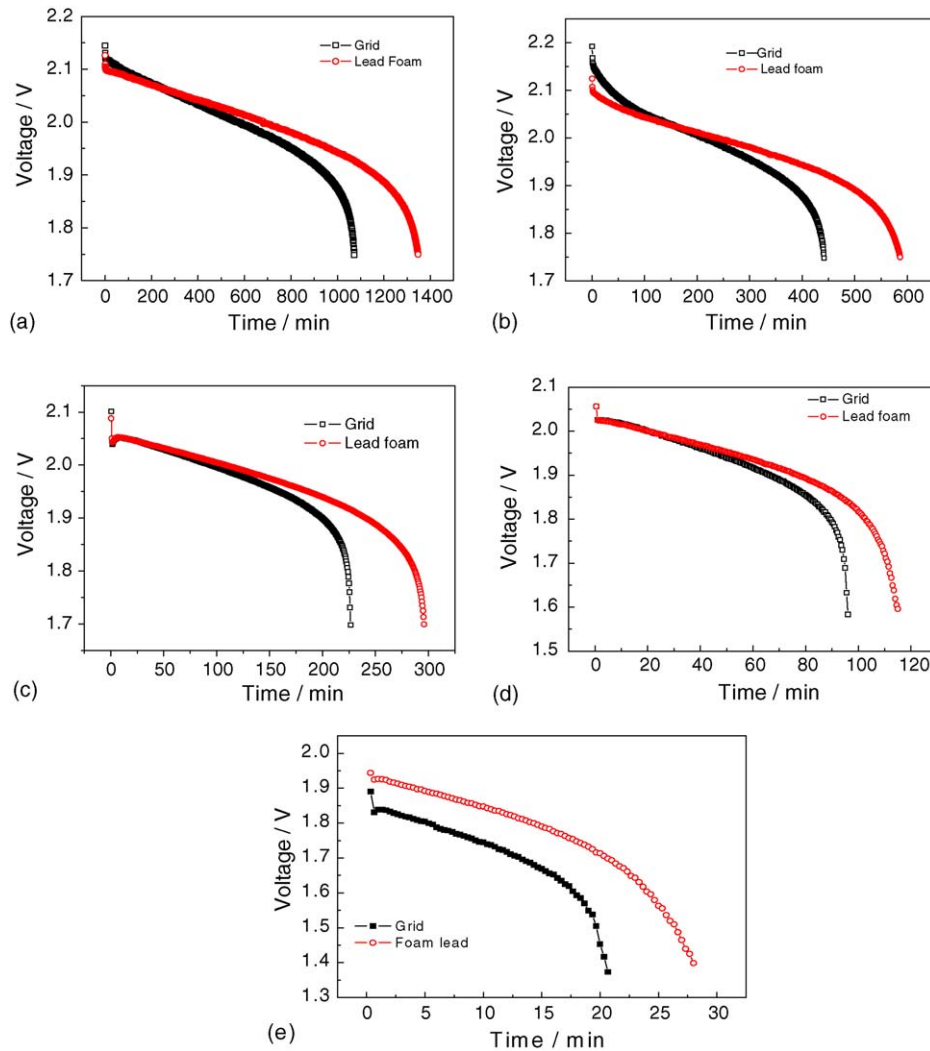


Fig. 2. The discharge curves of the two different batteries at: (a) 20 h, (b) 10 h, (c) 5 h, (d) 2 h rates and (e) high current rate.

and only a few of them were small. The solubility of smaller and looser  $\text{PbSO}_4$  crystals is higher than that of the bigger ones. Therefore, the smaller and looser  $\text{PbSO}_4$  crystals are easier to be reduced, that is, the lead foam is propitious to the charge reaction of a battery.

### 3.5. Effect of different grids on EIS of NAM

In order to study the difference in NAM reactivity between the lead-foam grid negative electrode and the cast grid one, the VRLABs were disassembled after several charge–discharge cycles. The electrochemical behavior of the lead-foam grid negative electrode and the cast grid negative one was researched by means of EIS in a  $4.80 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$  solution. Fig. 5 shows the Nyquist graphs of the two kinds of negative electrodes at states of charge and discharge. Table 2 lists the fitting results of the EIS of experimental data.

From Fig. 5, we can see that the difference between the ohmic resistances of the two negative electrodes was little, while the difference of the electrochemical reaction resistances was quite big at the same state. The electrochemical reaction resistance

of a lead-foam grid negative electrode was as low as one-eighth of that of the cast grid negative electrode. It may be explained by the facts that: (1) the lead foam has a three-dimensional net structure, so it has a bigger contact area with the active material, and the reaction of the negative active material is more uniform around the lead foam; (2) the thickness of the  $\text{PbSO}_4$  film has been reduced; (3) ions' transfer in a film is easier. Accordingly, the electrochemical reaction resistance of the lead foam was obviously reduced.

