



## Novel polymer-graphite composite grid as a negative current collector for lead-acid batteries



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### HIGHLIGHTS

- A novel conductive polymer graphite grid was demonstrated for lead-acid battery.
- A PbSO<sub>4</sub>-deposition surface treatment method for the novel grid was demonstrated.
- The specific capacity of 170 mAh g<sup>-1</sup> was achieved for NAM at 0.1 C-rate.
- The weight of the negative grid can be reduced more than 50% by using the new grid.

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### ABSTRACT

We design a novel polymer-graphite composite grid as the negative current collector for lead-acid batteries. With this novel grid, the negative active material (NAM) can deliver a specific capacity of 170 mAh g<sup>-1</sup> at a discharge rate of 0.1 C. After that, we conduct structural optimization and surface treatment on the grid to improve its performance. Through the structural optimization, additional lead pastes can be loaded and the cycle stability of the battery is enhanced. By using the optimized grid, the weight of the negative current collector can be remarkably reduced by more than 50%. To handle the serious hydrogen evolution on the graphite surface and the unfavorable adhesion between graphite and NAM, fine PbSO<sub>4</sub> particles are coated onto the surface of the graphite grids by chemical deposition. The cells employing the PbSO<sub>4</sub>-deposition grids exhibit excellent cycling stability as well as low polarization and then high Coulombic efficiency. We present here a possible mechanism that how PbSO<sub>4</sub> deposits effectively enhance the performance of negative plates based on the testing results.

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### 1. Introduction

Lead-acid batteries have occupied a large market share of the rechargeable batteries due to their low cost, simple design and the advantages of high reliability, high safety, and high recyclability, etc. [1–5]. Currently, with the rapid developments of renewable energy system (such as wind and solar energy) and electric vehicle industry, the energy storage demands for these fields increase continuously, and higher performance of batteries is required [5–8]. To address these challenges, lead-acid batteries also need to improve their performance to maintain the market competitiveness [6–8]. An effective approach to enhance the specific energy of

lead-acid batteries is to replace the traditional lead alloy with a lightweight material to produce a current collector (grid) [9–12]. Among the lightweight materials, carbonaceous materials have particularly attracted the attention of scientific community because of their low density, high conductivity and favorable corrosion resistance. Various carbonaceous grids, such as reticulated vitreous carbon (RVC) [12–17], carbon foam [18–21] and graphite foam [22], have been proposed so far. With the use of these grids in lead-acid batteries, the weight of the current collectors can be reduced, and then the specific energy of the batteries is improved [12,19]. The charge acceptance of the active mass is also enhanced due to the larger contact area between the carbonaceous grids and the active mass, then realizing the high utilization of the active mass [12,19]. However, these grids still have some shortcomings such as high processing cost and unfavorable physical properties, which limit

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their commercial application.

Conductive polymer-graphite composite, which was produced by pressing and sintering a mixture of graphite and conductive polymer adhesive [23,24], is worth being focused on due to its simple synthesis procedure, low cost and favorable physical properties. Its surface electronic conductivity is  $1250 \text{ S cm}^{-1}$ , far higher than that of RVC ( $1.3 \text{ S cm}^{-1}$ ); and its compressive strength is 128 MPa, also higher than that of RVC (763 kPa) and graphite foam (2.1–5.1 MPa) [12,22]. The polymer-graphite composite has been used as a bipolar plate in proton exchange membrane fuel cells [25]. Nevertheless, its application as a current collector in lead-acid battery has not been reported. Exploring its application potential in lead-acid batteries is crucial to reduce the cost and weight, and enhance the energy of lead-acid batteries.

Notably, some issues should not be neglected when using the carbonaceous grids as negative current collectors for lead-acid batteries, including poor adhesion of carbonaceous materials to lead particles and serious hydrogen evolution. These issues may have an adverse effect on the cycle stability of the battery [26]. When carbon substrates were coated with lead alloy/lead compounds through physical and/or chemical modification [12,17,19,26], the adhesion of carbonaceous materials to active material can be enhanced, and the serious hydrogen evolution caused by a low hydrogen evolution overpotential of carbonaceous materials can be inhibited [26,27]. As a result, surface treatment is an effective way to improve the performance of carbonaceous grids.

In this study, we designed a novel polymer-graphite composite grid as the negative current collector for lead-acid batteries and developed a structural optimization and  $\text{PbSO}_4$ -deposition method for treating graphite grids to optimize the cycle stability. X-ray diffraction (XRD), scanning electron microscopy (SEM), cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and charge-discharge testing of 2 V single cells were employed to investigate the structure and properties of the grid. We can reduce more than 50% of the weight of negative electrode grid by using the proposed grid. Moreover, it is observed that the  $\text{PbSO}_4$  deposits could inhibit the hydrogen evolution on the polymer-graphite composite grids and enhance the adhesion of grid to negative active material (NAM).

