Enhanced performance of Zn(II)-doped lead-acid batteries with electrochemical active carbon in negative mass

Jiayuan Xiang [a, *], Chen Hu [b, **], Liying Chen [a], Dong Zhang [c], Ping Ding [a], Dong Chen [a], Hao Liu [b], Jian Chen [a], Xianzhang Wu [a], Xiaokang Lai [b]

[a] Research Institute of Narada Power Source Co., Ltd, Hangzhou 311305, China
[b] China Electric Power Research Institute, Beijing, 100192, China
[c] Hangzhou City of Quality and Technical Supervision and Testing Institute, Hangzhou 310019, China

HIGHLIGHTS

- Gas evolution is reduced by 58−73% via adding Zn(II) additives.
- Low-temperature and high-rate capacity is improved by Zn(II) additives.
- Cycle life is prolonged under the co-effect of carbon and Zn(II) additives.
- The cell exhibits 90% reversible capacity after 2100 cycles at partial-state-of-charge duty.

ARTICLE INFO

ABSTRACT

The effect and mechanism of Zn(II) on improving the performances of lead-acid cell with electrochemical active carbon (EAC) in negative mass is investigated. The hydrogen evolution of the cell is significantly reduced due to the deposition of Zn on carbon surface and the increased porosity of negative mass. Zn(II) additives can also improve the low-temperature and high-rate capacities of the cell with EAC in negative mass, which ascribes to the formation of Zn on lead and carbon surface that constructs a conductive bridge among the active mass. Under the co-contribution of EAC and Zn(II), the partial-state-of-charge cycle life is greatly prolonged. EAC optimizes the NAM structure and porosity to enhance the charge acceptance and retard the lead sulfate accumulation. Zn(II) additive reduces the hydrogen evolution during charge process and improves the electric conductivity of the negative electrode. The cell with 0.6 wt% EAC and 0.006 wt% ZnO in negative mass exhibits 90% reversible capacity of the initial capacity after 2100 cycles. In contrast, the cell with 0.6 wt% EAC exhibits 84% reversible capacity after 2100 cycles and the control cell with no EAC and Zn(II) exhibits less than 80% reversible capacity after 1350 cycles.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

In order to cope with the challenge of high-rate-partial-state-of-charge (HRPSoC) duty in micro-hybrid electric vehicles and partial-state-of-charge (PSoC) duty in energy storage system for micro-grid, new technology in lead-acid batteries (LABs) should be developed to provide higher levels of charge acceptance to enhance system efficiency and delay common failure mechanism such as lead sulfate accumulation on surface of negative plate [1].

Introducing carbon in types of activated carbon, carbon black and expanded graphite to negative active mass (NAM) during paste preparation has been proved to be an effective way to improve charge acceptance and prolong cycle life under PSoC duty [2–4].

The understanding of possible mechanism by which a carbon component enhance the performances of LABs has also been developed from eight different functions [5] to just three candidates that are most likely to have a significant individual effect [6]: (i) capacitive buffer to absorb charge current in excess of which can be accommodated by the Faradic reaction [7]; (ii) the extension of the surface area on which the electrochemical charge and discharge processes can take place [8]; (iii) the physical processes that hinder the crystallization of lead sulfate and thus help to maintain a high surface area for the discharge product [9].

* Corresponding author.
** Corresponding author.
E-mail addresses: xjyzju@aliyun.com (J. Xiang), huchen@epri.sgcc.com.cn (C. Hu).

However, a risk of hydrogen evolution at the end of charge process maybe also brought in when adding carbon to LABs due to the low hydrogen evolution overpotential of carbon materials under the negative plate working conditions [10]. Attention needs to be paid to avoid harmful influences like more gas release, thermal runaway or even electrolyte dry-out. Introducing metal ions with high hydrogen evolution overpotential in LABs has been proved to be an effective way to retard hydrogen-evolution rate. For instance, In_2O_3, Bi_2O_3 and Ga_2O_3 were reported to be beneficial for suppressing hydrogen evolution and prolong HRPSoC cycle life of valve-regulated-lead-acid (VRLA) batteries with carbon [11,12]. But as is well known, residual metal element is always "harmful elements" for LABs since they may cause hydrogen and/or oxygen gassing and which, therefore, must be restricted or avoided. The influence of seventeen elements namely Sb, As, Bi, Gd, Gr, Co, Cu Ge, Fe, Mn, Ni, Se, Ag, Te, Tl, Sn and Zn in lead on hydrogen- and/or oxygen-gassing rates of LABs has been investigated [13], only Bi, Cd, Sn and Zn are considered as "beneficial elements" for VRLA batteries since they have little effect on gassing. The remaining metal elements are "harmful" since they will promote the gassing rate.

Therefore, the study of doping "beneficial elements" in LABs with carbon in negative mass and their influence on battery performances is valuable and urgent. But to date, there is few research about it. In the present work, the focus lies on effect of Zn(II) at the form of ZnO doping in negative mass or $ZnSO_4$ doping in electrolyte on hydrogen evolution and other performances of VRLA batteries with carbon. The purpose is to understand the function mechanism of high hydrogen-evolution-overpotential metal ions, provide a promising way to eliminate the water-consumption risk when adding carbon in negative mass, and improve the other performances of the LABs.

