

Effect of silica soot on behaviour of negative electrode in lead–acid batteries

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Abstract

The influence of the content of SiO₂ (in the form of a soot) on the capacity and the self-discharge of lead–acid batteries, as well as on the structure of gelled-electrolyte, is studied in detail by means of cyclic voltammetry (CV), electrochemical impedance spectroscopy and scanning electron microscopy. The content of SiO₂ and the viscosity of the gelled-electrolyte are important factors which affect the capacity of batteries. A comparison of cyclic voltammograms indicates a change in the electrochemical behaviour of the lead electrode in the presence of SiO₂. The reaction resistance increases as a function of the SiO₂ content. The mechanism of the effect of the content of silica soot on electrode capacity and on the performance of gelled-electrolyte is discussed. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The electrolyte of valve-regulated lead–acid (VRLA) batteries with gelled-electrolyte is a type of thixotropic colloid in a ‘soft solid’ state. It is prepared by mixing silicon gel or silica soot with sulfuric acid, in which the silicic acid condenses and forms a web with a framework texture which incorporates H⁺ and SO₄²⁻ ions. Compared with flooded-electrolyte batteries, gelled-electrolyte batteries have advantages in terms of: (i) convenient transportation; (ii) use in any orientation; (iii) no leakage of sulfuric acid, (iv) no acid stratification; (v) maintenance-free operation and (vi) long service life. The stability of the gelled-electrolyte, however, is unsatisfactory; the type and the content of gelling agent and the concentration of sulfuric acid can affect the performance of the gelled electrolyte. It is necessary, therefore, to determine the influence of these factors on the structure of the gel and on the electrochemical performance of the lead electrode in gelled-electrolyte batteries. In our previous work [1], the effect of the type of gelling agent on the performance of gelled-electrolyte was discussed. The influence of the content of SiO₂ on the thixotropy, the conductivity of gelled-electrolyte, and the capacity of lead–acid batteries is also known to be significant. In this paper, the effects of the content of SiO₂ contained in the gelled-electrolyte on the

electrochemical behaviour of the lead electrode are studied by means of electrochemical techniques. The mechanism of the effect of the content of silica soot on electrode capacity and the performance of gelled-electrolyte is also discussed.

2. Experimental

2.1. Electrode and electrolyte preparation

The working electrode was a flat lead electrode that was prepared by inserting a pure lead rod into a hard plastic pipe in which epoxy resin was filled for sealing. A copper wire was welded to one end of the electrode. The opposite end was used as the working electrode surface and had a geometric area of 0.283 cm².

The gelled-electrolytes were prepared by means of mixing silica solution which was obtained by blending silica soot and double-distilled water with sulfuric acid (relative density 1.60) in various proportions, with the acid concentration kept the same.

2.2. Electrochemical measurements

Electrochemical experiments were carried out in a three-electrode, single compartment cell with a Hg/Hg₂SO₄, K₂SO₄ (saturated) reference electrode and a platinum wire counter electrode. The experiments were performed at

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room temperature (20 ± 1 °C) with a M273 Potentiostat–Galvanostat (EG & G).

Prior to the experiment, the working electrode was polished with 1200[#] and 4000[#] waterproof silicon carbide paper. After washing with double-distilled water, the electrode was placed in the cell and cathodically polarized to remove the oxide film on its surface. Cyclic voltammetry (CV) was conducted over the potential range from -1.3 to -0.7 V at a scanning rate of 10 mV s^{-1} . The voltammogram for the 10th cycle was recorded in each experiment. Impedance measurements were taken at open-circuit potential (OCP) by means of a M388 Electrochemical Impedance System (EG & G) in the frequency range $100 \text{ kHz} - 0.005 \text{ Hz}$ and with amplitude of 10 mV .

2.3. Scanning electron microscopy

Scanning electron micrographs of the gelled-electrolytes were obtained with a JSM-6330F field emission scanning electron microscope.