At a state of charge the shapes of the Nyquist impedance diagrams of both the electrodes are semicircle, indicating that charge transfer is the rate-determining step at a state of charge,

Table 2

Fitting results of  $R_\Omega$  and  $R_{ct}$  of the lead-foam negative electrode and the cast grid negative electrode at different states ( $\Omega \text{ cm}^2$ )

	Charge state		Discharge state	
	Lead foam	Cast grid	Lead foam	Cast grid
$R_\Omega$	1.18	1.14	1.51	1.43
$R_{ct}$	1.79	13.26	2.51	21.18

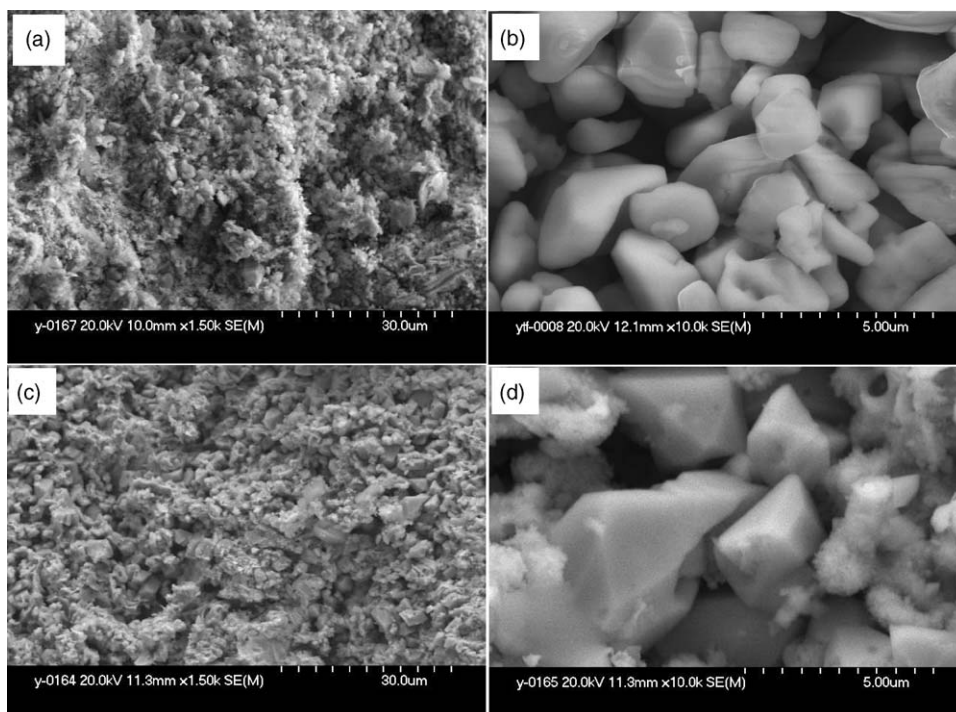


Fig. 3. SEM images of negative active material of the two different electrodes at state of charge: (a and b) lead-foam negative electrode and (c and d) cast grid negative electrode.

while the Nyquist impedance diagram of the cast grid negative electrode at a state of discharge shows the characteristic of diffusion being the rate-determining step. The Nyquist impedance diagram of the lead-foam negative electrode also shows the same

characteristic in a low frequency range [7]. The reason for the above results could be that the  $\text{PbSO}_4$  on the surface of cast grid negative electrode was more compact than that on the lead-foam one.

