



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

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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.

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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].

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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

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 cm².

The fumed silica involved in this work was Aerosil 200 (produced by Dedussa Co., Germany denoted as A200), and the colloidal silica was eka Bindzyl 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 H₂SO₄ 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 Chemie BV Co.) over a 10⁵–10⁻² 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/Hg₂SO₄, K₂SO₄ (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

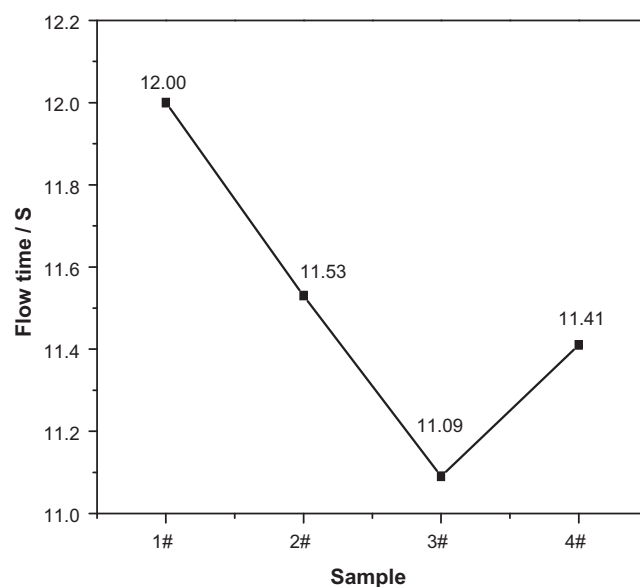


Fig. 1. Variation of gelled electrolyte liquidity with mixing ratio at room temperature (25 °C).

μC-XCF charge–discharge device (Jiangsu Golden Sail Power Technology Co., Ltd.).

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

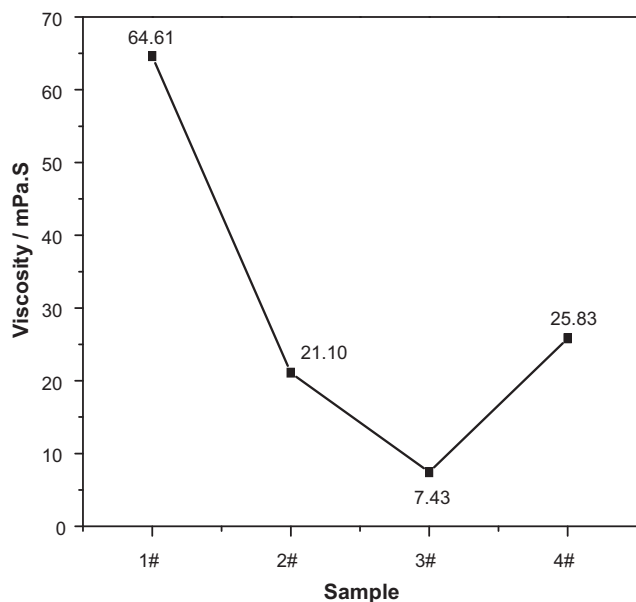


Fig. 2. Variation of gelled electrolyte viscosity with mixing ratio at room temperature (25°C).

the four CV curves in the potential range of -1.8 V to 1.5 V, which implies that the oxidation and reduction processes of the lead are similar for each gel electrolyte system.

Fig. 5 illustrates that the oxygen evolution potential is more positive for 2# mixed gel electrolyte, implying that the oxygen evolution reactions are greatly inhibited which may result from the formation of more stable three-dimensional network structure. Moreover, the corresponding peak currents of the mixed silica gel electrolyte (2#) are much lower than those of the single gelling agents (1# and 4#). And compared with 4# gel, 2# gel exhibits a lower current of oxygen evolution peak, so a conclusion can be drawn: a certain mixing proportion of gelled electrolyte can inhibit oxygen evolution to the greatest extent possible. This suggests that the new silica-based mixed gel electrolyte system will provide a lower self-discharge rate, much less water loss, and higher charge efficiency.