3. Results and discussion

3.1. Cyclic voltammetry

Cyclic voltammograms for a lead electrode in gelled-electrolyte containing different SiO_2 content are shown in Fig. 1. The oxidation and reduction capacity of the lead electrode decreases with increasing SiO_2 content. The relationship between oxidation or reduction capacity and SiO_2 content is presented in Fig. 2. The observed behaviour is probably due to the following reasons. First, as the amount of SiO_2 contained in the gelled-electrolyte increases, the action of silica gel in adsorbing the polar ions H^+ and SO_4^{2-} strengthens, so the reaction activity of H^+ and SO_4^{2-} ions is reduced. This will lead to a decrease in the oxidation and reduction capacity of the lead electrode. Second, the gelling agent used in the experiments is silica soot which has a small

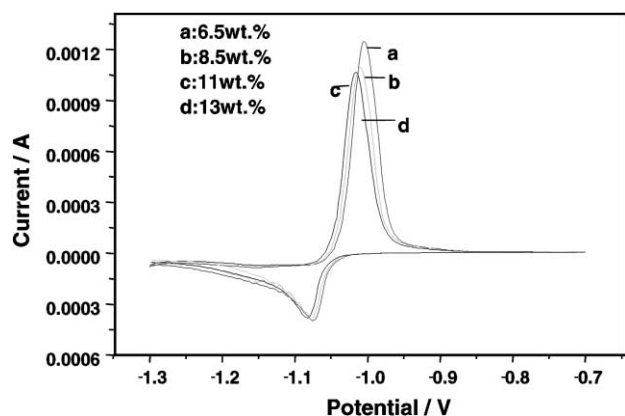


Fig. 1. CV for lead in gelled-electrolyte with different SiO_2 content (wt.%).

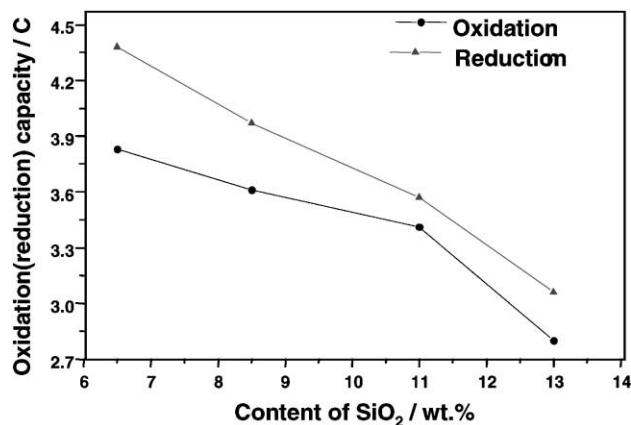


Fig. 2. Relationship between oxidation or reduction capacity of lead and SiO_2 content.

granular size and thus, forms a gel with a three-dimensional web structure [2], that encompasses particles with each composed of a SiO_2 colloidal nucleus and an adsorption layer [3]. The increasing content of SiO_2 in the gelled-electrolyte causes supersaturation of the solution. As a result, a great deal of colloidal nuclei grow and lead to the formation of small colloidal particles. This is beneficial to the formation of a fine pore structure, and thus explains the compactness of the web structure. This makes the transportation of reactants inhibited, and the internal resistance is increased and the capacity of electrode is decreased accordingly. A comparison of the oxidation (Q_a) and the reduction (Q_c) capacity of the lead electrode in different gelled-electrolytes, however, shows that the proportion of oxidation and reduction capacity is enhanced as the content of SiO_2 increases, see Table 1. This indicates that increasing SiO_2 content can help improve the percentage utilization of lead active material. This may be attributed to the formation of PbSiO_3 on the surface of lead electrodes in gelled-electrolyte. It has been reported [4] that crystals of PbSiO_3 and PbSO_4 have similar dimensions, and it is therefore likely that PbSiO_3 ‘infringes’ the crystal region of PbSO_4 and disrupts the continuity of the PbSO_4 film so that the penetrability of the film is improved. This makes it possible for the active-material within the bulk of the lead electrode to take part in the reaction, and the percentage utilization of lead active-material is thereby improved. The data in Table 1 show that the oxidation peak potential (E_{pa}) of the lead electrode is shifted slightly towards more negative values

