Journal of Power Sources 209 (2012) 262–268

Contents lists available at SciVerse ScienceDirect

Journal of Power Sources

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

The performance of a silica-based mixed gel electrolyte in lead acid batteries☆

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ARTICLE INFO

Article history:
Received 19 November 2011
Received in revised form 23 February 2012
Accepted 26 February 2012
Available online 6 March 2012

Keywords:
Silica-based mixed gel electrolyte
Lead-acid batteries

ABSTRACT

The gel electrolyte is a key factor affecting the performance of lead-acid batteries. Two conventional gelators, colloidal and fumed silica, are investigated. A novel gel electrolyte is prepared by mixing the gelators with sulphuric acid. The physical property testing demonstrates that the mixed gel electrolyte is more mobile, has a longer gelling time, greater stability and a better crosslinking structure than its counterparts as compared with any single gelling agent. The electrochemical properties indicate that the mixed gel electrolyte can suppress the oxygen evolution reaction, reduce the resistance to charge transfer at open circuit potential, increase the initial capacity, demonstrating that it is a promising gel electrolyte for lead acid batteries.

1. Introduction

It is well known that compared with conventional flooded or absorbent glass mat (AGM) batteries, the valve regulated lead acid (VRLA) batteries with a gel electrolyte have excellent performance in several fields [1–5]. The key factor affecting the performance of gel batteries is the gel electrolyte itself; the gelator has a significant impact on the properties of the gelled electrolyte.

Fumed and colloidal silica have been widely used as gelling agents [6,7]. Fumed silica has good thixotropy [8] and reliability under cyclic or deep-discharge conditions when used in gel electrolytes [9,10], but it has many shortcomings such as a shorter gelling time, higher viscosity, higher material and manufacturing costs, and an increased internal resistance, which limits the extensive application of this technology [11]. The gel electrolytes containing colloidal silica have advantages of simple preparation, storage and gel perfusion, and low cost. However, they usually contain a high content of iron and other impurities which decrease the overpotentials of hydrogen and oxygen evolution, causing an increase in water consumption in the gel batteries, and eventual battery failure [4,11,12].

Because of the widespread utility of fumed silica and colloidal silica as gelling agents, studies of the structure, and the properties of its surfaces have been carried out by researchers for many years [8]. The gelling agents do not participate in the electrochemical reactions within lead acid batteries; their main function is to form a three-dimensional network structure, entrapping the sulfuric acid solution. The schematics of gel formation with fumed silica and colloidal silica were separately provided [11,13], which both form a three-dimensional network structure but in a variety of ways. Careful analysis [14] indicated that the surface reactivity of the silica depends substantially on the quantity and structural arrangement of its surface hydroxyl groups. Fumed silica tends to form isolated silanols; while colloidal silica, produces hydrogen-bonded silanol groups with almost no isolated silanols [14].

Most researchers [15–17] focused their effort on inorganic and organic additives to improve the performance of gelled electrolytes. In this paper, fumed and colloidal silica were combined to prepare a novel mixed gel electrolyte for overcoming the disadvantages of gel electrolytes prepared with fumed or colloidal silica, thereby improving the physical and electrochemical properties and optimizing the overall performance of the gel electrolyte.

2. Experimental

2.1. Preparation of the electrodes and gelled electrolyte

The working electrode was prepared by inserting a pure lead rod into a hard plastic tube sealed with epoxy resin. A copper wire

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☆ This paper was presented at the LABAT'2011 conference, Albena, Bulgaria, 7–10 June 2011.

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doi:10.1016/j.jpowsour.2012.02.101

Table 1
Gelled electrolyte composition.

Sample	1#	2#	3#	4#
Colloidal silica/fumed silica[a]	0:5	1:4	2.5:2.5	5:0

[a] The ratios were calculated in terms of the silica content.

was welded to one end of the electrode. The opposite end was used as a flat, circular working surface with a geometric area of 0.5 cm^2.

The fumed silica involved in this work was Aerosil 200(produced by Dedussa Co., Germany denoted as A200), and the colloidal silica was eka Bindzzl 40% (produced by Akzo Nobel Co., Netherlands). Table 1 summarizes the composition of the gelled electrolytes. The net content of silica in each gel is 5 percent of total weight, and the weight ratios of colloidal silica to fumed silica were as follows: 0/5 (Sample 1#), 1/4 (Sample 2#), 2.5/2.5 (Sample 3#), 5/0 (Sample 4#). The H_2SO_4 concentration was maintained at 1.28 g cm^{-3} after dilution with the silica colloid. The mixture was stirred at a high speed in a homogenizer to form a colloidal solution. Electrochemical testing was performed after gelation of the colloidal solution.

