Electrochimica Acta xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Tracking the morphology evolution of nano-lead electrodeposits on the internal surface of porous carbon and its influence on lead-carbon batteries

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ARTICLE INFO

Article history:
Received 21 September 2016
Received in revised form 24 October 2016
Accepted 28 October 2016
Available online xxx

Keywords:
Porous carbon
Nano-lead electrodeposit
Internal surface
Ultrathin sectioning
Lead-carbon batteries

ABSTRACT

For studying the mechanism related to the microscopic internal structure of porous carbon additives in lead-carbon batteries, we conducted the electrochemical experiments with a three-electrode system on a lead-doped mesopore-dominated porous carbon (Pb@MC) composite in a Pb^{2+} containing H_2SO_4 electrolyte. Through the electrochemical measures, lead particles on the external surface of carbon could be not only electrodeposited into the nano-sized pores of carbon, but also attached on the pore wall with atomic state, which was observed for the first time by using High Resolution Transmission Electron Microscopy (HRTEM) and Aberration Corrected Scanning Transmission Electron Microscopy (ABF-STEM) with the help of ultrathin sectioning. The nano-lead electrodeposits on the internal surface of carbon didn't grow up because they were confined by the nano-sized pores of carbon. These nano-lead deposits could not only effectively inhibit the hydrogen evolution, but also contribute the pseudocapacitance and enhance the reversible reaction of $Pb/PbSO_4$, and thus result in the longer cycle performance of lead-carbon batteries.

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1. Introduction

The energy storage batteries are essential to steady output power, high power supply stability and reliability for solar, wind energy and other renewable green energy supply. The storage and application of renewable green energy require the energy storage batteries with high power output and good charge acceptance ability under High-rate Partial-state-of-charge (HRPSoC) conditions [1–4]. Lead-carbon batteries that add porous carbon materials into the negative plates of lead-acid batteries have long cycle life under HRPSoC conditions [5–7]. Elucidating the mechanisms of carbon additives is crucial to improve the application of lead-carbon batteries in energy storage field [8–11]. Researchers have studied the mechanisms of carbon additives in the lead-carbon batteries with aspects of conductive network [12,13], capacitance buffer [14,15], improving pore structure [11,16] and electrochemical kinetics [17,18]. These aspects were mainly related to the macroscopic properties of carbon materials, not to the microscopic internal structure. Recently there have been some studies reporting the lead deposition on the surface of carbon additives in the negative plates of lead-carbon batteries. B. Hong et al. [19] prepared nano-Pb/active carbon composites as the negative additives, and get a conclusion that the nano-Pb adsorbed on the surface of the carbon pores could increase the adsorption impedance of hydrogen, leading to the inhibition of hydrogen evolution. W. Zhang et al. [20] claimed that the Pb electrodeposits on the surface of activated carbon could provide more directions for current distribution, and reduce the charge-transfer resistance of the $Pb/PbSO_4$ redox couple, thus to enhance the charge acceptance of lead-carbon electrodes. In our past work [21], activated carbon materials with abundant acidic surface functional groups, which could act as the active sites of lead electrodeposition, were apt to be electrodeposited by Pb. The above studies confirmed the Pb electrodeposition on the external surface of porous carbon, and predicted the Pb electrodeposition on the internal surface, but without strong evidence. And the mechanism

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http://dx.doi.org/10.1016/j.electacta.2016.10.189
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Please cite this article in press as: L. Wang, et al., Tracking the morphology evolution of nano-lead electrodeposits on the internal surface of porous carbon and its influence on lead-carbon batteries, Electrochim. Acta (2016), http://dx.doi.org/10.1016/j.electacta.2016.10.189

related to the microscopic internal structure of porous carbon materials has been unclear.

It is well known that almost all of the high specific surface area of porous carbon mainly comes from internal surface [22,23]. If Pb could be electrodeposited on the internal surface of porous carbon, the surface area and the reactivity of Pb active materials would be effectively increased. For clarifying the mechanisms and improving the design, fabrication, and application of porous carbon materials in lead-carbon batteries, it is significant to characterize the nano-Pb electrodepositing on the internal surface of porous carbon. However, it is difficult to observe the morphology of nano-Pb electrodeposits on the internal surface of micropore-dominated porous carbon because of its super small (< 2 nm) pores and amorphous graphic structure. To solve this problem, we use a mesopore-dominated porous carbon (MC) to be the Pb electrodeposition substrate, which was cut into small flakes through ultrathin sectioning to be easily observed by TEM electron beam. To simulate the electrochemical process of carbon additives in the negative plates better, Pb@MC composite was prepared through vacuum impregnation followed by chemical-precipitation method, and then to be treated by potentiostatic method through a three-electrode system. We characterized the morphology evolution of nano-Pb electrodeposits on the external and internal surface of carbon, and clarified their contribution on inhibition of hydrogen evolution, pseudocapacitance enhancement, and improving the high-rate charge-discharge performance.

