

The Optimization of Gel Electrolytes on Performance of Valve Regulated Lead Acid Batteries

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The gel electrolytes were prepared with sulfuric acid and phosphoric acid, where hydrophilic fumed silica was used as a gelling agent. The influences of gel electrolyte on performance of the valve regulated lead acid (VRLA) batteries were investigated employing capacity tests, electrochemical impedance spectroscopy and scanning electron microscopy. The initial capacities of the sulfuric gel VRLA batteries were higher than that of phosphoric gel VRLA batteries. The sulfuric gel VRLA battery using 1.210 specific gravity of sulfuric acid with hydrophilic fumed silica exhibited the highest capacity of 0.828Ah. In the impedance measurements, the ohmic and charge transfer resistances for the phosphoric gel VRLA batteries were higher than that of sulfuric gel batteries. The morphology of electrodes of phosphoric gel VRLA batteries were more deteriorated in the SEM image.

Key Words : Gel electrolytes, Valve regulated lead acid, Impedance spectroscopy

Introduction

The lead acid battery has been developed and widely used as a secondary battery, since it had been invented by Plante.¹ This is a kind of the flooded type lead acid battery, which has many problems. It is necessary to reserve the special battery room because of acid-spray emission and gassing. It requires periodic maintenance in the formation of topping up or cleaning away of corrosion product. Using the maintenance free (MF) VRLA battery is one of solutions to overcome these problems. Thus, the VRLA batteries are widely used in the areas of automobile, UPS, telecommunications, computer, and codeless electronic devices.²⁻⁵

There are two technologies adopted to develop the VRLA batteries.⁶ One is AGM technology, where the liquid electrolyte is adsorbed in an absorptive glass mat (AGM) separators.⁷⁻¹⁵ The other is gel technology, where the electrolyte is gelled by organic or inorganic thixotropic agents, such as polyacrylamide polymer, sodium silica, colloidal silica, granular silica, and fumed silica.¹⁶⁻¹⁹ The gel VRLA batteries have many advantages, such as long service life and high reliability under deep discharge cycles, no acid stratification and installation any position, no leakage of acid mist, and good charge stability, compared with conventional flooded or AGM batteries.²⁰ Diverse researches and developments have been carried out on the AGM VRLA batteries, however, less researches have reported on the gel VRLA batteries.²¹ It is necessary to understand further the effect of the gel electrolyte on the performance of the batteries. It has been reported²² that the type of solvents, the content of gelling agent, and the concentration of acid can affect the characteristics of gel electrolyte.

In the present study, the effects of the gel formation in terms of solvents and specific gravity on the performance of VRLA battery and the electrochemical characteristics of

VRLA battery were investigated with capacity tests, capacity variation, and impedance measurements according to charge/discharge cycles.

Experimental

The preparation of gel electrolyte and VRLA batteries.

The sulfuric acid (Duksan Pharmaceutical Co. 95%) solutions having various specific gravities (s.g: 1.100, 1.210, 1.265, 1.300 at 25) were prepared with distilled water. The phosphoric acid (Duksan Pharmaceutical Co. 85%, s.g 1.685) solutions having various specific gravities (s.g: 1.100, 1.210, 1.265, 1.300 at 25) were also prepared. The hydrophilic fumed silica (Degussa, Aerosil 200) of 5 wt% was added to each acid solution and mixed under 400 rpm for 30 min.

The VRLA battery was assembled with one cathode, two anodes, and four separators. The dimension of each electrode was 25 × 30[mm²] and the substrate was Pb-Ca alloy. All the battery of the gel electrolytes composed sulphuric acid or phosphoric acid was firstly filled with sulfuric acid (s.g. 1.280) and charged, then it was discharged deeply. When the battery was discharged completely, the electrolyte in the battery was removed by dumping, and gel electrolytes were filled, and then it was recharged.