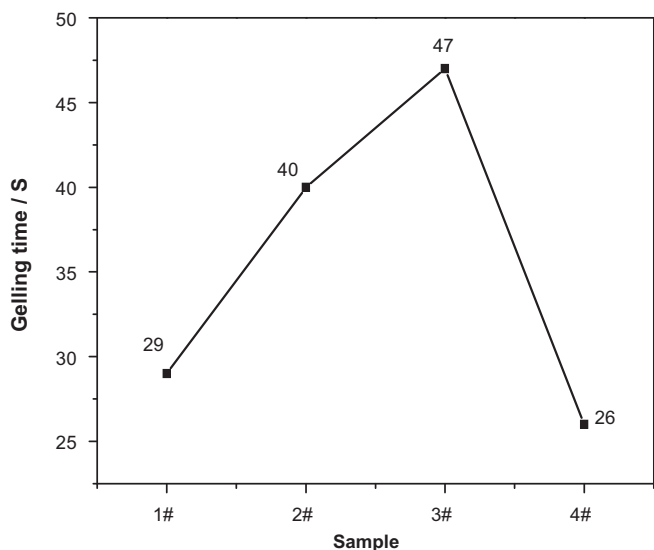


Fig. 3. Variation of gelled electrolyte gelling time with mixing ratio at room temperature (25°C).

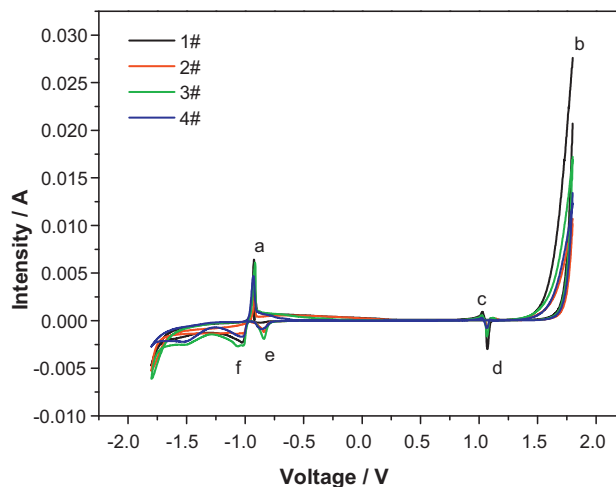


Fig. 4. Cyclic voltammograms of gelled electrolytes with varying mixing ratios at the 25th cycle (-1.8 to 1.8 V, $\nu = 10$ mV s $^{-1}$).

3.1.4. Electrochemical impedance spectra (EIS)

Fig. 6 shows the electrochemical impedance spectra of the gelled electrolyte obtained at open circuit potential. In our experiment, the open circuit potential of each samples is about at -0.98 V in the three-electrode cell, rising and falling not more than 0.01 V. A cathodic potential of -1.2 V was applied for 20 min to reduce any oxide formed on the Pb surface.

The results can be fitted well by the equivalent circuit of Fig. 7.

Where R_s represents the ohmic resistance consisting of the resistance of the corrosion products deposited on the electrode surface, the resistance of the electrolyte and the resistance of the electrical connections to the electrode, R_{ct} is the charge-transfer resistance of the rate-controlling electrochemical reaction of the corrosion process and C_d is the double-layer capacitance [18]. The plots for the four gel compositions are similar and all of them exhibit a semicircle at high frequency, indicating that charge transfer is a rate determining step. The semicircular radii for the silica-based mixed gel electrolytes are much smaller than those for the single gelling agents. It also can be seen in Fig. 8 that unequal proportions of colloidal and fumed silica (1:4) generate the lowest resistances and the most prominent result. Li et al. [17] reported that at the open circuit potential, the electrode surface is covered by many small

