



Effect of polyols on the electrochemical behavior of gel valve-regulated lead-acid batteries



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ABSTRACT

The effects of three types of straight chain polyols (propanetriol, butantetraol, and pentitol) and one branched chain polyols pentaerythritol as electrolyte additives on the electrochemical properties of gelled electrolyte valve-regulated lead-acid (GEL-VRLA) batteries were systematically studied. Our result shows that a moderate mechanical dispersion of fumed silica in H₂SO₄ solution is beneficial to improve the electrochemical properties of the gelled electrolyte. Adding of straight chain polyols (propanetriol, butantetraol, and pentitol) can decrease not only the optimum dispersion time, but also the electrolyte resistance of the gel. The optimum dispersion time needed is pure (90 minutes) > adding pentitol (80 minutes) > adding butantetraol (70 minutes) > adding propanetriol (60 minutes). Furthermore, the optimum agitation time can be reduced by 88% with adding of branch chain polyols pentaerythritol. Also, the charge-transfer resistance (R_{ct}) of gel can be reduced by more than one order of magnitude. More important, the peak current (capacity) of the lead electrode is stable with agitation time, which is significant for practical application. The adding of pentaerythritol makes the gel more uniform and porous, demonstrating that it is a promising gel electrolyte for VRLA batteries.

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1. Introduction

Gel valve-regulated lead-acid (GEL-VRLA) batteries have many advantages such as high reliability, long service life, small self-discharge, deep-cycle performance and so on [1,2]. It is well known that the properties of gelled electrolyte have great influence on the performance of GEL-VRLA batteries [3,4]. Various gelling agents are used in GEL-VRLA batteries [5–8], and the most commonly used is fumed silica for its good thixotropy and reliability under cyclic or deep-discharge conditions in GEL-VRLA batteries [9–11]. However, the gel suffers from high viscosity and large resistance, which leads to a low capacity of the battery [12]. To address these problems, some inorganic and organic substances such as phosphoric acid [13], ionic liquids [14], siloxane derivatives [15], polyacrylamide, polypyrrole, poly (methyl methacrylate) and vaniline [16] have been explored as additives to improve the battery capacity and cycling life. Despite these achievements, it is still a challenge to develop a simple and effective method to reduce the viscosity and internal resistance of the fumed silica gel.

There are both “isolated” and “hydrogen-bonded” silanols on the fumed silica surface as indicated in reference [10]. When fumed silica is used in GEL-VRLA batteries, most of its isolated surface silanols link to form weak hydrogen bonds with each other to give a three-dimensional network gel structure, entrapping the sulfuric acid solution. Whereas, some isolated silanols form hydrogen bonds with the water molecules create a “hydration force”, which is a repulsive force against the forming of a gel. Recent reports have showed that the silica gel was readily formed with the alcohols contents, especially polyols [17,18]. In addition, it has also been demonstrated that alcohols such as methanol, ethanol can displace water molecules from the hydration sheath around silica, which is benefit for the gelation process, and the displace tendency varies with the carbon chain structure of alcohols [17]. On the other hand, the carbon chain length and hydroxyl number have great influence on the properties of the polyols. However, to the best of our knowledge, the effects of polyols and their carbon chain length of different polyols on the fumed silica gel are still none reported.

To understand the effect of polyols on fumed silica gel and reduce the high internal resistance of the fumed silica gel, we therefore undertake a fundamental study on the electrochemical properties of fumed silica gel with different polyols content.

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Besides, to find out the influence of carbon chain length of different polyols to the fumed silica gel, four kinds of polyols (propanetriol, butantetraol, pentitol and pentaerythritol) possessing similar hydroxyl contents were investigated, respectively.

2. Experimental

2.1. Physical characterization of fumed silica

The fumed silica involved in this work was Aerosil 200 produced by Degussa Co., Germany [19,20].

A JEM-2010HR transmission electron microscope (TEM) was employed to observe the morphology and microstructure of the silica particles.

2.2. Preparation of the electrode and electrolyte

The working electrode was prepared by inserting a pure lead rod into a hard plastic tube and sealing with epoxy resin. A copper wire was welded to one end of the electrode. The opposite end was used as the flat, circular working surface, with a geometric area of 0.5 cm^2 .

The gelled electrolyte was prepared by mixing (5 wt.%) Aerosil 200 fumed silica, 36 wt.% H_2SO_4 solution ($d = 1.285 \text{ g mL}^{-1}$) and the same quality (1 wt.%) of different polyols (propanetriol, butantetraol, pentitol and pentaerythritol). The mixture was dispersed in a homogenizer at the stirring rate of 4000 rpm, at room temperature (about $28\sim 30^\circ\text{C}$) to form a colloidal solution. Electrochemical testing was performed after gelation of the colloidal solution.

