



Beneficial effects of activated carbon additives on the performance of negative lead-acid battery electrode for high-rate partial-state-of-charge operation

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H I G H L I G H T S

- We report a 12 V Pb–C battery with as-designed activated carbon in NAM.
- Carbon additives optimize NAM microstructure and enhance electrode reaction kinetics.
- The battery exhibits more than 110,000 cycles under HRPSoC condition.
- The battery exhibits 20% improved charge acceptance comparing to the common one.
- Carbon acts as porous-skeleton builder, electrolyte supplier and capacitive buffer.

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Experiments are made with negative electrode of 2 V cell and 12 V lead-acid battery doped with typical activated carbon additives. It turns out that the negative electrode containing tens-of-micron-sized carbon particles in NAM exhibits markedly increased HRPSoC cycle life than the one containing carbon particles with much smaller size of several microns or the one containing no activated carbon. The improved performance is mainly attributed to the optimized NAM microstructure and the enhanced electrode reaction kinetics by introducing appropriate activated carbon. The beneficial effects can be briefly summarized from three aspects. First, activated carbon acts as new porous-skeleton builder to increase the porosity and active surface of NAM, and thus facilitates the electrolyte diffusion from surface to inner and provides more sites for crystallization/dissolution of lead sulfate; second, activated carbon plays the role of electrolyte supplier to provide sufficient H₂SO₄ in the inner of plate when the diffusion of H₂SO₄ from plate surface cannot keep pace of the electrode reaction; Third, activated carbon acts as capacitive buffer to absorb excess charge current which would otherwise lead to insufficient NAM conversion and hydrogen evolution.

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1. Introduction

The environment concerns over the use of fossil fuels and their resource constraint have spurred great interest in low-emission transport like electric vehicles, and also the wind/solar energy storage and utilization. No matter in hybrid electric vehicles (HEV) or in intermittent energy storage systems, the battery has to operate continuously at partial-state-of-charge (PSoC) duty and accept charge at extremely high rates when vehicle braking or wind is heavy. In addition, high-rate discharge is necessary for engine cranking and power-assist. That is, the battery is said to undergo

high-rate partial-state-of-charge duty (HRPSoC) [1,2]. However, under such a duty, conventional lead-acid batteries, such as those designed for SLI (starting, lighting and ignition) or deep-cycle use, would quickly accumulate lead sulfate on the surface of negative plate [3], which cannot be converted efficiently back to spongy lead during charge, then thus limit the cycle life of the batteries.

Therefore, the lead-acid battery developed over decades for SLI duty, telecommunications or UPS applications must be modified significantly in order to provide the power capability and adequate service-life demanded by future automobile electrical systems and energy storage systems. The key objective is to overcome the processes that give rise to the accumulation of sulfate on the negative plate in HRPSoC duty.

Nakamura, Shiomi and co-authors [4,5] have established that introduction of carbon black to the negative active material (NAM)

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Table 1
Characteristics of carbon additives under investigation.

Type of material	Mean particle size (D_{50} , μm)	BET surface ($\text{m}^2 \text{g}^{-1}$)	Pore volume ($\text{cm}^3 \text{g}^{-1}$)	Average pore size (nm)	Capacitance under 0.05 A g^{-1} (F g^{-1})	Conductivity (S cm)
Activated carbon 1#	4.0	1156	0.615	2.12	249	0.33
Activated carbon 2#	68.0	2826	1.662	2.35	367	0.34
Graphite	18.5	7.4	0.042	22.73	–	82.33

retards substantially the sulfation of the negative plates during the simulated HRPSoC test of batteries for HEV applications. Newnham et al. [6] have found that the specific surface area of NAM is an important parameter as it sustains the potential of the negative plates below the hydrogen evolution potential. In recent years, it is widely accepted that incorporation of elevated concentration of carbon (a few wt.% instead of the traditional 0.2 wt.%) is a promising route to alleviate the tendency for sulfate accumulation and possesses a long operating life in HRPSoC duty [7–11]. The types of carbon additives could be carbon black, activated carbon, graphite, or mixture of them. Micka's group [12,13] has pointed out that the effect of carbon is due to steric hindrance of the sulfate crystallization rather than the electric conductivity of graphite via investigating HRPSoC cycle life of the negative plate not only by adding graphite but also adding isolated titanium dioxide. Pavlov and co-workers [8] have established that, during cycling of cells under HRPSoC condition, the electrochemical reactions of charge at the negative plates occur not only on the lead sulfate, but on the surface of the carbon as well. They proposed a parallel electrochemical mechanism of charge and came to the conclusion that carbon must be incorporated in and impact the structure of NAM to influence the battery performance under HRPSoC duty [14].