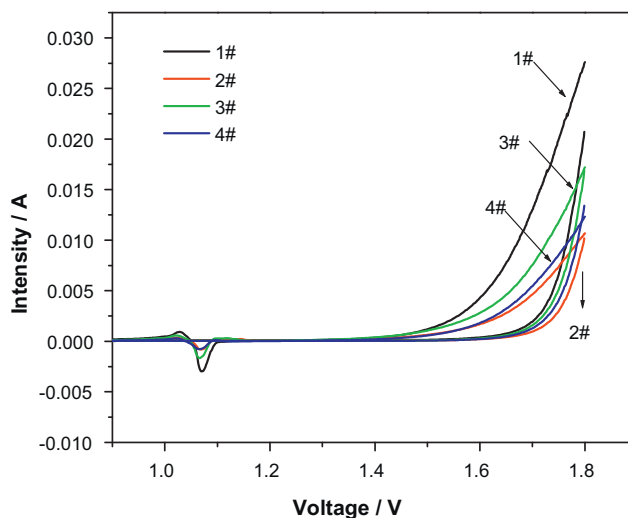


Fig. 5. Cyclic voltammograms of gelled electrolytes with varying mixing ratios at the 25th cycle derived from Fig. 4 (0.9 – 1.8 V, $\nu = 10$ mV s $^{-1}$).

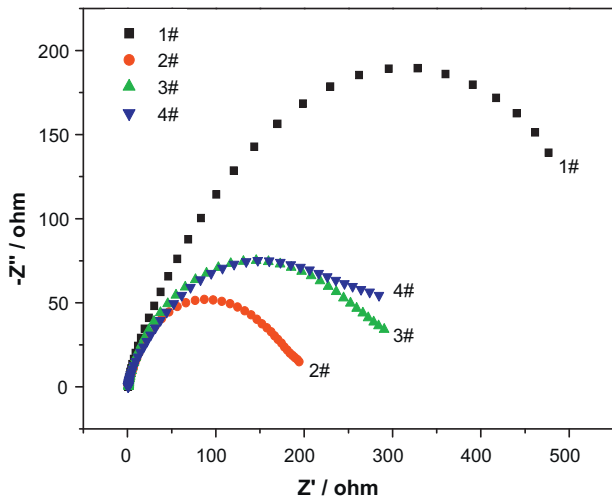


Fig. 6. EIS for gelled electrolyte prepared with different mixing ratios at open circuit potential.

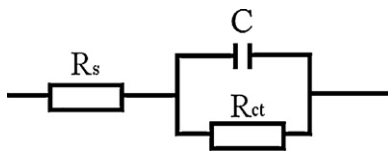


Fig. 7. Equivalent circuit used to fit the impedance data (Fig. 6).

PbSO₄ crystals. When fumed silica and colloidal silica are combined to prepare the silica-based mixed gels (2#, 3#), the growth of tiny PbSO₄ crystals into big crystals can be stimulated, which will stimulate the electron transfer. It is also found that, when gelling agents are mixed, the formation of lead sulfate from the lead is increased, implying that the activity of negative discharge reaction is improved and the capability of lead-acid battery is upraised, which is generally consistent with capacity testing below.

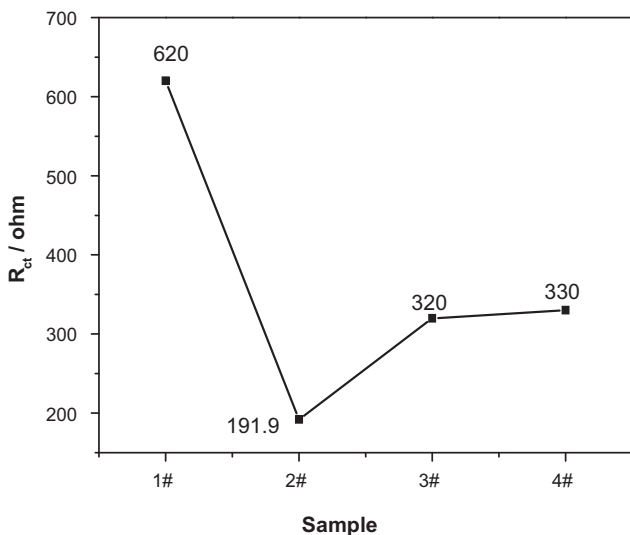


Fig. 8. Variation of charge transfer resistance (R_{ct}) with mixing ratio (derived from Fig. 6).

