Application of High Modulus Silica Sol Electrolyte in Lead-acid Battery

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Abstract: High modulus silica sol of n/m=52 sodium silicate aqueous sol was prepared by compressing and filtering sodium silicate aqueous solution without loss of SiO2 content. The SiO2 content can increase from 14.2% to 30%. The high modulus silica sol are mixed with acidic water to prepare a high modulus silica sol electrolyte, which is then produced into 6-DZM-20 Ah electric bicycle batteries. A combination of intermittent current-changing charging process, simple electrolyte production process, brings about reduced energy consumption and cost. The battery with the high modulus silica sol electrolyte shows enhanced stability, deep cycling performance, long service life, strong resistance to harsh environments, low self-discharge rate, low floating current, and excellent heat resistance.

1. Introduction
The non-flowing electrolyte technology in the maintenance-free sealed lead-acid battery refers to the electrolyte existing in the adsorbent glass-like form, so that the electrolyte does not overflow under the specified conditions and does not need to be refilled [1]. With proper stirring, the colloidal electrolyte can change to a low viscosity. After the battery is sealed, the colloidal particles of small molecules collide and combine with each other due to thermal motion. These colloids further polymerizes to a three-dimensional spatial network structure with silica as the skeleton, which can provide the channel for the oxygen cycle under fast charging, and the polymer becomes hard, thereby forming a strong silicon gel [2]. The electrolyte in the colloidal electrolyte battery is homogeneously distributed in the colloidal network structure, and there is no concentration stratification of acid electrolyte in the vertical direction.

The total electrolyte amount in the gel battery is more than that in the conventional AGM battery. The battery has better charge acceptance performance and less water loss. Therefore, the gel battery is unlikely to cause thermal runaway, and the high current discharge performance is excellent. The recovery performance after deep discharge is significantly better than the low-liquid valve-controlled battery [3]. In this paper, a electrolyte with high modulus silica sol will be proposed in a cost and energy effective manner.

2. Experimental

2.1. Characteristics
The gel battery uses silica sol to fix the sulfuric acid electrolyte. In the gel battery, the role of the silicon gel is as follows: ① fixing the sulfuric acid electrolyte so that the electrolyte is not layered to ensure the stability and reliability of the battery performance; ② storing a large amount of sulfuric acid electrolyte to ensure that the gel battery is a liquid-rich design; ③ preventing the positive electrode active material from falling off, and therefore extending the service life of the battery; ④ suppressing the battery sulfation especially under deep discharge, resulting in better discharge performance, and longer service life.

The composition and structure of the silica sol electrolyte have a crucial influence on the performance of the battery. The composition and manufacturing process of the silicon gel electrolyte is the core and key technology of the gel battery [4, 5].

2.2. Preparation

The n/m=2 raw material sodium silicate aqueous solution (mNa₂O·nSiO₂) were de-watered without loss of SiO₂ content. The process of compression filtration will remove Na₂O component from the raw material to reach the level of n/m=52. Through this compression filtration, SiO₂ content increased from 14.2% in raw materials to 30%. Its oxygen electronegativity is close to the SiO₂ aqueous dispersion slurry, but it overcomes the shortcomings of SiO₂ nano powders. The latter was inclined to coarsening and stratification after adding acid water.

The high modulus silica sol electrolyte was prepared by mixing 94.4% acid water, 1% sodium silicate aqueous solution, 4.6% water and a small amount of OES additives. The acid water, above mentioned, is composed of 36.1% H₂SO₄, 1.5% Na₂SO₄, 0.1% SnSO₄ and 0.05% CMC.

3. Specifications of Electrolyte

Table 1. Specification comparison of different electrolytes

|                             | High modulus silica sol electrolyte | Conventional electrolyte |
|-----------------------------|-------------------------------------|---------------------------|
| Average particle size of electrolyte (nm) | 676.6                               | 803.8                     |
| Average particle size of electrolyte after heat treatment at 45 °C (nm) | 746.8                               | 1145                      |
| Electrolyte layering time at 25 °C (h) | >72                                 | 24                        |
| Electrolyte layering time at 45 °C (h) | 36                                  | 4                          |
| Specific heat capacity (J·g⁻¹·K⁻¹) | 3.21                                | 3.13                      |
| Surface Tension at 25 °C (mN·m⁻¹) | 57.2                                | 63.3                      |
| Surface Tension at 45 °C (mN·m⁻¹) | 53.1                                | 56.6                      |
| Hydrogen evolution potential (V) | -1.693                              | -1.532                    |
| Oxygen evolution potential (V) | 1.691                               | 1.669                     |