The main possible functions of carbon additives to negative plate performed in HRPSoC cycling have been summarized by P.T. Moseley [15]: (i) enhancing the overall electrical conductivity of NAM; (ii) restricting lead sulfate crystal growth; (iii) absorbing excess charge current as a capacitor; (iv) reducing the hydrogen over-potential and thus facilitating hydrogen emission. However, not all carbon forms that exhibit high conductivity or increase the specific surface area of NAM could be favorable for battery cycle life under HRPSoC operation [7]. So far, the optimum type of carbon additives and actual effect mechanism for improved HRPSoC cycling performance of lead-acid batteries are still unclear and need further investigation.

In the present work, we prepare two groups of possible suited activated carbon materials, and add them to the negative plate. The HRPSoC cycling performance, charge acceptance ability and other properties of Pb–C negative plate are evaluated in both simulated 2 V test cells and 12 V batteries. The correlation between electrochemical properties of cells/batteries and microstructures of NAM is paid close attention. The aim of the present investigation is to disclose the positive function mechanism of activated carbon additives on the electrochemical processes of the negative plate in HRPSoC duty.

2. Plate preparation and battery design

2.1. Carbon materials added to NAM

The as-prepared carbon additives were of very high active surface area and different particle size range from several microns to tens of microns. Graphite with much low BET surface but relative high electrical conductivity was also selected for comparison. The characteristics of carbon additives are summarized in Table 1.

2.2. Negative paste preparation and characterization

Experimental groups of carbon additives doped to negative pastes are listed in Table 2. Paste without carbon was also prepared and used for assembling reference plates. All the plates were cured and dried at 65°C for 24 h.

The samples of NAM after formation and HRPSoC cycling were characterized by scanning electron microscope (SEM, Hitachi S-3400N) and BET Surface Analyzer (Gemini VII 2390).

2.3. Simulated test cell and battery design

The influence of carbon additives on the performance of negative lead-acid battery plate was investigated both in 2 V simulated test cells and 12 V batteries.

The design characteristics of 2 V simulated test cells are presented in Table 3. Before cell assembly, the negative plates were formed in 1.04 sp. gr. H_2SO_4 . The process of formation composes of a charge at 0.22 C_{10} for 10 h, a discharge at 0.1 C_{10} for 0.5 h and a further charge at 0.2 C_{10} for 10 h. In each 2 V test cell, one negative plate was assembled with two positive plates, and AGM separator (Sinoma International) with a thickness of 1.65 mm at 10 kPa (93% porosity) were used at 25% compression. The cells were filled with H_2SO_4 of 1.304 sp. gr. and sealed. 12 V Prototype battery with 20-h capacity of 75 A h was also produced as shown in Fig. 1. For contrast, 2 V cell and 12 V battery consisted of same positive and negative plates without carbon additives were also produced.

3. Electrochemical performances of test cells and batteries

3.1. Simplified HRPSoC cycling

The effects of carbon materials on HRPSoC performance were evaluated in simulated test cell using a simplified profile imitating the micro-hybrid driving mode. The first step in this cycling profile was discharging at 1 C rate to 50% SoC. After that, the cells were subjected to cycling according to the following procedures: charge at 2 C rate for 90 s (upper voltage limit of 2.54 V), rest for 10 s, discharge at 2 C rate for 60 s, rest for 10 s. The cell voltage was measured at the end of the discharge pulses and the test was stopped when the cell discharge voltage fell down to 1.70 V.

The results of simplified HRPSoC cycling were shown in Fig. 2. The reference, AC1 and AC2 cells reached the end of their lives at about 7000, 10,700 and 15,600 cycles, respectively. Obviously, the cell with 2 wt.% activated carbon prolongs the cycle life under the

Table 2
Experimental groups of carbon additives to negative plate.

Signature	Composition	Concentration in NAM (wt.%)
Ref	–	–
AC1	Activated carbon 1#	2%
AC2	Activated carbon 2#	2%
AG	Activated carbon 2# + graphite	1% + 1%

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