



Original article

Lead oxide/carbon black composites prepared with a new pyrolysis-pickling method and their effects on the high-rate partial-state-of-charge performance of lead-acid batteries

Huan Yang^a, Yubing Qiu^{a,b,*}, Xingpeng Guo^{a,c}^a School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan 430074, PR China^b Key laboratory of Material Chemistry for Energy Conversion and Storage (Huazhong University of Science and Technology), Ministry of Education, PR China^c Hubei Key Laboratory of Materials Chemistry and Service Failure, Wuhan 430074, PR China

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ABSTRACT

A new pyrolysis-pickling method was developed to prepare various lead oxide (PbO)/carbon black (CB) composites as the additives in the negative plates of lead-acid batteries to improve their high-rate partial-state-of-charge (HRPSoC) performance. Compared with CB, the PbO/CB composites prepared by the pyrolysis-pickling method have higher content of alkaline surface functional groups (C_{alkaline}) and less content of carboxyl surface functional groups (C_{COOH}) on CB particles which are still covered with small amount of PbO, meanwhile they have smaller BET surface area, but larger pore volume and average pore width. The hydrogen evolution process in the negative plates containing the PbO/CB composites is inhibited effectively due to the increased C_{alkaline} on CB, while the redox processes ($\text{Pb} \leftrightarrow \text{PbSO}_4$) in these negative plates are accelerated obviously owing to the changes in their microstructure. The PbO/CB composites can impede the growth of PbSO_4 crystals and significantly increase the HRPSoC cycle life of the simulated test cells. In general, the PbO/CB composites with a lower PbO content may be the appropriate additives for the negative plate of lead-acid batteries.

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1. Introduction

Lead-acid battery has been widely used in hybrid-electric vehicles (HEVs) or in stop/start systems, in which they have to be operated continuously in partial-state-of-charge (PSoC) states tending to be of short duration but high rate. Under this condition, lead-acid batteries will fail rather quickly due to the irreversible sulfation of negative plates [1,2].

In order to deal with these problems, two different strategies have been proposed: one combines an asymmetric supercapacitor with a lead-acid battery in a single unit, named UltraBattery [3–6]; another is denoted as lead-carbon battery, which introduces various carbon materials in the negative plates of lead-acid batteries. Carbon materials have good construction of electric network [7,8], higher double layer capacitance [9,10], more electrolyte supplement and reactivity sites [11,12], which can prevent the growth of PbSO_4 crystals [13,14] and improve the

HRPSoC cycle life of lead-acid batteries. So a lot of studies focus on the additives of carbon materials in the negative plates [12–17]. However, under the working conditions of lead-acid batteries, carbon materials can produce serious hydrogen evolution, which will make the electrolyte in the battery dry out [18].

Some research try to overcome this problem by modifying the surface functional groups of activated carbon materials using heat treatment, acid and alkali treatment, liquid/vapor phase oxidation and microwave treatment so as to change their catalytic and adsorbent performance [19–21]. L.Y. Wang et al. [22] reported that alkaline surface functional groups of activated carbon (AC) can inhibit hydrogen evolution process, while acidic surface functional groups can promote it. However, acidic groups of AC are beneficial to the active sites of lead electrodeposition, which may inhibit the hydrogen evolution effect of AC and the irreversible sulfation of lead-carbon batteries. Other research employed the metals or metal oxides with higher hydrogen evolution over-potential (η_{H}) to form composites [23–25] or mixtures [26,27] with carbon materials. It is reported that nano-lead-doped AC composites [23], nano-Pb(PbO)/AC composites [25] and lead-containing active carbon composites [24] can increase the η_{H} of negative plates, while the problems of the bad adhesion and great density

* Corresponding author at: School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan 430074, PR China.
 E-mail addresses: qiyubin@mail.hust.edu.cn, qybstone@msn.cn (Y. Qiu).

difference between carbon and lead particles are solved. Furthermore, Gao et al. [25] pointed out that the active surface of lead oxide (PbO)/AC may react with sulfuric acid and lead oxide powder, which can enhance the binding force between PbO/AC composites and negative electrode active materials (NAM) during HRPSoC cycles. Apparently, Pb oxide/C composites with modified surface functional groups will combine the above effects and may be suitable additives for the negative plates of lead-acid batteries.

In this paper, a new pyrolysis-pickling method was developed to prepare various Pb oxide/carbon black (CB) composites, which were used as additives in the NAM of battery to form negative plates and simulated test cells. The Pb oxide/CB composites were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), energy disperse spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS), thermal gravimetric analysis (TGA) and specific surface area and porosity analyzer. The effects of these additives on the electrochemical performance of the negative plates and the HRPSoC cycle performance of the simulated test cells were studied using polarisation curves, cyclic voltammetry (CV) and galvanostatic charge-discharge methods. The influence of these additives on the microstructure and crystal morphology of the negative plate were also analysed using SEM and specific surface area and pore analyzer. The mechanisms involved were discussed.