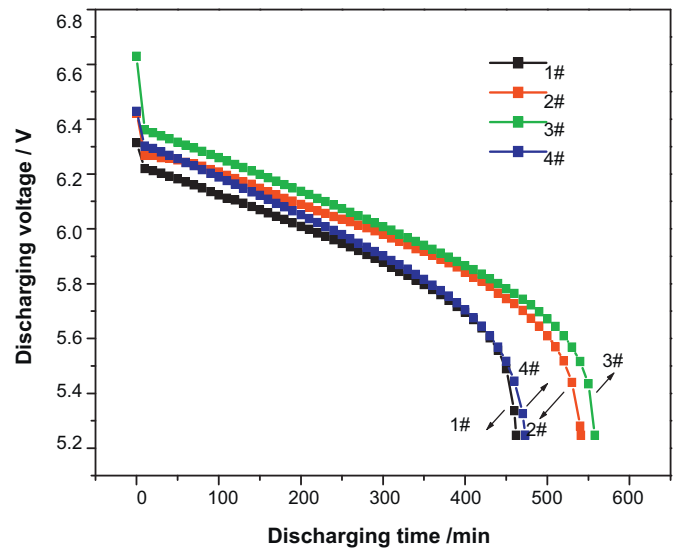


Fig. 9. Initial discharge curves (at a 10 h rate) for gel batteries (6V/4.5 Ah) using gelled electrolyte prepared with different mixing ratios.

3.2. Gel batteries performance

3.2.1. Initial capacity testing

Fig. 9 illustrates the initial discharge curves at a 10 h rate for gel batteries (6V/4.5 Ah) having electrolytes with different mixing ratios of the two silicas. Different gel batteries are both assembled in the same conditions. The mixed gel batteries exhibit a higher discharge voltage and larger discharge capacity than those with a single gellator. The micropores in silica-based mixed gel electrolytes may provide an enhanced pathway for diffusion of reactive species between the positive and negative plates, thereby reducing the concentration polarization during charge and discharge and consequently providing superior rate capability.

3.2.2. Charge retention ability testing

From the measurement of charge retention (Table 2), it is found that the charge retention ratio of mixed gel batteries was obviously more than that of batteries with single gelling agent at 0.1 C after being stored for 28 days at 25 °C.

3.3. Morphological analysis of gels

Scanning electron micrographs of fumed silica, dry colloidal silica and dried gel electrolytes with different mixing ratios are presented in Fig. 10. Fumed silica has a continuous and porous network with uniform particles of 20–30 nm, whereas the dry colloidal silica particles are prone to aggregate and display a predominantly spherical shape; their particles are 70–80 nm in diameter. It can be seen from Fig. 10 that after gelling with sulfuric acid, both the mixed silica-based (sample 3) and gel fumed silica-based (sample 1) electrolytes display three dimensional network structures due to inter- or intra-particle crosslinking. The particles are prone to aggregate

Table 2

The charge retention ability of gel battery with different mixing proportional electrolyte.

Sample	Capacity before 28 days	Capacity after 28 days	Charge retention ratio
1#	3.7670	3.5693	94.75%
2#	4.0034	3.9771	99.34%
3#	4.0875	3.9064	95.57%
4#	3.7153	3.4854	93.81%