2.3. Electrochemical test

The cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were carried out in a three-electrode configuration with a Hg/Hg₂SO₄, K₂SO₄ (saturated) reference electrode, and a platinum sheet as the counter electrode at room temperature. The CV tests were performed using a PARSTAT 2273 electrochemical workstation (Princeton Applied Research, USA) and the EIS using GSTAT302N (Autolab, Metrohm Autolab B. V. company).

Prior to the experiment, the working electrode surface was polished with 1500# and 2000# waterproof silicon carbide papers. After washing with distilled water, the electrode was placed in the cell and cathodically polarized to remove the oxide film from its surface. CV curves were conducted over the potential range from -1.3 to -0.7 V at a scanning rate of 10 mV s^{-1} . The voltammogram of

the 25th cycle was recorded in each experiment. EIS measurements were taken at the open-circuit potential (OCP) in the frequency range $100 \text{ kHz}\sim 0.01 \text{ Hz}$, with an AC amplitude of 10 mV ; and 71 points were recorded per decade.

2.4. Morphology characterization of the gel electrolyte

The gel samples were processed in an oven at 115°C for 30 days. The morphologies were observed by a JSM-6701F field emission scanning electron microscopy (FESEM) Instruments (JEOL Ltd. Japan).

3. Results and discussion

3.1. Characterization of fumed silica

The TEM images of A200 fumed silica in Fig. 1 show that the average diameter of the A200 is about $10\sim 12 \text{ nm}$, and the Brunauer-Emmett-Teller (BET) surface area is $\sim 200 \text{ m}^2\cdot\text{g}^{-1}$ [21]. It tends to link with each other forming the chain-like aggregates. This aggregated structure is responsible for the unique properties of fumed silica.

It is reported that this kind of native, unmodified fumed silica possesses a surface covered with silanol (Si-OH) groups to the tune of $2.5 \text{ [SiOH] groups}\cdot\text{nm}^{-2}$ or equivalently about $0.84 \text{ mmol}\cdot\text{g}^{-1}$ [22], which includes hydrogen-bonded silanols and isolated silanols. When the diameter of the particles decreases to 10 nm , the surface density of the isolated silanols increases, which resulting in strong agglomerations [23]. Consequently, the dispersion of fumed silica plays an important role in the property of the colloidal system. However the dispersion of fumed silica in GEL-VRLA batteries has generally been neglected.

3.2. Dispersion of fumed silica

Fig. 2 shows the CV results of the lead electrode in gelled electrolytes without any additive. The current of redox peaks increases with agitation time and reaches a maximum at about 90 minutes, and then decreases with further increase of dispersion, which clearly indicates the moderate agitation time is better to improve the electrochemical performance of lead electrode. In order to better understand the resistance of the gel, we performed the electrochemical impedance spectra (EIS) experiments. The Nyquist and Bode curves are shown in Fig. 3. As observed, there are two time constants in the Bode curves, indicating that the charge

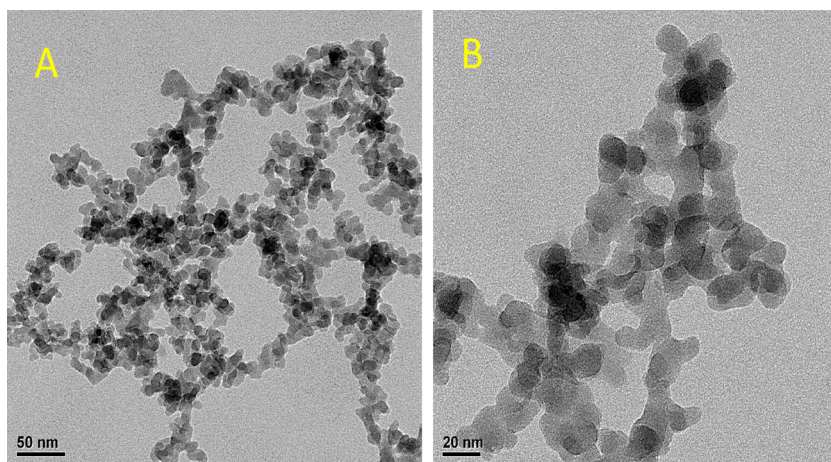


Fig. 1. TEM images of fumed silica: (A) 50,000 \times and (B) 100,000 \times .

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