



Effect of activated carbon surface functional groups on nano-lead electrodeposition and hydrogen evolution and its applications in lead-carbon batteries



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ABSTRACT

The effect of activated carbon (AC) surface functional groups on the cycle performance of lead-carbon batteries was studied from hydrogen evolution and nano-lead electrodeposition on the surface of the AC. AC materials were modified by oxidation methods (hot air or acid treatment) to increase acidic groups and reduction processes (alkaline treatment or heat treatment in N₂) to increase alkaline groups. The surface functional groups were characterized by X-ray photoelectron spectroscopy and Boehm titration method. We used cyclic voltammetry and a three-electrode system to prepare nano-lead deposits on the surface of the AC, and studied its influence on hydrogen evolution of AC. The results show that acidic groups are beneficial to lead electrodeposition. In addition, the lead deposits with high activity covering the surface of AC could inhibit hydrogen evolution and the irreversible sulfation in lead-carbon batteries, and then result in longer cycle life under High-rate Partial-state-of-Charge conditions.

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1. Introduction

Countries all over the world are competing to develop solar, wind energy and other renewable green energy because of the increasing consumption of natural fossil energy sources and the environmental pollution caused by the release of harmful gases from the burning of fuel. However, the new energy supply has the problems with the power fluctuation, the poor power supply stability and reliability, which needs the energy storage batteries to stabilize the access and the output. The storage and application of the new energy requires that the batteries have a high power output and good charge acceptance ability under High-rate Partial-state-of-Charge (HRPSoC) conditions [1,2].

Lead-carbon batteries is a new type of lead-acid batteries with carbon materials as negative additives, which have excellent deep discharge capacity and long cycle life under HRPSoC conditions [3–6]. Much research focus on the mechanisms of carbon materials in the lead-carbon batteries, mainly including the construction of electric network [7,8], electric double layer capacitor [9,10],

preventing the growth of PbSO₄ crystals [11–13], electrolyte supplement and increasing reactivity sites [14,15] to improve HRPSoC cycle life of the batteries. However not all carbon materials could improve the performance. The physicochemical parameters of carbon materials involved in each reaction step of the battery should be further studied in quantitative or semi quantitative level. In addition, the hydrogen evolution overpotential of carbon materials is low, which would make the batteries hydrolyzed easily in operation, thus resulting in dehydration to make the batteries failure [16,17]. The surface functional groups have obvious influence on the behavior of hydrogen evolution of AC materials [18–20]. Therefore, it is necessary to study the effect of the surface functional groups on hydrogen evolution of activated carbons, and its energy storage mechanism in lead-acid batteries.

The surface functional groups of AC materials mainly include the oxygen-containing and nitrogen-containing functional groups. Oxygen-containing functional groups are divided into acidic functional groups, such as carboxylic, lactonic and phenolic groups; neutral functional groups, such as benzoquinonyl and other groups; alkaline groups, such as quinonoid carbonyl, pyrone and benzopyranyl groups [21,22]. Researchers modify the AC surface chemical properties through heat treatment, acid and alkali treatment, liquid/vapor phase oxidation and microwave treatment to affect their catalyst and adsorbent performance

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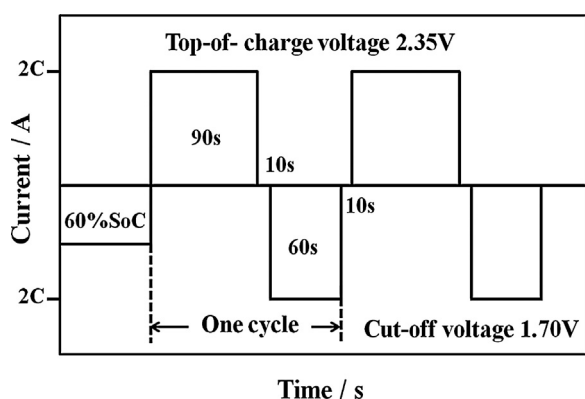


Fig. 1. Diagrammatic sketch of HRPSoC cycling condition.

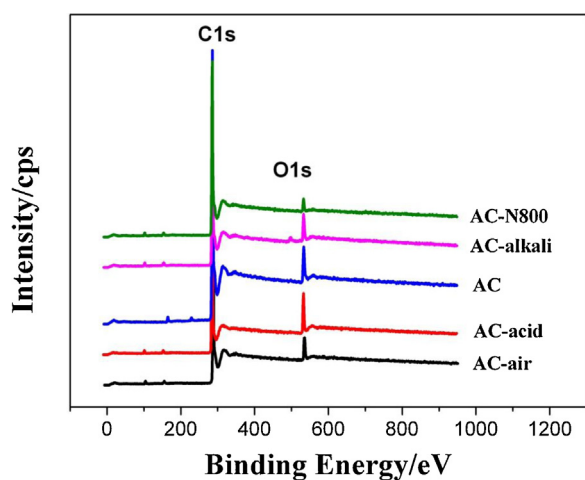


Fig. 2. XPS spectra of AC samples.