Instruments and measurements. The battery was discharged by constant current at 0.06A (10 h discharging rate current) to cut-off voltage of 1.75 V. After confirming the capacity of battery, the cycle life test was conducted under the following conditions. Each cycle consisted of a constant current discharge at 0.06A to cut-off voltage of 1.75 V followed by the constant current-constant voltage recharge to 130% of the discharge capacity. The battery capacity and cycle life were obtained by a Potentiostat/Galvanostat (KST-P1, Kosentech, Korea)²³ and a battery cycler system

(WBCS3000, Won A Tech, Korea). The morphologies of electrodes were observed by a scanning electronic microscope (SEM, S-4200, HITACHI, Japan) before and after the cycle life test. The morphology was characterized with SEM as previous reported. The electronic impedance spectroscopy (EIS) of VRLA battery was measured at open circuit potential by an electrochemical impedance system (IM6, ZAHNER Elektrik, Germany) with the frequency range 100 kHz-10 mHz and amplitude of 10 mV. The equivalent circuit of VRLA battery was derived by using a complex least square fitting program (ZView2, Scribner Associates, USA). The data were fitted and analyzed with the same software.

Results and Discussion

The variation of capacity during cycling. All the batteries were tested for the cycle life during 50 cycles after measuring the capacities of batteries. The capacities were checked at every 10 cycles.

Figure 1(a) shows the variations of discharge capacity during cycle life test for gel batteries with sulfuric acid. As shown in Figure 1(a), the gel battery with sulphuric acid of s.g 1.210 has the highest initial capacity, such as 0.828 Ah after 10 cycles. The gel batteries with sulphuric acid main-

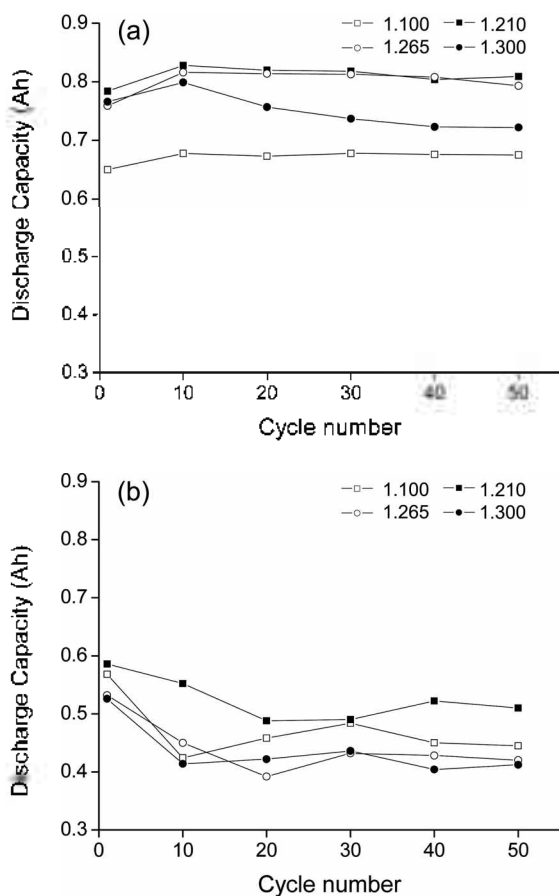


Figure 1. The variations of capacity during cycles for gel batteries with (a) sulphuric acid and (b) phosphoric acid.

tained the initial capacity during the cycle life test.

Figure 1(b) shows the variations of discharge capacity during cycle life test for gel batteries with phosphoric acid. The initial capacities of gel batteries with phosphoric acid were lower than that of gel batteries with sulfuric acid. Among the gel batteries with phosphoric acid, the highest capacity was obtained for one with phosphoric acid of s.g 1.210. However, the value of discharge capacity of the gel batteries with phosphoric acid exhibited lower discharge capacity than 0.6Ah. In addition, the capacities of gel batteries with phosphoric acid changed according to the number of cycle. The gel battery with sulphuric acid (s.g 1.210) showed good initial capacity and capacity retainment. The discharge capacities of the gel batteries with sulfuric acid were higher than that of the gel batteries with phosphoric acid. It has been reported that the addition of phosphoric acid to the conventional flooded lead acid battery improved capacity and cyclability.²⁴ Sulphuric acid in the