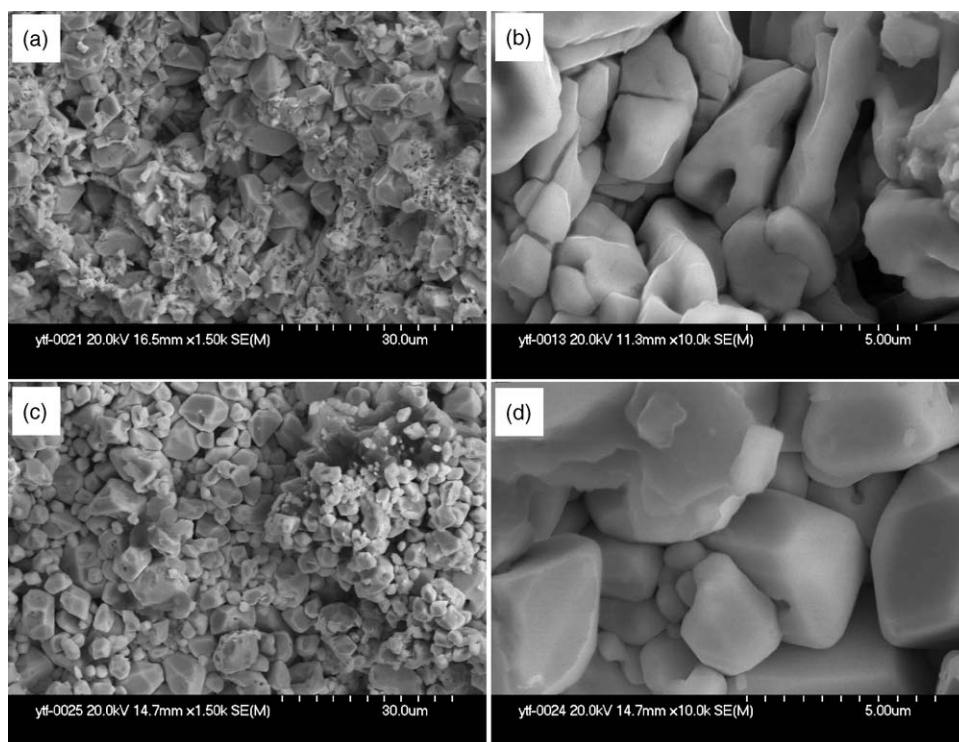


Fig. 4. SEM images of the negative active material of different electrodes at a state of discharge: (a and b) lead-foam negative electrode and (c and d) cast grid negative electrode.

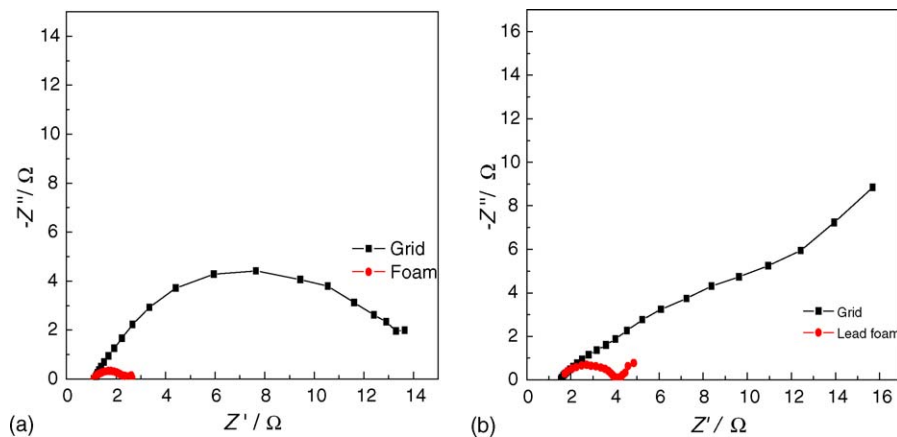


Fig. 5. EIS of different negative electrodes at: (a) charge state and (b) discharge state.

Table 3

Specific surface areas of negative electrodes at different states per square centimeter ( $\text{cm}^2 \text{cm}^{-2}$ )

Charge state	
Lead foam	350.63
Cast grid	302.35
Discharge state	
Lead foam	140.34
Cast grid	45.43

### 3.6. The measurement of specific surface area of negative electrodes

A chronoamperometer in the CHI 630 electrochemistry workplace was applied for measuring the specific surface areas of the different negative electrodes. The specific surface areas of the two different negative electrodes at different states were tested, and the results of data processing are shown in Table 3.

Table 3 shows that the specific surface areas of the lead-foam grid negative electrode were higher than those of the cast grid one at different states. At a charge state and a discharge state, the specific surface areas of the lead-foam grid negative electrode were 16% and 209% higher than those of the cast grid one, respectively.

## 4. Conclusions

The specific surface area of the lead-foam grid measured by chronoamperometry is about  $5700 \text{ m}^2 \text{ m}^{-3}$ , which is about as 17 times as that of the cast grid and the  $\gamma$  value can be decreased. The VRLA battery of the lead foam has a better charge acceptance and better discharge performance. The lead foam has a

bigger specific surface area and a bigger contact surface area with the active material, which results in a lower degree of the electrochemical polarization on the electrode surface, a lower electrochemical reaction resistance compared with that of the cast grid one, and a lower charge–discharge current density passing through the electrode. These characteristics of the lead foam are advantageous to the uniform conversion of the active material and the enhancement of the proceeding degree and the electrode reaction rate. At the same time, the active material utilization efficiency can be improved. The electrochemical reaction resistance of the lead-foam grid negative electrode is about one-eighth of that of the cast grid negative electrode at all the states. The specific surface area of the lead-foam grid negative electrode is 16% higher than that of the cast grid one at a charge state, and the content of the spongy Pb on the lead-foam grid negative electrode surface is higher than that on the cast grid negative electrode surface at a charge state. However, the  $\text{PbSO}_4$  content and the electrochemical reaction resistance of the lead-foam grid negative electrode are less than those of the cast grid one, and the specific surface area of the lead-foam grid negative electrode is 209% higher than that of the cast grid one at a discharge state.

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