



Characterization of nano-lead-doped active carbon and its application in lead-acid battery



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HIGHLIGHTS

- We researched the bad influences of AC used in lead-acid battery.
- Nano-Pb/AC inhibited HER through increasing the adsorption impedance of hydrogen.
- Nano-Pb/AC could overcome the negative effects of AC in lead-acid battery.
- Nano-Pb/AC in negative plate can improve the performances of lead-acid battery.

ARTICLE INFO

Article history:

Received 9 April 2014

Received in revised form

16 June 2014

Accepted 22 July 2014

Available online 31 July 2014

Keywords:

UltraBattery
Lead–carbon battery
Lead-acid battery
Doped active carbon
Hydrogen evolution

ABSTRACT

In this paper, nano-lead-doped active carbon (nano-Pb/AC) composite with low hydrogen evolution current for lead-acid battery was prepared by ultrasonic-absorption and chemical-precipitate method. The nano-Pb/AC composite was characterized by SEM, EDS and TEM. The electrochemical characterizations are performed by linear sweep voltammetry (LSV), electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) in a three-electrode system. Since intermediate adsorption is the rate-determining step, the hydrogen evolution reaction (HER) is markedly inhibited as the intermediate adsorption impedance of nano-Pb/AC increased. Meanwhile, the working potential of nano-Pb/AC is widened to the whole potential region of Pb negative plate (from -1.36 V to -0.86 V vs. Hg/HgSO_4) in lead-acid battery. In addition, nano-Pb can improve the interfacial compatibility between AC and Pb paste, accordingly relieve the symptoms of carbon floatation. Finally, 2.0 V single-cell flooded lead-acid batteries with 1.0 wt.% nano-Pb/AC or 1.0 wt.% AC addition in negative active materials are assembled. The cell performances test results show that the 3 h rate capacity, quick charging performance, high current discharging performance and cycling performance of nano-Pb/AC modified battery are all improved compared with regular lead-acid battery and AC modified lead-acid battery.

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1. Introduction

Batteries working under hybrid electric vehicle (HEV) service are exposed to a duty cycle, which is quite different from any other function that lead-acid batteries have been required to perform. The batteries operate at partial-state-of-charge (PSoC) rather than a fully charged condition, and charges and discharges tend to be of short duration but high rate. Under this condition, lead-acid batteries that have been designed for conventional tasks (e.g., SLI or deep cycle), fail rather quickly due to irreversible sulfation of negative plates [1].

For solving the above-mentioned problems, two different strategies were proposed. The one named lead–carbon battery (Pb–C

battery), which usually added some carbon materials into the negative paste. The other, combined an asymmetric supercapacitor and a lead-acid battery in a single unit, named UltraBattery. Nakamura [2] investigated the influence of small additions of certain (not specified) sorts of carbon into the negative paste for the first time and found a favourable effect on the hindrance of sulfation. The beneficial effect of carbon was attributed to the formation of conducting bridges through carbon particles surrounding the sulfate crystals. This idea was further elaborated by A.F. Hollenkamp and sponsored by ALABC [3]. It was found that the addition of up to 2% of carbon black or graphite powder into the negative paste could hinder the sulfation of negative electrodes. They observed that the addition of graphite to the negative active materials (NAMs) in the unformed state improved the conductivity of the plate. However, M. Calábek [4] opined that the improvement of the cycle life of negative plate was attributed to the inhibition of the

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growth of lead sulfate crystals deposited in the electrode pores, but not the improving of conductivity. Afterwards, D. Pavlov [5] discovered that the addition of electrochemical active carbon could decrease the overpotential of reaction $\text{Pb}^{2+} + 2\text{e}^- \rightarrow \text{Pb}$, which will improve the charge acceptance and discharging capacity of the negative electrode. Common-wealth Scientific and Industrial Research Organization (CSIRO) and Furukawa Battery developed the UltraBattery [6–8], which was reported to have the advantage of being long lasting, cost effective and more powerful than past technologies used in HEVs. The supercapacitor, acting as a buffer during high-rate discharge and charge, enhances the power and lifespan of lead-acid battery. Thus, the UltraBattery in HEVs is able to deliver and absorb charge rapidly during vehicle acceleration and regenerative braking, respectively. This technology has been described in literature in detail [8–10].

However, we must pay more attention to the harmful influences of carbon materials on lead-acid batteries. First, under the negative plate working conditions of lead-acid battery (−0.86 to −1.36 V vs. Hg/HgSO₄, 5 mol L^{−1} sulfuric acid), carbon materials will perform low capacity and serious hydrogen evolution [11] whether as negative additive or a single asymmetric supercapacitor. As a result, more gas will be given off towards the end of charging and cause the thermal runaway or even electrolyte dry-out [12,13]. Second, the addition of carbon will reduce the charge retention ability as a galvanic cell may form by Pb and C which have been testified in this paper. Moreover, bad miscibility, great differences in specific surface and gravity between C and Pb make them difficult to mix evenly. This may cause the carbon floatation and carbon penetration phenomenon, which would limit the beneficial effects of C. But up to now, few researches have been reported on these aspects.