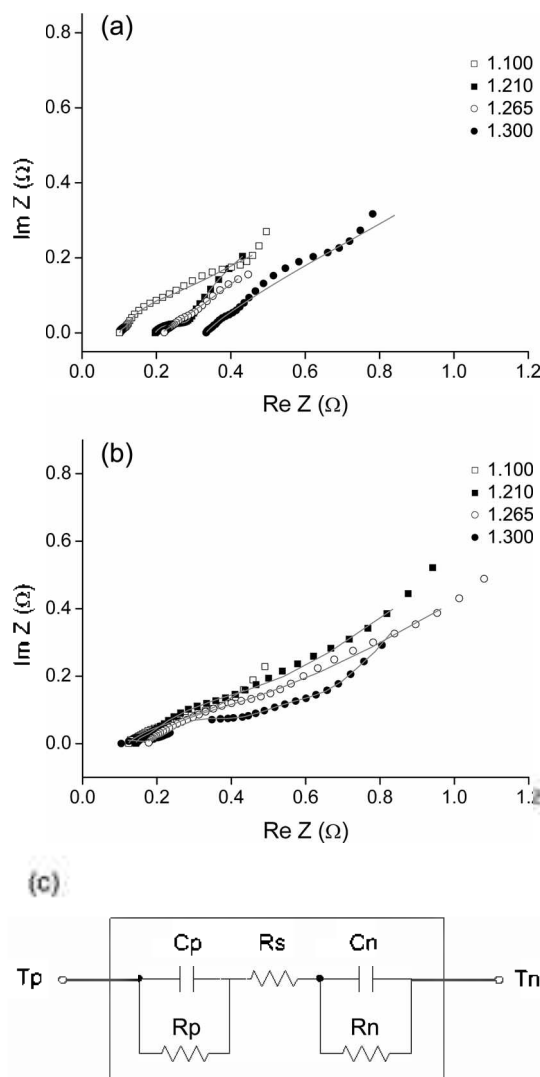


Figure 2. The nyquist plots for (a) sulphuric gelled and (b) phosphoric gelled electrolyte batteries before cycle. (c) The equivalent circuit for VRLA battery.

pores of the electrodes, however, diffused out and then adsorbed with the gelled electrolytes of phosphoric acid during discharging, thus the utilization of sulphuric acid was reduced. The surface of electrodes with gel electrolyte of phosphoric acid became more compact, and the pore size was reduced. Due to this, the capacity of gel batteries with phosphoric acid might be more decreased.

Impedance measurements. The nyquist plot for various gelled batteries before charge-discharge cycle is shown in Figure 2, where the solid lines represent the fitted results and the points do the experimental data. The values of resistances were several tens $m\Omega$ which is similar to the resistance which has been reported in previous studies.²⁵ The equivalent circuit model to fit the impedance data is shown in Figure 2(c) where, T_p and T_n are the battery terminals. R_s is the ohmic resistance due to the electrolyte and separators. R_p and R_n are the charge transfer resistance of the electrodes. C_p and C_n are the capacitances due to space charge distribution in the double layers. The subscripts p and n refer to the cathode and the anode. Figure 3 shows the variation of R_s with the cycles for various different gelled electrolyte batteries. As shown in Figure 3(a), the R_s of all gel batteries with sulphuric acid are below 0.1Ω after 10 cycles and the values of R_s increased with the cycles. In Figure 3(b), the R_s of all gel batteries with phosphoric acid were also increased with cycles, the values are drastically increased after 50

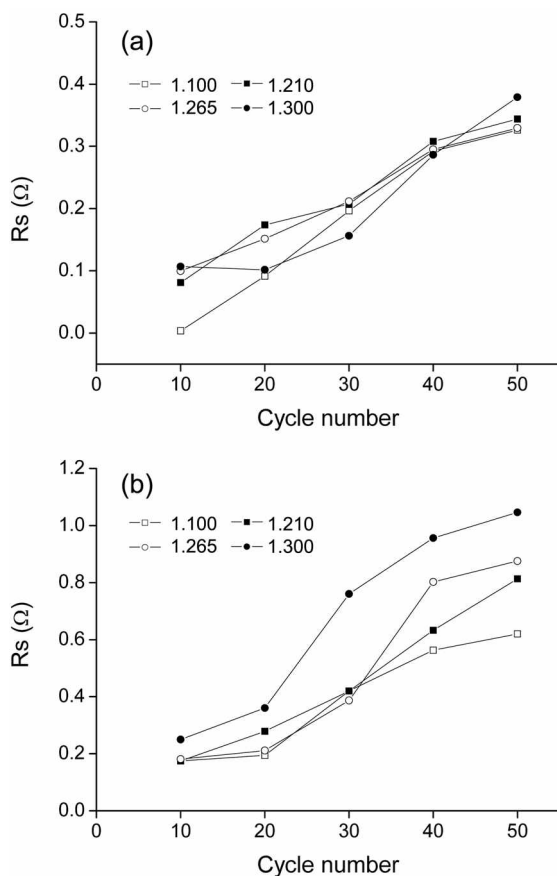


Figure 3. The variation of R_s with cycle for (a) sulphuric gelled electrolyte VRLA and (b) phosphoric gelled VRLA batteries.