Table 1
CV measurements for four kinds of gelled-electrolytes

SiO_2 content (wt.%)	E_{pa} (V)	I_{pa} (mA)	E_{pc} (V)	I_{pc} (mA)	Q_a/Q_c (%)
6.5	-1.005	-1.247	-1.076	0.398	87
8.5	-1.011	-1.092	-1.076	0.394	90
11	-1.016	-1.067	-1.082	0.383	95
13	-1.016	-0.8653	-1.082	0.374	97

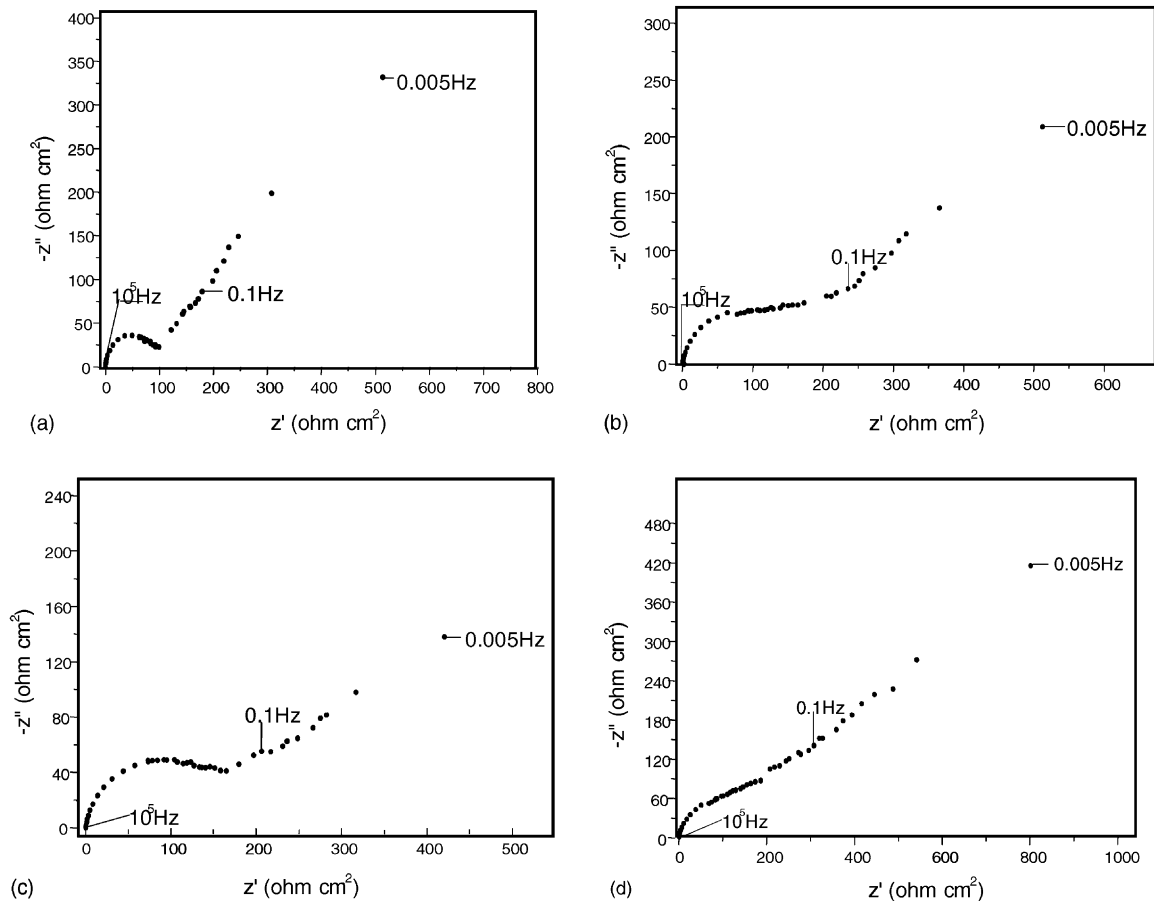


Fig. 3. Impedance spectra of lead electrode in gelled-electrolyte with different contents of SiO₂: (a) 6.5 wt.%, (b) 8.5 wt.%, (c) 11 wt.%, (d) 13 wt.%.