2.2. Physical characterization of the gel electrolyte

The liquidity testing was carried out in the "Leoch Cup" and the viscosity was determined by using a Ubbelohde viscometer (capillary diameter 0.7–0.8 mm) and recording the flow time in each case. To determine the gelling time, the penetration of lead balls (3 mm in diameter) into the gel at different times was recorded. Physical characterization of colloidal sol was carried out when gel electrolytes stop stirring. In our experiment, the interval time from stopping agitation to starting test can be neglected since the four gels were prepared under the same conditions. And above tests were all measured at room temperature (25 °C). The zeta potential measurement was performed with JS94J microelectrophoresis (Shanghai Zhongchen Digital Technology Equipment Co. Ltd., China), with dried gel sample dispersed in deionized water by ultrasonic waves for 5 min before the measurement. Fourier-infrared (FT-IR) spectroscopy (IR Prestige-21 (Shimadzu, Japan)) elucidated the functional groups of the dried gelled electrolyte. Scanning electron microscopy (SEM), utilizing a Quanta 400 thermal FE environment scanning electron microscope (Philips FEI Ltd., Holland), was used for the morphological studies of the samples. The morphology and microstructure of the silica particles was observed using a JEM-2010HR transmission electron microscope (TEM). Thermogravimetric analysis (TGA) was conducted to determine the thermal stability of the three-dimensional network structure in the dry gelled electrolytes. The dry samples for the SEM observation, TEM measurement, Zeta potential test, FT-IR and TG analysis were prepared as follows: place the gel in an oven for 30 days with a constant temperature of 120 °C.

2.3. Electrochemical test

Electrochemical impedance spectroscopy (EIS) was performed at open circuit potential on an Autolab PGSTAT-30 (Eco Echemie BV Co.) over a 10^5–10^{-2} Hz frequency range at an amplitude of 10 mV. At the beginning of each experiment, the working electrode was mechanically polished with emery paper and deoxidized at −1.2 V in a three-electrode cell with an Hg/Hg_2SO_4, K_2SO_4 (saturated) reference electrode and a platinum sheet as the counter electrode to remove impurities. The batteries were filled with a variety of electrolyte formulations using a vacuum system to improve the gel distribution. The initial capacity of each battery was tested with a μC-XCF charge–discharge device (Jiangsu Golden Sail Power Technology Co., Ltd.).

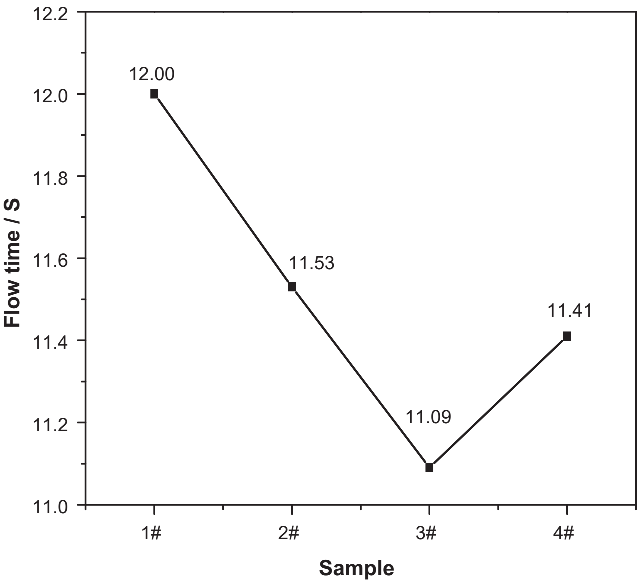

Fig. 1. Variation of gelled electrolyte liquidity with mixing ratio at room temperature (25 °C).

3. Results and discussion

3.1. Gelled electrolyte characterization

3.1.1. Liquidity and viscosity

Improved liquidity reduces the time required to pour the gelled electrolyte into the battery, allowing an even distribution and fuller penetration into the active substance. As illustrated in Fig. 1, the flow time is decreased initially with increasing amount of colloidal silica, and then the flow time is increased with only colloidal silica. This fact shows that the mobility of gelled electrolyte with an equal ratio of the two forms of silica is superior to that with a single gelling agent.

The viscosity demonstrates a similar variation trend with mixing ratio at room temperature (25 °C), as seen from Fig. 2. In both cases, the mixing of fumed silica and colloidal silica can help improve the mobility of the gel by reducing the viscosity, a synergetic action thus allowing easier absorption of the gel electrolyte. A possible reason for such is that when colloidal silica and fumed silica are mixed, the silica particles of different size may interact with each other and improve the dynamic properties of the particles.

3.1.2. Gelling time

Fig. 3 shows the gelling time as a function of mixing ratio at room temperature (25 °C). Gelling time is a process parameter that affects electrolyte processability during battery assembly (filling and formation). The optimum electrolyte would remain liquid during the entire battery manufacturing processes and would then gellify [4].

The gelling time of mixed silica gel electrolytes was much longer, possibly due to the formation of stable three-dimensional cross-linked structures, as was indicated by SEM analysis.

3.1.3. Cyclic voltammetry (CV)

Fig. 4 presents the CV curves of the gelled electrolytes. The additional peaks due to secondary redox reactions of the silica compounds do not appear in the voltammograms of the mixed gel electrolytes, demonstrating that all gelators studied are stable in the operating range of the battery [4]. Similar peaks are found in