

Effect of graphene oxide with different oxygenated groups on the high-rate partial-state-of-charge performance of lead-acid batteries



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ARTICLE INFO

Keywords:

Lead-acid battery
High-rate partial-state-of-charge
Graphene oxide
Oxygenated groups
Hydrogen evolution performance

ABSTRACT

Four graphene oxide samples with different oxygenated groups are prepared and characterized, and then employed as the additives in the negative active materials to investigate the effect of different oxygenated groups of graphene oxide on the H₂ evolution performance of negative plates and the high-rate partial-state-of-charge cycle life of simulated lead-acid batteries. The results indicate that the H₂ evolution and the reduction of PbSO₄ processes are largely accelerated by the graphene oxide additives. An increase in C–O groups (C–OH and C–O–C) of graphene oxide can largely promote the H₂ evolution process. The addition of the graphene oxide additives largely increases the surface area and total pore volume of the negative plates, meanwhile obviously increases the hydrophilicity of negative active materials to facilitate the diffusion of acid into the inner of the plate. The high-rate partial-state-of-charge cycle life of the simulated test cells containing the graphene oxide samples is prolonged significantly, and especially those containing graphene oxide with less C–O groups and more carbonyl and carboxyl groups have the longest cycle life, which seems to be more appropriate as the additive of negative plates.

1. Introduction

Working under conditions of high-rate partial-state-of-charge (HRPSoC) continuously, lead-acid batteries will suffer quick battery failures owing to the irreversible sulfation of negative plates [1,2]. In recent years, various carbon materials, including carbon black (CB) [3–5], activated carbon (AC) [6–10], graphite [11,12], carbon nanotube [13–16], graphene [17–19], etc., were directly introduced into the negative active materials (NAM) to prevent the progressive sulfation of negative plates and significantly prolong the HRPSoC cycle life of lead-acid batteries [20]. However, these lead-carbon batteries suffer serious hydrogen evolution to dry out their electrolyte quickly [21].

In order to overcome this H₂ evolution problem, the carbon materials were modified with various methods [6,7,22], e.g. the modification of their surface functional groups [8], the development of metals (or metal oxides)/carbon materials composites [9,10,23] and the combination of these two methods [24]. It was reported that acidic surface functional groups of AC could promote the H₂ evolution in negative plates, while those alkaline surface functional groups could inhibit it [8]. We also found that the surface functional groups of CB in

PbO/CB composites displayed the similar effect [24]. Different surface functional groups of carbon materials may play an important role in their H₂ inhibition performance.

Based on our previous work [25], adding graphene oxide (GO) in negative plates can significantly prolong the HRPSoC cycle life of lead-acid batteries, however, also promote the H₂ evolution in the negative plate obviously. According to the effect of functional groups of AC and CB, different oxygenated groups of GO may produce a different effect on the H₂ evolution process. But few studies have focused on this. In this paper, GO with different oxygenated groups were prepared and characterized, and then their influence on the H₂ evolution ability of negative plates and on the HRPSoC cycle life of simulated test cells was investigated to identify the detailed effect of different oxygenated groups of GO. The results of this work may benefit the selection of appropriate GO for the further modification of its functional groups or the preparation of metals (metal oxides)/GO composites for lead-acid batteries.

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<https://doi.org/10.1016/j.est.2018.06.004>

Received 23 March 2018; Received in revised form 7 June 2018; Accepted 7 June 2018
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Table 1
Content of the materials used in negative pastes (wt. %, versus the lead oxide).

| | Acetylene black | Short fibers | BaSO ₄ | Humic Acids | H ₂ SO ₄ ⁺ | H ₂ O | GO samples |
|----------|-----------------|--------------|-------------------|-------------|---|------------------|------------|
| Blank | 0.2 | 0.05 | 0.4 | 0.7 | 12.5 | 10 | 0 |
| GO added | 0.2 | 0.05 | 0.4 | 0.7 | 12.5 | 13 - 15 | 1.0 |

* Density = 1.25 g cm⁻³.

2. Experimental

2.1. Preparation of GO

A water-enhanced oxidation method, which belongs to a modified Hummer's method, was employed to prepare GO samples with different species of oxygenated groups [26,27]. In an ice-bath (< 10 °C), 1.0 g graphite powder (99.95%, supplied by Qingdao Huatai, China) and 3.0 g KMnO₄ were added in 46 mL concentrated H₂SO₄ with the different initial addition of distilled water ($V_{\text{H}_2\text{O}}^0 = 0, 4 \text{ and } 12 \text{ mL}$) and were stirred continuously, then maintained at 40 °C for 2 h. According to the different $V_{\text{H}_2\text{O}}^0$ (0, 4 and 12 mL), the obtained GO is denoted as GO1-M, GO2-M, GO3-M, respectively. The fourth GO sample was synthesized in the system without the initial addition of distilled water ($V_{\text{H}_2\text{O}}^0 = 0$). But after the oxidation at 40 °C for 2 h, 100 mL distilled water was slowly added into the reaction system and maintained at 90 °C for 15 min. The obtained GO is denoted as GO4-H [28]. After centrifuging, washing by distilled water, and vacuum drying, the final GO samples were prepared for the further test in this work. Except for graphite powder, other reagents and chemicals used in this preparation step were analytical grade (AR).