2. Experimental

2.1. Preparation of different composites with the pyrolysis-pickling method

Table 1 shows the brief processing steps for different composites. The detailed processing procedures are as follows:

2.1.1. Pretreatment

2.0 g CB (VXC-72R, specific characteristics according manufacturer: particle size 30 nm; BET surface $254 \text{ m}^2 \text{ g}^{-1}$) was dispersed in 100 mL 80% ethyl alcohol by ultrasonication for 10 min, then they were poured into 300 mL 0.1 mol L^{-1} $\text{Pb}(\text{NO}_3)_2$ and further dispersed by electromagnetic stir for 2 h. Subsequently, 25 mL 15 mol L^{-1} ammonia was dropped into the above mixture and was dispersed by ultrasonication for 10 min. At last, the mixture was filtered and dried at 80°C for 12 h. The obtained sample is denoted as Pb-C-alkali.

2.1.2. Pyrolysis

Pb-C-alkali was heated in N_2 atmosphere with a heating rate of $10^\circ\text{C min}^{-1}$ and maintained at 500°C for 2 h, then cooled in N_2 atmosphere. The obtained sample is denoted as Pb-C-N500.

2.1.3. Pickling

1.5 g Pb-C-N500 was dispersed in 300 mL 5 mol L^{-1} HCl by electromagnetic stir for 30 min at 25°C , then the supernatant solution was sucked out with a dropper. The above process was

repeated twice. Subsequently, the sample was filtered out and washed with deionized water until the water pH = 7.0. Finally, the sample was dried at 80°C for 12 h, which is denoted as Pb-C-N500- 25°C . The pickling temperature was changed to 50°C and other conditions were maintained as above to prepare the sample that is denoted as Pb-C-N500- 50°C .

Because both the surface functional groups of CB and Pb oxides may influence the hydrogen evolution performance of the negative plates, their effects need to be differentiated. For this purpose, CB was treated with the pyrolysis-pickling method at 50°C without adding $\text{Pb}(\text{NO}_3)_2$ in the pretreatment procedure. The obtained sample is denoted as C-N500- 50°C .

2.2. Preparation of negative plates

The negative plates were prepared using lead oxide power (oxidation degree = 76%), acetylene black (0.2 wt.%, **versus the lead oxide, the same as below**), short fibers (0.05 wt.%), barium sulfate (0.4 wt.%), humic acids (0.7 wt.%), H_2SO_4 ($12.5 \text{ wt.}\%$, 1.25 g cm^{-3}), H_2O ($12.5\text{--}15 \text{ wt.}\%$) and CB or different Pb oxide/CB composites (1.0 wt.%). In this paper, the negative plate without CB or different Pb oxide/CB composites is considered as the blank (NAM) plate, while CB or different Pb oxide/CB composites are considered as additives in the NAM. The negative pastes were prepared according to the procedures described in detail in our previous paper [28]. Then, the prepared paste (1.0 g) was coated on a Pb-Sn-Ca grid with a geometric area of $1.0 \times 1.5 \text{ cm}^2$ to prepare the negative plates. All as-prepared negative plates were cured under carefully controlled conditions, and then these cured negative plates were formed in H_2SO_4 solution (1.05 g cm^{-3}) with the current of 8.5 mA g^{-1} and 17 mA g^{-1} under a commercial formation procedure. After formation, the negative plates were washed with deionized water to remove the formation acid, and then they were used for electrochemical tests or cycle life tests.

2.3. Electrochemical measurements

All electrochemical experiments in this work were performed using a CS350 electrochemical workstation (Wuhan Corrtest, China) with a conventional three-electrode system in a single compartment cell at room temperature ($\sim 25^\circ\text{C}$). The prepared negative plate with a geometric area of $1.0 \times 1.5 \text{ cm}^2$ was used as the working electrode. Two platinum electrodes with relatively large area were used as the counter electrodes and a Hg/Hg₂SO₄ electrode as the reference electrode. The electrolyte was H_2SO_4 with a density of 1.28 g cm^{-3} . The cathodic polarization curves were measured at a scan rate of 1 mV s^{-1} , starting from the open circuit potential (E_{ocp}) to -1.5 V vs. Hg/Hg₂SO₄. CV measurements were performed in the potential range from -1.5 V to 0.4 V vs. Hg/Hg₂SO₄ at a scan rate of 10 mV s^{-1} , starting from 0.4 V vs. Hg/Hg₂SO₄, and 5 cycles were recorded. All the above electrochemical tests were repeated at least three times to ensure the reliability of the results.

Table 1
Brief processing steps for different composites.

CB	Pb(NO ₃) ₂ stirring	NH ₃ .H ₂ O ultrasonication	N ₂ -500°C pyrolysis	25°C –pickling	50°C –pickling	Composites
✓	×	×	×	×	×	CB
✓	✓	✓	×	×	×	Pb-C-alkali
✓	✓	✓	✓	×	×	Pb-C-N500
✓	✓	✓	✓	✓	×	Pb-C-N500-25°C
✓	✓	✓	✓	×	✓	Pb-C-N500-50°C
✓	×	✓	✓	×	✓	C-N500-50°C

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