with increase in SiO₂ content, and this implies that SiO₂ increase assists slightly the oxidation of lead to PbSO₄ and thus causes a rise in capacity. With increasing content of SiO₂ in the gelled-electrolyte, however, the viscosity of the gelled-electrolyte is enhanced resulting in a reduction in both the charge and the discharge capacities. In the work reported here, this latter and unfavourable effect possibly dominates so that there is an overall decrease in the oxidation and reduction capacities.

The thixotropy of the gelled-electrolyte is strengthened with increasing SiO₂ content. It has been shown [5] that increase in the SiO₂ content can shorten the distance between the colloidal particles with other conditions remaining the same. This feature encourages the formation of hydrogen bonds. The good thixotropy of gelled-electrolyte can be ascribed to the weakness of the hydrogen bonds. On the other hand, with increasing content of SiO₂ in the gelled-electrolyte, the gelling time shortens and the capacity tends to diminish. Therefore, the SiO₂ content of gelled-electrolytes should be carefully controlled.

3.2. Impedance measurements

Impedance measurements are widely used to analyze the interfacial processes, the variation in the internal resistance,

the state of charging and the residual capacity of lead–acid batteries [6–10]. This method is accurate, fast and non-destructive in nature [11]. In this study, the influence of gelled-electrolyte on the surface of the lead electrode is studied by the impedance method at OCP. The Nyquist plots for a lead electrode in gelled-electrolyte with different SiO₂ content are shown in Fig. 3. A high frequency semi-circle (arc) and low frequency straight line are observed in all cases. The radius of high frequency semi-circle increases regularly with increasing SiO₂ content. This demonstrates that the electrochemical performance of the lead electrode differs in the different gelled-electrolytes. According to impedance theory [12], the radius of the high frequency semi-circle in the Nyquist plot represents the charge-transfer resistance of an electrochemical process, which reflects the resistance to self-discharge of the lead electrode. The low

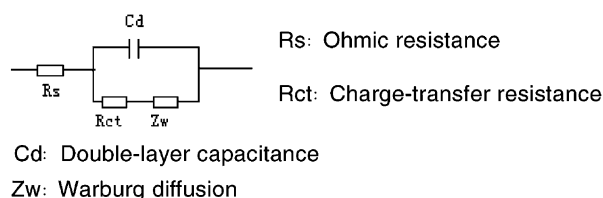


Fig. 4. Equivalent circuit.