2.2. Preparation of negative plates and simulated test cells

Lead oxide power (oxidation degree = 82.6%) was supplied by a commercial battery company. The content (versus the lead oxide) of other materials in negative pastes is listed in Table 1, in which humic acids ($\geq 90\%$, Aladdin) and BaSO₄ (AR) are reagents, and acetylene black and short fibers are supplied from commercial battery companies. The apparent density of the negative pastes was about 4.2 g cm⁻³, which was adjusted by distilled water. The negative plate was prepared using a Pb-Sn-Ca grid (1.0 × 1.5 cm²) and 1.0 g negative paste, and then cured carefully and formed under a commercial formation procedure (H₂SO₄ density: 1.05 g cm⁻³; constant formation current: 8.5 mA g⁻¹ and 17 mA g⁻¹; total charge delivered to NAM: 535.5 mAh g⁻¹) [25]. The negative plates containing GO1-M, GO2-M, GO3-M, and GO4-H are nominated as GO-1, GO-2, GO-3, and GO-4,

respectively, and those without GO are blank plates. A prepared negative plate (1.0 × 1.5 cm²) and two commercial positive plates (2.8 × 2.8 cm²) were separated with a glass mat (AGM, thickness = 2 mm) separator, and then 65 mL H₂SO₄ (1.28 g cm⁻³) was added to form a flooded simulated lead-acid test cell [25].

2.3. Electrochemical measurements and HRPSoC cycle tests

The cathodic polarization curves of the prepared negative plates (Blank, GO-1, GO-2, GO-3 and GO-4) were measured in H₂SO₄ (1.28 g cm⁻³) at room temperature (25 °C) using a GAMRY Reference 3000 electrochemical workstation. Two platinum electrodes and a Hg/Hg₂SO₄ electrode were used as the counter electrode and the reference electrode, respectively. The polarization potential range is from the open circuit potential (E_{OCF}) to -1.5 V vs. Hg/Hg₂SO₄ and the scan rate is 1.0 mV s⁻¹.

Before the HRPSoC cycle test, the 2C current was determined from the measured Peukert plots for the different kinds of simulated test cells and the state-of-charge (SoC) of the test cells was discharged to 50%. The schedule of the HRPSoC cycle test was: charge (2C, 30 s); rest (10 s); discharge (2C, 30 s); rest (10 s). The limit of end-of-discharge voltage ($V_{\text{discharge}}$) and end-of-charge voltage (V_{charge}) was 1.60 V and 3.0 V, respectively. After the first cycle-set test (2C-1 set), the second (2C-2set) and the third cycle-set (2C-3set) test were conducted according to the same procedures. All these tests were performed at room temperature (25 °C) and repeated at least three times.

2.4. Physical characterization

The as-prepared samples of GO1-M, GO2-M, GO3-M, and GO4-H were characterized using X-ray diffraction (XRD, XRD-7000S, Japan) with Cu K α radiation, Fourier transform infrared spectroscopy (FTIR, Vertex 70, Germany) in reflectance mode, and X-ray photoelectron spectroscopy (XPS, VG Multilab 2000) analyses (the binding energies were calibrated relative to the C 1 s peak from GO sample at 284.6 eV). The morphology of the negative plates was observed using scanning electron microscope (SEM, Nova NanoSEM 450, America). The specific surface and porosity analysis for the negative plates, which had been dried in vacuum at 120 °C for 2 h, was conducted using an ASAP2020 M analyzer (America). The water contact angle of the prepared negative plate was measured with a JC2000 contact-angle meter (Shanghai Zhongchen Digital Technic Apparatus, China).

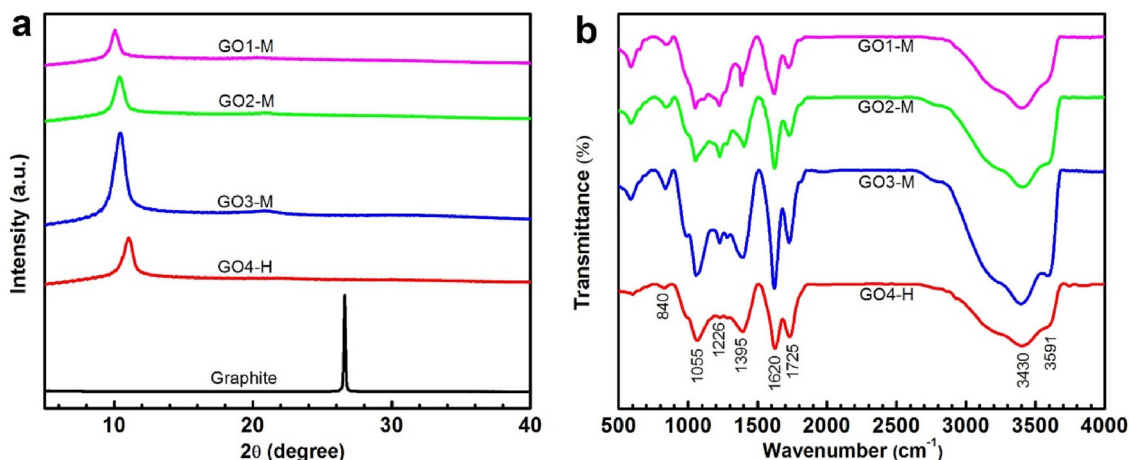


Fig. 1. (a) XRD patterns and (b) FTIR spectra of different GO samples.

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