2. Experimental

2.1. Preparation of Pb@MC composite and nano-lead electrodeposition

Fig. 1(a) shows the preparation process of Pb@MC composite through vacuum impregnation followed by chemical-precipitation method. Firstly, phenolic resin as a carbon precursor was used to prepare MC materials with $CaCO_3$ nanoparticles (~50 nm) as a template [24]. And then 1 g MC was immersed in 150 mL 0.1 mol L^{-1} $Pb(NO_3)_2$, which was added dropwise under the vacuum. After filtering, the sample was vacuum impregnated into 150 mL 0.1 mol L^{-1} H_2SO_4 dropwise. Meanwhile, $PbSO_4$ was precipitated on the surface of MC. After being washed with deionized water to neutral and dried at 120 °C for 4 h, the Pb@MC composite was obtained.

In order to simulate the constant current-constant voltage charging mode of lead-carbon batteries, Pb@MC composites were used for the lead electrodeposition by charging to −1.135 V (vs Hg/Hg_2SO_4) at 200 mA g^{-1} and then potentiostatic charging for 5 h with a three-electrode system, which made the Pb^{2+} of $PbSO_4$ particles gain electrons to be reduced to Pb particles in Fig. 1(a).

2.2. Electrochemical experiments

All the electrochemical experiments were tested under a three-electrode system (Electrochemical Testing Station, Solartron 1280Z) at room temperature. The electrolyte was 5 mol L^{-1} H_2SO_4 aqueous solution with some lead powders. The three-electrode device consisted of a platinum plate counter electrode, a Hg/Hg_2SO_4 reference electrode (Sat. K_2SO_4), and carbon film with 120 ± 10 μm thickness used as the working electrode. The electrode potential of Hg/Hg_2SO_4 electrode (Sat. K_2SO_4) is about 0.4056 V higher than that of Saturated Calomel Electrode (SCE) at room temperature. The preparation of carbon film and the design of the working electrode were shown in supplementary materials. Both of the preparation of working electrode and the following electrochemical experiments could be duplicately carried out.

The high-rate charge-discharge performance of MC and Pb@MC films were tested with the three-electrode system by simulating HRPSoC conditions of lead-acid batteries according to the following procedures: charge at 1000 mA g^{-1} for 45 s (upper voltage limit of −1.2 V, vs Hg/Hg_2SO_4), rest for 5 s; discharge at 1000 mA g^{-1} for 30 s, rest for 5 s. The cell voltage (vs Hg/Hg_2SO_4) was measured at the end of the discharge pulses. To further clarify how the lead electrodeposition on the external and internal surface of carbon affect the hydrogen evolution and the pseudocapacitance, the hydrogen evolution behavior and the capacitive property of films after 100, 300 and 600 cycle times would be tested. All the different cycles' testing were stopped in the recharging state. The hydrogen evolution behavior of all films before and after different electrochemical experiments were obtained by cyclic voltammetry (CV) procedures with the voltage ranged from −0.7 to −1.5 V (vs Hg/Hg_2SO_4) at 1 mV s^{-1} in 5 mol L^{-1} H_2SO_4. The capacitive property of all films with the thickness of 280 ± 10 μm were compared by CV curves from 0 to −1.2 V (vs Hg/Hg_2SO_4) at 0.7 mV s^{-1} in 5 mol L^{-1} H_2SO_4.

2.3. Characterization of nano-lead on the surface of MC

The Pb@MC films before and after different electrochemical experiments were cut into some flakes about 70 nm in thickness by ultrathin sectioning in Fig. 1(b). The morphology evolution of nano-lead on the internal surface of MC was observed by HRTEM (Tecnai F20), and the lead on the external surface was characterized using a Field Emission Scanning electron microscopy (FESEM,

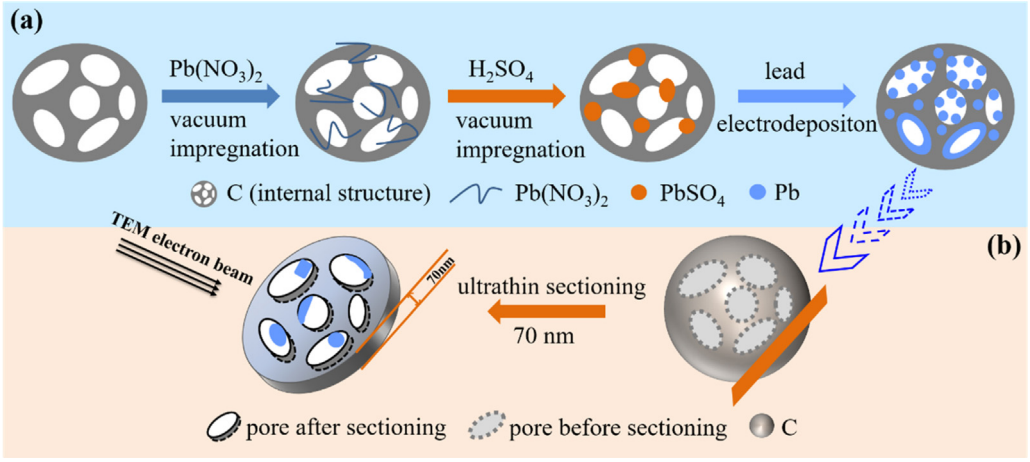

Fig. 1. (a) Preparation of Pb@MC composite and nano-lead electrodeposition; (b) diagrammatic sketch of ultrathin sectioning of MC.

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