The specification of the high modulus silica sol electrolyte are compared with those of conventional electrolyte in Table. 1. The particle sizes of the high modulus silica sol electrolyte before and after heat treatment are both smaller than those of the conventional electrolyte. The size stability of the high-modulus silica sol electrolyte under heat treatment is also better. It is well known that the specific heat capacity of the electrolyte is inversely proportional to the temperature rise of the battery during operation. The larger the specific heat capacity value, the smaller the temperature rise of the battery. The smaller temperature rise of the battery helps to extend the battery life. At 25 °C, the surface tension of the high-modulus silica sol electrolyte is lower than that of the conventional electrolyte. The high-modulus silica sol electrolyte companies with fewer bubbles on the surface after the initial acid addition into the battery, which means easier controlling electrolyte quantity. At 45 °C (simulating the temperature of battery formation), the surface tension of the high modulus silica sol electrolyte is also smaller. It can be observed that the bubbles on the surface of the acid kettle are more likely to break up and not accumulate during the formation, and the bubbles remaining in the battery are also more likely to flow up.
The cyclic voltammetric curves of the two electrolytes are measured, and the high modulus silica sol electrolyte is more difficult for hydrogen evolution and oxygen evolution reactions.

![Figure 1. Cyclic voltammetric curves](image)

### 4. Application and Advantages

#### 4.1. Battery manufacturing and testing standards

The positive grid alloy adopts Pb-Cd-Sn alloy, which is currently considered as the best alloys suitable for deep cycle charging and discharging with large current. The negative grid adopts the conventional Pb-Ca alloy. The positive active material (PAM) is improved with a small amount of stannous sulfate, pore-forming agent, 3%–5% PbO₂ and conductive substance based on conventional PAM. The apparent density of PAM is 4.30±0.05 g·cm⁻³. The negative active material (NAM) is improved with barium sulfate 1.0%, acetylene black 0.5% based on conventional NAM. The apparent density of NAM is 4.40±0.05g·cm⁻³. The curing is carried out with the curing temperature increasing step by step under high humidity conditions, and finally dried at 80 °C. The PbO₂ content in PAM is controlled above 90%wt. The separator adopts AGM type with a thickness of 400±10 μm. The pole group is assembled into a 6-DZM-20 battery with 7 positive electrodes and 8 negative ones.

Intermittent current formation is adopted to activate battery capacity. The maximum charging current is 4 A. After continuous charging for 8 hours, the battery is allowed to stand still. The net charging capacity is 187.5 Ah, and the activation charging rate is reduced to 2.66 times. The single circuit reduces the charging capacity by 16 Ah, with each circuit saving 5 kW·h of electricity compared with the conventional process.

The initial capacity test after battery activation shows that the average sulfuric acid content of the high modulus silica sol battery is 1328 g, discharge time is 126 min, and the initial capacity is 21 Ah. Calculations show that the PAM utilization rate is 29.8%, the NAM utilization rate is 35.4%, and the sulfuric acid utilization rate is 83.7%.

3 times 2 hr capacity test, low temperature capacity test, normal temperature capacity, and charge acceptance test have been conducted according to Chinese Standard GB/T 22199-2008 "Sealed Lead-acid Batteries for Electric Mopeds" for the batteries with high modulus silica sol electrolyte. The main results are listed as follows:

1. The 2 hr capacity should reach 100% of the rated capacity within three cycles, with the voltage difference being not more than 700 mV.
2. Under -15 °C, first low temperature discharge time is not less than 85 min.
3. High current discharge duration is not less than 20 min.
4. The ratio of the charging current value Ica to C2/10 after 10 min should not be less than 2.

Corresponding data are shown in Table 2.
Table 2. Comparison of battery performance test

|                        | High modulus silica sol battery | Conventional battery |
|------------------------|---------------------------------|-----------------------|
|                        | Capacity: 22.83 Ah              | Capacity: 22.50 Ah    |
|                        | Voltage difference: 385 mV      | Voltage difference 459 mV |
|                        | Discharge time: 101 min         | Discharge time: 94 min |
| ①                      | Capacity: 16.83 Ah              | Capacity: 15.67 Ah    |
| ②                      | 28 min                          | 26 min                |
| ③                      | I_{ca}=4.95 A; C2/10=2.62       | I_{ca}=5.23 A; C2/10=2.48 |

4.2. Advantages

4.2.1. Uniformity and high-efficiency. The electrolyte is not layered, the sulfuric acid is evenly distributed, the charging efficiency and active material utilization rate are higher, the discharge capacity is better, and the service life is longer. In a conventional lead-acid battery, especially a battery with a long length, the density of sulfuric acid electrolyte are different due to the density difference of pure sulfuric acid and water. That is, the electrolyte is layered in vertical direction. Insufficient acidity is on the top of the electrode plate, which results in unsatisfying charging capacity. The electrolyte layering will also bring about the active material overcharge phenomenon[6]. On the other hand, the bottom will be difficult to charge due to the too much sulfuric acid. Due to the concentration difference between the upper and lower parts the working voltage and capacity of the battery decrease. Too high density of sulfuric acid at the bottom will also accelerate the corrosion at the bottom of grid and the sulfation of the electrode plate, thereby shortening the battery life. In the high modulus silica sol electrolyte battery, the electrolyte is effectively fixed in the gel of the three-dimensional network with SiO₂ as the skeleton. During the charging process, it can effectively avoid sulfuric acid deposition and make sulfuric acid density distribution homogeneous. The active substances can be fully utilized, which means a higher charge/discharge capacity.