[23–25]. C.A. Toles et al. [26] increased acidic surface functional groups by phosphoric acid activation in air atmosphere, which could accelerate the charge transferring on the surface of carbon and reduce the absorption of Cu^{2+} . L. Geng et al. [27] adjusted oxygen-containing functional groups of graphene oxide through 100–200 °C heat treatments. The results showed that the lower processing temperature produced more carboxyl groups that could improve the catalytic activity of graphene oxide to the oxidation of benzyl alcohol, thus increasing the conversion rate of benzene methanol in the air. R. Zhong et al. [28] prepared carbon nanofibers with carboxyl, carbonyl, phenolic and nitrogen-containing functional groups by acid oxidation, air oxidation, and reaction with LiAlH_4 or melamine, respectively. Studies have indicated that the incorporation of N atoms changed the electronic structure of the adjacent C atoms, which could increase the positive charge region to attract more oxygen atoms to form OH^- , thus improving the catalytic activity of CNF electrode.

For lead-carbon batteries, the chemical environment and modified demand of activated carbon as negative additives are different from the above-mentioned carbon material. The lower limit of working voltage of the negative plates is under the hydrogen evolution potential, so it is needed to promote lead electrodeposition to inhibit hydrogen evolution. However, the effect of activated carbon with modification on lead electrodeposition and its applications in the lead-carbon batteries was rarely studied. In addition, the components of lead electrode are very complex, so it is necessary to take out AC to simulate the electrochemical processes of AC in lead-carbon electrode. In this paper, we modified the AC materials by oxidation and reduction methods to change surface functional groups. The nano-lead deposits on the surface of the AC were prepared by cyclic voltammetry (CV) with a three-electrode system. The effect of AC surface functional groups on nano-lead electrodeposition and hydrogen evolution were studied. Its applications in lead-carbon batteries were obtained by testing the cycle performance of 2 V simulated lead-acid batteries under HRPSoC conditions.

2. Experimental

2.1. Surface modifications of activated carbon

The activated carbon as starting material has been submitted to different surface modifications including oxidation and reduction process. The oxidized samples were achieved by two methods as follows, 4 g AC immersed in HNO_3 solution (5 mol L^{-1} , 50 mL) for 4 h as AC-acid, and treated at 300 °C for 1 h in air atmosphere as AC-air.

The reductive AC were prepared by thermal treatment in N_2 atmosphere from 25 to 800 °C under a rate of 6°C min^{-1} , then maintained at 800 °C for 2 h. This sample was denoted as AC-N800. The 4 g AC were immersed in NaOH solution (5 mol L^{-1} , 50 mL) for 4 h as AC-alkali. All of the above mentioned samples were boiled and filtered by deionized water until the filtrer liquid was neutral, then dried at 120 °C for 4 h.

2.2. Characterization of activated carbons

The porous structure of the modified ACs were characterized by N_2 -adsorption/desorption isotherms measured at 77 K (ASAP 2020, Micromeritics, USA). All the AC samples were degassed at 300 °C for 8 h before the adsorption experiments. Specific surface areas were calculated by the BET (Brunauer–Emmett–Teller) model. The total pore volume was estimated by the amount of N_2 adsorption at a relative pressure of 0.95, and the pore size distributions were obtained by DFT (Density-Function-Theory) model.

The surface functional groups of the modified ACs were obtained by Boehm titration method and X-ray photoelectron spectroscopy. The detailed steps of Boehm titration method were as follows [29]: AC sample (0.5 g) was placed in 12 mL of 0.1 mol L^{-1} solution of sodium hydroxide, sodium carbonate, sodium bicarbonate and hydrochloric acid. The conical flasks were sealed and

Table 1
Porous structure properties of AC samples.

Sample	BET surface area/ $\text{m}^2 \text{ g}^{-1}$	Average pore size/nm	Pore volume/ $\text{cm}^3 \text{ g}^{-1}$	Micropore volume/%
AC-air	1424	1.90	0.68	55.9
AC-acid	1138	1.87	0.53	67.9
AC	1351	1.94	0.65	42
AC-alkali	1205	1.86	0.56	69.8
AC-N800	995	1.89	0.47	62.1

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