cycles. The largest value of 1.0Ω was obtained in gelled battery using 1.300 specific gravity. Sulphuric acid used in the activation step was captured into the gelled electrolytes of phosphoric acid that became more difficult to react with the electrode materials. It led to lower the performance due to the generation of heat, dry-out of gel electrolyte, and increase of internal resistances of gel electrolyte.

Figure 4 shows the variations of battery resistance, R , which is summed up with R_{ct} , R_p and R_n , with cycles. For gel batteries with sulphuric acid, the resistance of each battery was almost the same except with one of s.g. 1.300. For gel batteries with phosphoric acid of s.g. 1.300, battery resistances were drastically increased.

The morphology of electrodes. In order to study the effect of gel electrolyte on the electrode morphology, the morphology of electrodes were investigated using scanning electron microscopy (SEM). Several factors may limit the capacity and cycle life of the lead acid batteries but one of the most important factors is related to the structural stability. It is important to keep the agglomerate skeleton in the cathode and to prevent the shrinkage in the anode. The agglomerate structure of the cathode collapsed and the links between crystals were weaker, and then they shed with cycling. It resulted in the capacity loss of the battery. In addition, the reduction of pore size in the anode has been origin of capacity loss. Figure 6(a) shows the morphology of

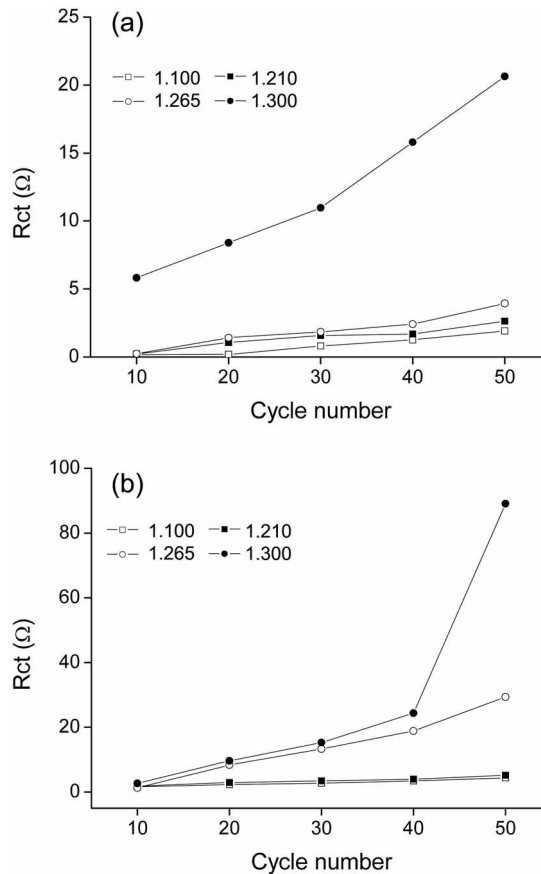


Figure 4. The variation of R_{ct} for (a) sulphuric gel (b) phosphoric gel batteries with cycles.

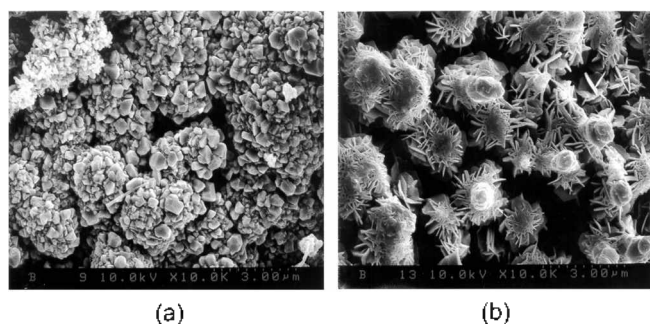


Figure 5. SEM images of (a) the fresh cathode and (b) the anode surfaces.