## 2. Experimental

### 2.1. Grid preparation and surface treatment

The polymer-graphite composite grids (denoted as graphite grids) whose shape and size were designed by our group, were prepared by Shanghai Heixia Carbon Products Co., Ltd. with a density of  $1.96 \text{ g cm}^{-3}$ , an average dimensions of  $64 \times 32 \times 1 \text{ mm}$ , a compressive strength of 128 MPa and a surface electronic conductivity of  $1250 \text{ S cm}^{-1}$  (measured by the four-probe method). As shown in Fig. 1, sample CG(I) refers to a simple designed grid with a rectangular cross section (2.00 g per grid), and sample CG(II) corresponds to an optimal designed one with an octagonal cross section (1.60 g per grid). Commercial lead alloy grids (Pb-0.095%Ca-0.2%Sn-0.025%Al, sample PG) were used as reference grids. The related parameters of the grids were listed in Table 1.

The surface of the graphite grids were treated with chemically deposited  $\text{PbSO}_4$  particles to further enhance their performance. As shown in Fig. 2, the graphite grids were first soaked in a  $0.5 \text{ mol L}^{-1}$  lead nitrate solution for approximately 24 h, and then they were removed into a  $5 \text{ mol L}^{-1}$  sulfuric acid solution for the next reaction. After washing with deionized water and drying at  $120 \text{ }^\circ\text{C}$  (1 atm) for 4 h, the  $\text{PbSO}_4$ -deposited graphite grids were obtained.

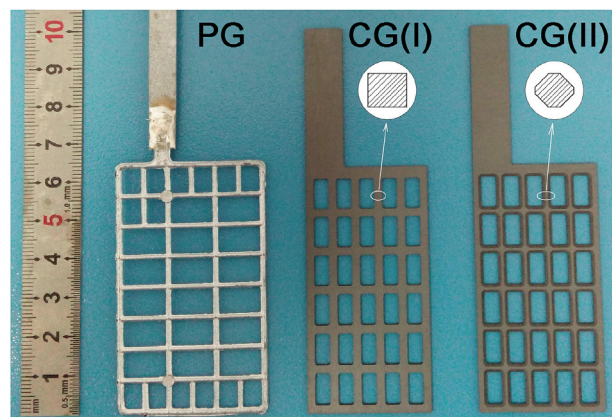


Fig. 1. Photograph of the Pb-Ca alloy grid and graphite grid.

### 2.2. Negative plate manufacture and cell assembly

The graphite grids (before and after surface treatment) and Pb-Ca alloy grids were used to prepare the negative plates through manual pasting. After that, all plates were cured and dried at  $65 \text{ }^\circ\text{C}$  for 24 h. Before cell assembly, the plates were formed in  $0.6 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$  solution. The formation process was composed of a charge at 0.22 C (“C” represents 10-h discharge capacity) for 10 h, a discharge at 0.1 C for 30 min and once more charge at 0.2 C for 10 h [28].

In each 2 V test cell, one negative plate was assembled with two positive plates (Narada, China), and they were separated by absorptive glass-microfibre separator (AGM, Sinoma International) and nipped between perforated glass plates and polytetrafluoroethylene screws with AGM thickness of 1.65 mm (93% porosity). The cells were immersed in  $5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$  aqueous electrolyte for 24 h in vacuum and then sealed in a cell container with a pressure-regulating valve.

### 2.3. Structure characterization and performance testing

The microstructures of the grids and the negative plates were observed using SEM (JSM-6010LA, JEOL Ltd.), and the composition of the formed NAM was investigated by energy spectrum analysis (EDS). The crystallographic structures of the graphite grids before and after surface treatment were determined by a powder XRD system (M21X, MAC Science Ltd.) equipped with Cu  $K\alpha$  radiation ( $\lambda = 0.154 \text{ nm}$ ) in the  $2\theta$  range from  $10^\circ$  to  $90^\circ$ .

CV and EIS of various current collectors, which included the graphite grids (before and after surface treatment) and the Pb-Ca alloy grid, were measured for investigating the hydrogen evolution behavior by using an electrochemical test station (Solartron, 1280Z, UK). The measurements were conducted in a three-electrode system in  $5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$  solution. The grid with an area of  $25 \text{ cm}^2$  was used as the working electrode,  $\text{Hg}/\text{Hg}_2\text{SO}_4$  ( $\text{K}_2\text{SO}_4$  sat.,  $E = 0.64 \text{ V vs. NHE}$ ) electrode and positive plate as the

Table 1  
Negative plate design parameters.

Sample	Grid materials	Mass of negative grid/g	$\alpha$ (ratio of collector to plate weight)	$\gamma$ (ratio of NAM to collector surface area)/ $\text{g cm}^{-2}$
PG	Pb-Ca alloy	8.2	0.37	0.56
CG(I)	Graphite	2	0.22	0.21
CG(II)	Graphite	1.6	0.17	0.31

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