In this paper, we prepared a nano-Pb/AC composite with low hydrogen evolution and good miscibility. Furthermore, hydrogen inhibition mechanism was evaluated by EIS. The electrochemical behavior of AC and nano-Pb/AC negative electrodes working in lead-acid battery was studied. Then, some single-cell flooded lead-acid batteries with AC or nano-Pb/AC additions were assembled. The performances including initial capacity, quick charging ability, high current discharging ability, hydrogen evolution rate and cycle life were tested in the ensuing experiments.

2. Experimental

2.1. Preparation of nano-Pb/AC composite

Nano-Pb/AC composite was prepared by the ultrasonic-absorption and chemical-precipitation method with three steps.

Pretreatment: 2g AC raw material (YP-50, produced by Japan Kuraray) was immersed in 100 mL 80% ethyl alcohol for 2 min.

Ultrasonic-absorption: 300 mL 0.1 mol L^{−1} Pb(NO₃)₂ solution was poured into the wetted raw material under ultrasonic oscillation for 10 min. Then the sample was filtered out and washed with deionized water.

Chemical-precipitation: The sample was dipped into 300 mL 0.1 mol L^{−1} H₂SO₄ solution under ultrasonic oscillation for 10 min, and then PbSO₄ was generated and precipitated in the pores. Followed by filtering and washing with deionized water to pH = 7.0, drying at 60 °C for 10 h, the nano-Pb/AC composite was obtained.

2.2. Preparation of testing samples

For electrochemical testing, AC paste (contents: 80 wt.% AC, 10 wt.% PVDF, 10 wt.% acetylene black) was evenly painted on Ti foil and then dried at 60 °C for 8 h. The working area was 1.0 cm × 1.0 cm.

For battery testing, a serial of 2.0 V single-cell flooded lead-acid batteries with one negative plate sandwiched between two PbO₂ positive plates were assembled. There were three kinds of negative plates, the common Pb paste negative plate for regular lead-acid battery (LB), the 1.0 wt.% (relative to the Pb active materials) blank AC addition in negative plate for AC modified lead-acid battery (ACLB) and the 1.0 wt.% nano-Pb/AC composite addition in negative plate for nano-Pb/AC modified lead-acid battery (nano-Pb/ACLB). All positive and negative plates had a size of 4.0 cm × 6.8 cm (height × width) and geometric area of 27.2 cm². The thickness was 0.30 cm for the positive plates and 0.20 cm for the negative plates. The positive plates and common negative plates were all produced by Henan Yuguang Gold & Lead Co., Ltd.

2.3. Instruments

The electrochemical experiments were carried out in a three-electrode system. The counter electrode was Pt plate with a geometric area of 16.00 cm². The mercury/mercurous sulphate reference electrode (Hg/HgSO₄) was used as the reference electrode. All potentials in this paper were reported with respect to this reference electrode unless specified. The electrolyte was 5 mol L^{−1} sulfuric acid solution.

Electrochemical experiments such as cyclic voltammetry (CV), linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS) were performed using a PARSTAT 2273 electrochemical workstation controlled by the Powersuit software. The frequency interval of EIS measurement was from 10⁵ to 10^{−2} Hz, and the AC amplitude was 10 mV. Battery testing was performed using LAND battery test system. JEM-2010 Transmission Electron Microscope (TEM), JSM-6360F Scanning Electron Microscope (SEM) and Energy Dispersive Spectrometer (EDS) was used to observe the microscopic surface morphology and determine elementary composition of as-prepared nano-Pb/AC composite. Porous structure of the sample was tested by nitrogen adsorption/desorption isotherms at −196 °C with the Monosorb produced by Quantachrome Instruments Company. Content of Pb in nano-Pb/AC was analyzed with Inductively Coupled Plasma Atomic Emission Spectrometry (IRIS1000ICP) produced by Thermo Fisher Scientific.

3. Results and discussion

3.1. Properties of nano-Pb/AC composites

3.1.1. Characterization

Fig. 1 provides the morphology of AC and nano-Pb/AC characterized by SEM, EDS and TEM. It can be seen that both samples mainly consist of large AC lumps (2–10 μm) and plentiful small AC particles (less than 2 μm). This proves that no serious structural damage of AC occurred in this modification process. But, a small amount of tiny white particles can be observed in nano-Pb/AC composite (Fig. 1b). EDS testified that the white particles were Pb containing materials (Fig. 1d). As shown in Fig. 1c, the nano-Pb compound particles are found abundantly in AC particles with the size of 5–10 nm. The average content of Pb is about 3.32 wt.% measured by ICP.

The nitrogen adsorption/desorption isotherms of AC and nano-Pb/AC are shown in Fig. 2a. The isotherms are supposed to be type IV, which occurs on adsorbents possessing a mixture of microporosity and mesoporosity. The slope at the end of the isotherm was due to a limited uptake of nitrogen at higher relative pressures, indicating capillary condensation took place in mesopores [14]. The BET surface area of AC is 1528 m² g^{−1} and that of nano-Pb/AC is 1192 m² g^{−1}. Pore-size distributions gauged by HK mode (for micropores) and BJH mode (for mesopores) are shown in

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