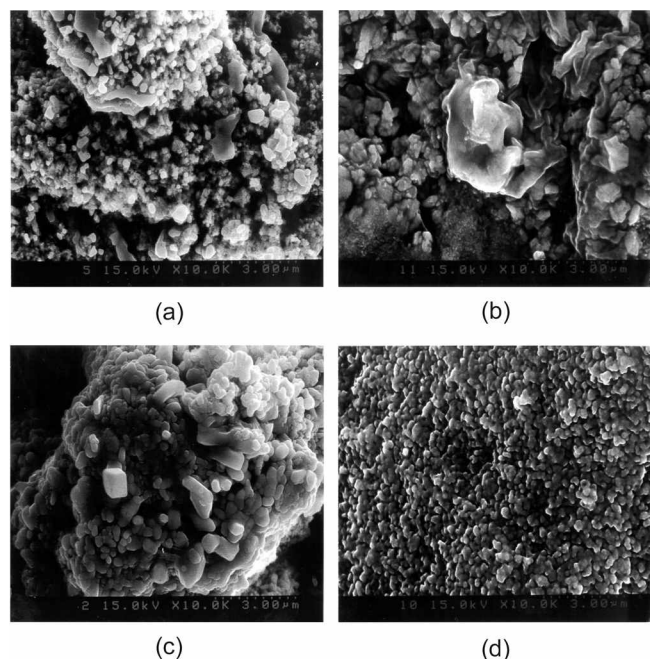


Figure 6. SEM images of the electrodes after 50 cycles (a) the cathode of gel battery with sulfuric acid (s.g. 1.210), and (b) the cathode of gel battery with phosphoric acid (s.g. 1.210). (c) the anode of gel battery with sulfuric acid of s.g. 1.210, and (d) the anode of gel battery with phosphoric acid of s.g. 1.210.

the cathode before cycling. The individual particles are small and granular in shape. Several particles interconnect to form agglomerates and adhere tightly each other. The macrostructure is composed of large, shapeless, and continuously connected agglomerates with a rock-like appearance. Figure 6(b) presents the surface morphology of the anode before cycling. The particles in the anode are larger than those in the cathode. The particles like an echinoid were distributed on the surface of electrode. Figure 6 shows the SEM images, of the cathodes which the gel batteries with sulfuric acid and with phosphoric acid of s.g. 1.210, were cycled 50 times, separately. In comparison of the surface morphology of electrode before and after cycles, the morphology of particles were changed to inhomogeneous after cycles shown in Figure 6(a), and the electrode surface was less porous. On the other hand, the agglomerate structure has been disappeared along with that the particle size

became larger, as shown in Figure 6(b). That may increase the resistance of electrode and then result in the capacity loss of the battery. It was shown that the electrode of gel battery with phosphoric acid became more deteriorated. As a result, the phosphoric acid in the gel battery may cause the deformation of electrodes. The particles like an echinoid shown in Figure 5(b) changed to polygonal crystal form and interconnected to agglomerates in the anode of gel battery with sulfuric acid, as shown in Figure 6(c). Additionally, the surface was covered with small particles and there have been little pores in the anode of gel battery with phosphoric acid as shown in Figure 6(d). That may increase the resistance of electrode and then resulted in the capacity loss in the battery. It was shown that the electrode of gel battery with phosphoric acid became more deteriorated. As a result, the phosphoric acid in the gel battery may cause the deformation of electrodes. The battery resistance was increased with the shrinkage of active material. This is in which means that the ionic transfer had been disturbed, thus the capacity was degraded. It was found that anode of gel battery with phosphoric acid is more deteriorated than that of gel battery with sulfuric acid good agreement with the capacity test results of sulphuric and phosphoric VRLA batteries.

Conclusion

In the present study, the electrochemical characteristics of various gel batteries have been investigated. It was found that the gel batteries with sulfuric acid showed higher initial capacity and better cycle durability rather than that with phosphoric acid. The ohmic and charge transfer resistance for various gel batteries increased with the cycles, in addition, the resistance of gel batteries with phosphoric acid were higher than that of gel batteries with sulfuric acid. It is found that the deteriorations of the cathode and the anode of phosphoric gel batteries were more serious.

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