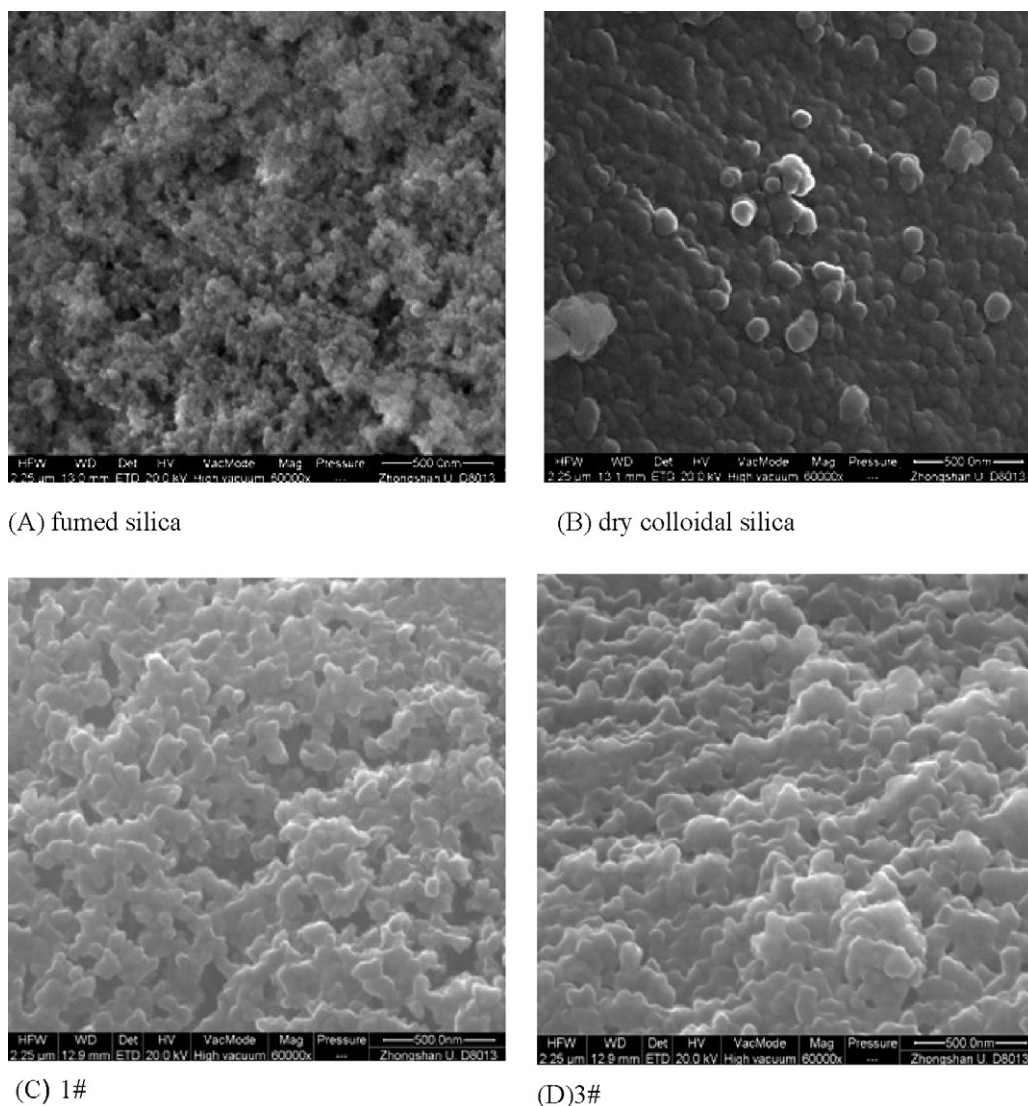


Fig. 10. SEM images of fumed silica (A), dry colloidal silica(B), sample 1# (C) and sample 3# (D).

and have irregular shapes. The reticulate structure is stronger in the mixed silica-based gel electrolyte.

Fig. 11 gives TEM images of fumed silica and the dry gelled electrolyte of sample 3. The average diameters of the fumed silica particles are consistently in the 10–20 nm range, and the interaction between particles results in the agglomerates of fumed silica. The xerogel of sample 3, with a moderate average particle size, possesses a three-dimensional network allowing formation of a uniform gel structure. The results coincide with the SEM measurements.

3.4. Xerogel analysis

3.4.1. Zeta potential

Fig. 12 shows the zeta potentials of the gelled electrolytes. The zeta potential is usually used to understand the electrokinetic properties of interfaces [19]. Generally, the higher the absolute value of the zeta potential, the greater the stability of the colloidal dispersion system. The stability of the gelled electrolyte has a significant effect on the gel battery performance, since stable uniform dispersed gelled electrolyte is beneficial for the formation of a well-balanced three dimensional gel structure, which is helpful for the batteries in the maintenance of a good gel structure through the

charge and discharge process, as well as a good extension of battery life.

It can be seen that the zeta potential value of mixed silica gel electrolytes is higher than that for their single component counterpart, the highest value occurring at an equal mixing ratio and being more than 50% higher than single component. The maximum zeta potential for mixed gel electrolyte appeared in Fig. 12 might be explained by assuming that: fumed silica and colloidal silica have the same colloid nucleus (SiO_2). Due to the concentration of sulfuric acid used in our experiments, the pH value of the electrolyte is lower than the isoelectric point of silica (<2), which results in the sols being positively charged due to the ionization of the silanol groups ($-\text{SiOH}_2^+$). So a gel electrolyte with any gelling agent was prepared, then a hydration shell will exist on the surface of colloid nucleus. When the two gelling agents were prepared to a mixed gel, the two single colloidal with identical colloid nucleus incorporate under the protection of hydration shell, forming a mixed sol with more positive charge on the surface of sol particles, thus leading to a greater zeta value.