2. Experimental

2.1. Materials and characterization

Carbon added to negative mass is provided by Cabot Corporation, with BET surface area of 1350 m^2 g^{-1} and particle size (D_{50}) of 13 μm. Due to its high surface area and great contribution to the electrochemical reactions of charge, we labelled the carbon as electrochemical active carbon (EAC) as some previous literature named [8].

Leady oxide (80% PbO) is manufactured in Narada Company from 99.99% pure lead by ball milling. Vanisperse-A and $BaSO_4$ is added in NAM as expander. ZnO and $ZnSO_4$ is analytical reagent from Xilong Chemical Co., Ltd. Battery grade sulfuric acid (1.40 sp. gr.) is used during paste mixing.

X-ray diffraction (XRD-7000, Shimadzu) was used to detect the phases of negative mass. Scanning Electron Microscope (SEM, Hitachi S-3400N) and BET Surface Analyzer (Gemini VII 2390, Micromeritics) were used to characterize the morphology and active surface area of carbon and negative mass. Particle Size Analyzer (Malvern-2000) was used to measure the particle size of carbon material. Mercury Intrusion Porosimetry (Autopore 9500, Micromeritics) was used to test the porosity of negative mass. Inductive Coupled Plasma-Atomic Emission Spectrometry (ICP-AES, Optima 7000 DV) was used to measure the content of Zn element in negative mass and electrolyte. Gas chromatograph-mass spectrometer (GC-MS, Agilent 5977) is used to determine the hydrogen and oxygen ratio of the accumulated gas from the cells during 2.40Vpc charging.

2.2. Cell design and manufacturing

Experimental groups of EAC and Zn(II) additives doped to negative pastes are listed in Table 1. Based on the negative plate containing 0.6 wt% EAC, ZnO and $ZnSO_4$ as Zn(II) additives were added in the cells, respectively. ZnO with doping level of 1.0 wt% of EAC was firstly mixed with EAC and then added in negative mass (0.006 wt% of NAM), and $ZnSO_4$ with doping level of 1 mg ml^{-1} was directly added in electrolyte. For comparison, the cell containing no carbon and Zn(II) additives was also prepared. In order to describe clearly, the four groups are simply named as control, EAC, EAC + ZnO, EAC + $ZnSO_4$. Each negative plate contains 0.05 wt% sodium lignosulphonate (Vanisperse-A) and 0.45 wt% $BaSO_4$.

2 V prototype cell with 10h-rate capacity (C_{10}) of 15 A h was fabricated and tested. The cell characteristic is shown in Table 2.

2.3. Electrochemical measurement

Linear sweep voltammogram was performed on CHI660C electrochemical workstation to characterize the hydrogen evolution behavior of negative plate in sulfuric acid (1.30 sp. gr.) at scanning rate of 0.1 mV s^{-1} from −1.0 V to −1.7 V versus Ag/Ag_2SO_4. Cyclic voltammogram was also performed on CHI660C electrochemical workstation to study the electrochemical behavior of EAC electrode in different electrolyte at scanning rate of 0.1 mV s^{-1} from −0.6 V to −1.4 V versus Ag/Ag_2SO_4. Nyquist plots of the electrodes was measured on ModuLab XM electrochemical workstation from 10 kHz to 0.01 Hz with amplitude of 5 mV to investigate the conductivity of the electrodes.

Discharge capacity was test at three conditions: (i) regular duty that discharge current was 1.5 A with cut-off voltage of 1.80 Vpc and ambient temperature was 25 °C; (ii) low temperature duty that discharge current was 1.5 A with cut-off voltage of 1.80Vpc and ambient temperature was −10 °C; (iii) high rate duty that discharge current was 3C (45 A) with cut-off voltage of 1.50 Vpc and ambient temperature was 25 °C.

Gas evolution property was evaluated under floating charge condition. After the cells were floating charged at 2.40Vpc for 72 h, collected the gas generated during the following 192 h with also 2.40Vpc floating charging.

Charge acceptance was evaluated as follows: (i) discharged the cells with 1.5 A until the SoC level reached to 50%; (ii) rest for 24 h at temperature of 0 °C; (iii) charged the cells with constant voltage of 2.40 V and no current limitation; (iv) recorded the current I_{10min} as charged for 10 min, and calculated the ratio of I_{10min}/I_{10} (I_{10} is the 10 h-rate current).

PSoC cycling performance was evaluated using a simplified profile imitating the energy storage mode: (i) firstly discharged the cells from fully-charged-state to 30%SoC at 5 A; (ii) charged to 80% SoC at 2 A with 2.35 V limited; (iii) discharged to 30%SoC at 5 A; (iv) repeated step (ii) to step (iii) for 150 times; (v) fully recharged the cells at 2 A; (vi) determined the discharge capacity at 2 A; (vii) fully charged the cells and then went back to step (i). The cell voltage was measured at the end of discharge, the discharge capacity was recorded, and the test was stopped when the cell discharge voltage fell down to 1.80 V or the cell capacity fell below 8 Ah.

3. Results and discussion

The XRD patterns of the formed negative mass are presented in Fig. 1a. The diffraction peaks of the control plate is mainly indexed to Pb (PDF No. 65−2873), only some minor peak indexed to α-PbO (PDF No. 85−1739) is detected. EAC doping in negative mass makes the XRD pattern change remarkably that the peaks of α-PbO become much stronger while the peak intensity of Pb decrease accordingly. It means the surface activity of spongy lead is enhanced with EAC, which might cause more lead oxidation reaction happen when the negative plate placed in air. As EAC added