4.2.2. Suppression of battery aging. High modulus silica sol electrolyte enables deep discharge of lead-acid batteries, suppresses the formation of large particles of lead sulfate, and extends the battery's cycle life. The conventional sealed lead-acid battery must be in time recharged after deep discharge. Otherwise, the lead sulfate generated on the electrode plate will gradually be converted from small active particles into large inert particles. In that case, the sulfate of the negative plate will occur, which decreases the battery capacity. The high modulus silica sol electrolyte has a good inhibitory effect on the sulfate coarsening. The presence of silicon gel on the positive plate also suppresses the shedding of the positive electrode active material and extends the service life of the gel battery.

4.2.3. Thermal stability. Battery with high modulus silica sol electrolyte can withstand the impact of ambient temperature changes and is not prone to thermal runaway and water loss. Table 2 also shows that the battery with high modulus silica sol electrolyte has better low-temperature and large-current performance than conventional batteries. This may be due to the adsorption of the silicon gel reducing the supersaturation of lead sulfate in the liquid layer near the electrode plate and reducing the coverage of the negative electrode surface, thereby improving the low-temperature performance of the gel battery. The specific heat capacity of the colloid is larger, with more electrolytes contained in the battery. Under the same heat absorption, the temperature rise of the battery is lower, while internal heat capacity of the high modulus silica sol battery is relatively large. When the battery is float-charged at the same voltage, the float current is smaller, and also is the heat generated. The gel in the battery fully contacts with the battery tank, and the thermal conductivity of the electrolyte is better, which is beneficial to the heat diffusion, thereby reducing the risk of heat runaway of the battery [7]. The reasons for the low water loss are listed as following: 1) when charging at the same current,
the charging voltage is low, with small water decomposition; 2) due to the presence of colloids, the vapor pressure of water, together with the water evaporation is reduced; 3) when the gas is precipitated, the colloidal electrolyte has a blocking effect on the gas escape, reducing acid fog, reducing the possibility of battery drying failure, and prolonging the service life[8].

Table 3. Water loss during battery cycling

|                        | High modulus silica sol battery | Conventional battery |
|------------------------|---------------------------------|----------------------|
| Weight loss after 10 cycles/g | 0.2                             | 0.5                  |
| Weight loss after 20 cycles/g | 0.2                             | 0.3                  |
| Weight loss after 30 cycles/g | 0.1                             | 0.2                  |

4.2.4. **security and better quality.** Battery with high modulus silica sol electrolyte is not prone to micro short circuit and has a longer service life. After dissecting the two experimental batteries, the appearance of the polar plates are observed, as shown in Figure 2. A large number of white spots can be observed on the lower part of the positive plate of the conventional battery. The battery with high modulus silica sol electrolyte adopts a liquid-rich design. Usually, the sulfuric acid electrolyte is excessive. At the end of the battery discharge, there is still a considerable amount of sulfuric acid electrolyte in the battery. Because the concentration of lead ions in the battery is always low, it is not easy to generate lead sulfate dendrites[9]. In the gel battery, due to the presence of gel, sulfuric acid is evenly distributed in the battery. There is no large concentration difference between the upper and lower parts of the polar plate, with the reduction of lead being relatively uniform on the polar plate, and it is not easy to form lead dendrites. Large part of sulfuric acid electrolyte is adsorbed in the high modulus silica sol of the batteries, which leads to a lower apparent acid density than conventional batteries. At a lower acid density, the corrosion rate of the grid is lower. Moreover, the battery's charge acceptance is also significantly improved. The silicon gel electrolyte enables the battery to have better deep discharge recovery performance and also can inhibit the softening and shedding process of PAM, thus greatly extending the service life of the battery.

![Figure 2.](image)
a: Polar plate after dissection of high modulus silica sol battery.
b: Polar plate after dissection of conventional battery.

5. **Conclusions**
The high modulus silica sol can fix the sulfuric acid electrolyte in lead-acid battery. Combined with the intermittent current formation process, the high-modulus silica sol battery proposed in this study has a simple and low cost process of electrolyte production, and reduces energy consumption during the activation process, and shows better low-temperature performance, deep discharge recovering ability and longer service life.

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