3.4.2. FTIR spectrum

Xerogels of the electrolytes with different mixing ratios were also characterized by infrared absorption spectroscopy (Fig. 13).

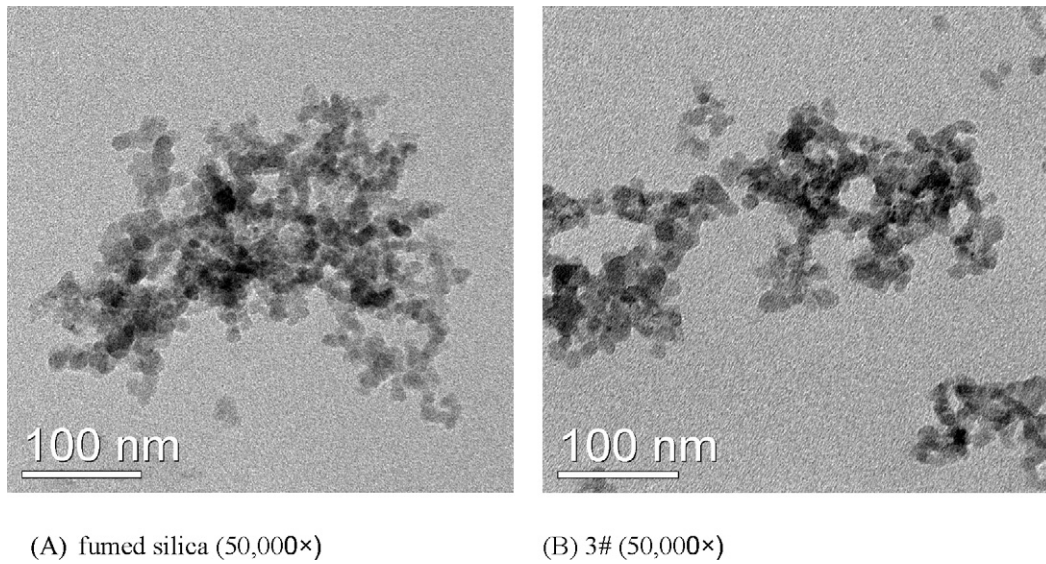


Fig. 11. TEM images of fumed silica (A) and dry gelled electrolyte 3# (B).

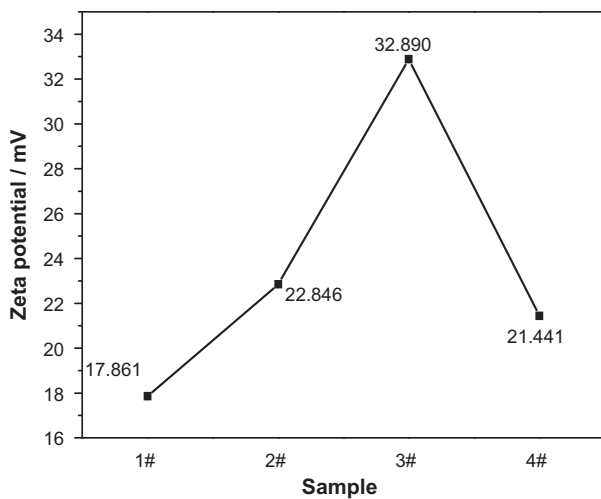


Fig. 12. Variation of zeta potential of dried gelled electrolyte with various mixing ratios.