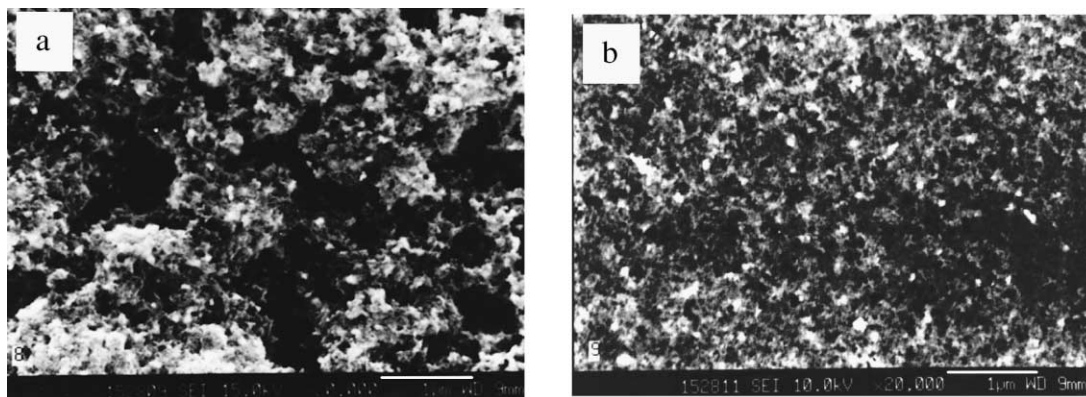


Fig. 5. Scanning electron micrographs for gelled-electrolyte containing: (a) 11 wt.%SiO₂ (b) 13 wt.%SiO₂.

frequency linearity indicates a process which is mass-transfer controlled. The intercept of the semicircle with the real axis indicates mainly the ohmic resistance of the solution.

It is evident from Fig. 3 that the electrochemical behaviour of a lead electrode in gelled-electrolyte at OCP includes charge-transfer as well as mass-transfer processes. In our opinion, this represents the self-discharge reaction of lead electrode and the diffusion processes of H⁺ and SO₄²⁻ ions via the PbSO₄ film formed on the surface of the lead electrode. The equivalent circuit of the data in Fig. 3 is given in Fig. 4.

Parameters derived from the impedance data are listed in Table 2, the values of the double-layer capacitance (C_d) are calculated according to the procedure reported in [13]. In Table 2, R_s is the resistance of the gelled-electrolyte, R_{ct} is the charge-transfer resistance and C_d is double-layer capacitance. The results show that the ohmic resistance and the charge-transfer resistance increase with increasing SiO₂ content, but the value of the double-layer capacitance trends to decrease. This can be explained in terms of the enhanced viscosity of the gelled-electrolyte, and that the web structure of the gel becomes too compact with increasing SiO₂ content. On the other hand, the diffusion of H⁺ and SO₄²⁻ ions to the surface of the electrode becomes more limited. This makes the self-discharge reaction on the surface of the lead electrode ($\text{Pb} + \text{H}_2\text{SO}_4 \rightarrow \text{PbSO}_4 + \text{H}_2$) become more difficult. With charges passing through the double-layer, the double-layer capacity is reduced.

3.3. Scanning electron microscopy

Scanning electron micrographs of samples of gelled-electrolyte containing different SiO₂ content are given in

Table 2
Effect of different gelled-electrolytes on impedance properties of lead electrode

SiO ₂ content (wt.%)	R_s ($\Omega \text{ cm}^2$)	R_{ct} ($\Omega \text{ cm}^2$)	C_d ($\mu\text{F cm}^2$)
6.5	0.34	108	796
8.5	0.52	138	803
11	0.52	168	716
13	0.69	204	537

Fig. 5. These clearly demonstrate the marked effect of SiO₂ content on the structure of the gelled-electrolyte. The micrograph of the gelled-electrolyte containing 11 wt.%SiO₂ shows that the colloidal particles and pores are both larger than those in the gelled-electrolyte with 13 wt.%SiO₂. The gelled-electrolyte with the lower amount of SiO₂ has a loose, porous structure, which is beneficial to the transportation of H⁺, SO₄²⁻ and O₂ by diffusion. The oxygen produced during charging of the positive electrode can be ‘recombined’ to water on the negative electrode through a series of processes [14]. This can reduce water loss in gelled-electrolyte batteries. With increase in SiO₂ content, the structure of the gel becomes more compact, and the pore size is thus reduced. Consequently, the diffusion of reactants is inhibited, and the capacity of lead–acid batteries is decreased.

4. Conclusions

The content of SiO₂ is an important determinant of the electrochemical performance of gelled-electrolytes. The colloidal particles become smaller with increasing SiO₂ content, so the three-dimensional web structure of the gel becomes more compact. This reduces the capacity of lead–acid batteries. Therefore, the SiO₂ content of gelled-electrolytes should be carefully controlled.

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