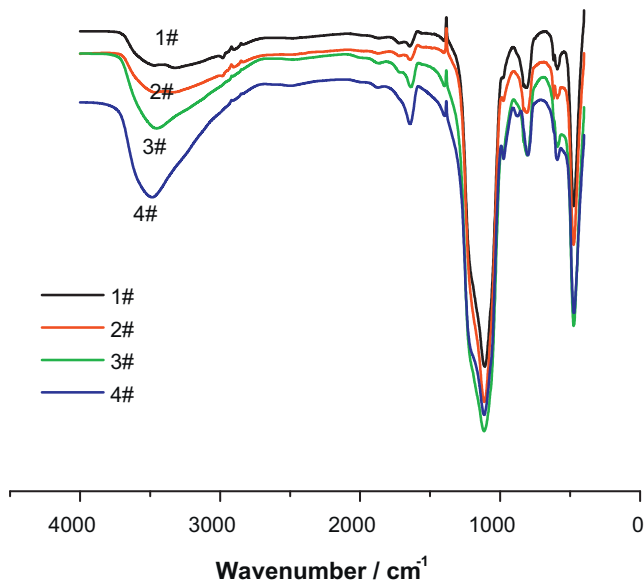


Fig. 13. IR spectrograms of dry gelled electrolyte with different mixing ratios.

The absorption peak at 3428 cm^{-1} corresponds to $-\text{OH}-$ groups in water molecules. The broad band at 1110 cm^{-1} substantiated the hydrolysis and formation of $\text{Si}-\text{O}-\text{Si}$ bonds. $\text{Si}-\text{O}$ covalent bond was found at 470 cm^{-1} . The peaks were roughly identical for all electrolytes, and consistent with those of silica in the standard spectra [20], indicating that the fumed and colloidal silica are merely physically mixed.

3.4.3. Thermogravimetric analysis (TGA)

Fig. 14 provides TG curves of gelled electrolytes dried under the same conditions (120°C for 30 days). There are still quality losses before 120°C though the samples have been treated before. Since the sulphuric acid and water has been tightly wrapped in the three-dimensional gel structure when a gel electrolyte formed, it is not easy to evaporate the inner water from sulfuric acid solution completely, thus water loss took place below 120°C .

The mass of the xerogels decreases before 500°C , remaining relatively stable beyond 500, but the mass loss of the mixed gel electrolytes is much greater than that with a single gelling agent, indicating that the mixed gel electrolyte can form a more stable and

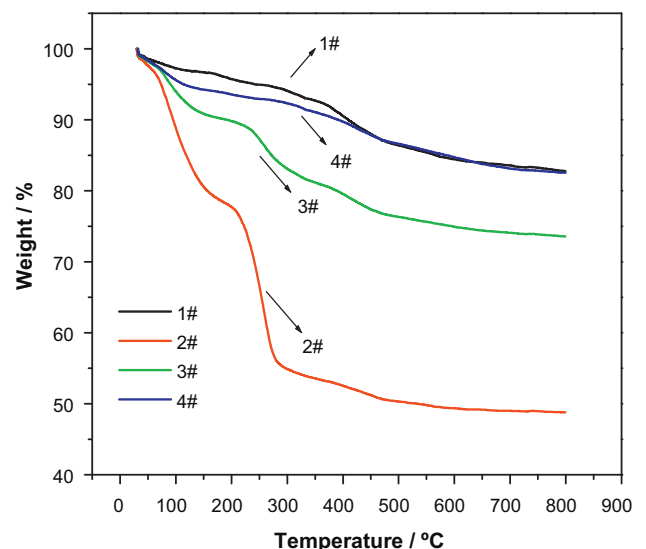


Fig. 14. TG curves of dry gelled electrolyte with different mixing ratios.

more porous three-dimensional network structure which retains more sulfuric acid and water molecules, which is consistent with the zeta potential and SEM measurements of the mixed gel electrolyte.

4. Conclusions

Different gel formulations of VRLA battery for energy storage systems and advanced automotive applications have been studied to determine both their physical (liquidity, viscosity, gelling time, zeta potential and IR, SEM, TEM, TGA) and electrochemical (CV, EIS and initial capability) characteristics.

The mixed colloidal and fumed silica-based gelled electrolyte show better liquidity, longer gelling time and greater stability than its counterparts with a single gelling agent. Mixing of gelators can effectively suppress oxygen evolution reaction, reduce the resistance of charge transfer at open circuit potential and increase initial capacity of gel batteries.

Mixed gel electrolytes can form a stronger three-dimensional network structure than electrolytes with a single gel. Mixing of the gelling agents is of purely physical nature, but the mixing in a certain proportion allows formation of an appropriate three-dimensional gel structure that can retain more sulfuric acid. Therefore the novel gel electrolyte, a blend of colloidal and fumed silica, has great potential for application in the gelled electrolyte valve-regulated lead-acid batteries.

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