Influence of Safety Valve Pressure on Gelled Electrolyte Valve-Regulated Lead/Acid Batteries Under Deep Cycling Applications

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Cycle life tests have been carried out to evaluate the influence of safety valve pressure on valve regulated lead/acid batteries under deep cycling applications. Batteries were cycled at 5 hour rates at 100% DOD, and safety valve pressure was set to 1.08 and 2.00 bar, respectively. The batteries lost 248.3 g and 235.3 g of water for each case after about 1,200 cycles, but the cyclic performances of the batteries were comparable. Most of the gas of the battery during discharging was hydrogen, and the oxygen concentration increased to 18% after 3 hours of charging. The micro structure of the positive active materials was completely changed and the corrosion layer of the positive grid was less than 50 μm, regardless of the pressure of the safety valve after cycle life tests. The cause of discharge capacity decrease was found to be water loss and the shedding of the positive active materials. The pressure of safety valve does not give little effect to the cyclic performances and the failure modes of the gelled electrolyte valve-regulated lead acid batteries.

Keywords : Lead acid battery, Cyclic performance, Safety valve, Failure mode.

Introduction

The sealed valve-regulated lead acid (VRLA) battery was developed in the early 1960s for use with portable equipment. VRLA batteries are used in a number of applications, challenging their conventional counterparts in almost all applications.[1,2] For stationary applications, in particular, these designs are replacing conventional, flooded electrolyte batteries. There are two types of VRLA batteries: batteries with gelled electrolyte and batteries with absorptive glass-mat (AGM) separator. Each type has been developed to serve different purposes. The design of gelled electrolyte tubular batteries is optimized for low-rate applications where the discharge duration is one hour or more. For high-rate applications, batteries using flat pasted plates and AGM separators are specified. In gelled electrolyte batteries, loss of water during overcharge, either as hydrogen or oxygen, is negligible, and no topping-up is necessary. These types of batteries are useful in specific applications, such as rural area power supplies and solar energy storage, unlike their flooded counterparts.[3]

The decrease in the cycle-life performance of lead acid batteries is often caused by deterioration of the positive plates.[4-6] The compression influences, positive-grid growth, electrolyte stratification, cell design and uniformity across a series string of cells caused early failure of the VRLA battery during deep cycling service.[7-9]

In the present study, the influence of safety valve pressure of VRLA batteries on the deep cycle applications was tested. The rubber safety valve was modified by a variable pressure valve to increase the opening pressure. Valve modified and controlled batteries were cycled, leading to discharge capacity change, weight loss, internal pressure, gas composition, and micro-structure of the positive plate.

Experimental Section

Gelled electrolyte VRLA batteries (Model VGS 200, Global Hi-Tech Co., Ltd., Korea) were tested by cycle life tester(Bitrode LCN 50-12, USA) under deep cycling applications. Table 1 shows the test conditions of 2 V VRLA batteries that contained four positive plates and five negative plates. The VC3 battery, whose safety valve pressure was 1.08 bar, had a rubber safety valve, and the VC3P battery's safety valve pressure was set to 2.00 bar, using a variable pressure valve (Circle Seal Controls Inc., USA).

To investigate the effect of valve pressure under deep cycling applications, test batteries with a capacity of 150 Ah in 3 hour rates were discharged at 50 A (C_3 rate, 100% depth of discharge) to 1.75 V and recharged at 40 A to 2.40 V for 5 hours.

The gas composition of the test battery was analyzed by a precision gas mass (M271, Finnigan). Gases filling the void volume over plates in the battery during cycling were sampled using a gas tight syringe through a preset silicon septum attached to the case.

The decrease in battery weight was measured by a electronic balance (SR 32001, Mettler) after every 50 cycles. Internal pressure changes during cycling were measured by a pressure transducer (PCDR 911, Drucks), which was attached to the upper case of the battery and pressure

Table 1. Test conditions of the batteries

Sample name	Pressure of safety valve/bar	Cycle test conditions	
		Discharge	Charge
VC3	1.08	C_3 rate (50A) to 1.75 V	40A to 2.40V for 5h
VC3P	2.00		

indicator (DPI 264, Drucks).

The crystallographic structure of the positive active materials was analyzed using XRD (D/MAX-RC, Rigaku). A porosimeter (Autopore II 9220, Micromeritics) was used to measure the porosity of the positive active materials.

After cycle life tests, samples of the positive plates were washed with distilled water and vacuum impregnated with epoxy resin, and then polished with 1 μm alumina slurry. The micro structure of the positive active materials was analyzed by SEM (ISI DS-130, Akasi).

Results and Discussion

VRLA batteries can not be used in deep cycling application because of their short cycle life. Generally, the failure of VRLA batteries was attributed to the positive electrode or water loss, and they became the focus of attention.[4-6,10,11] However, little has been reported on the pressure of the safety valve relating to deep cyclic performances.

Figure 1 shows the changes in discharge capacity and water loss of the VRLA batteries during cycle life tests. As the tests progressed, the discharge capacity of the VC3 battery decreased more rapidly to below 0.8 C than the discharging capacity of the VC3P battery. Interestingly, the battery that led in discharge capacity decrease lost more water. This indicates that the decrease in discharge capacity was relative to the amount of water loss. VC3 and VC3P batteries had lost 248.3 g and 235.3 g of water after 1,200 cycles, respectively, but the cyclic performances of both batteries were comparable.

A second noteworthy feature concerned the recovery of discharge capacity after 600 cycles to above 0.8 C in both batteries. This resulted from the structural change in the positive active materials during repetitive charge-discharge
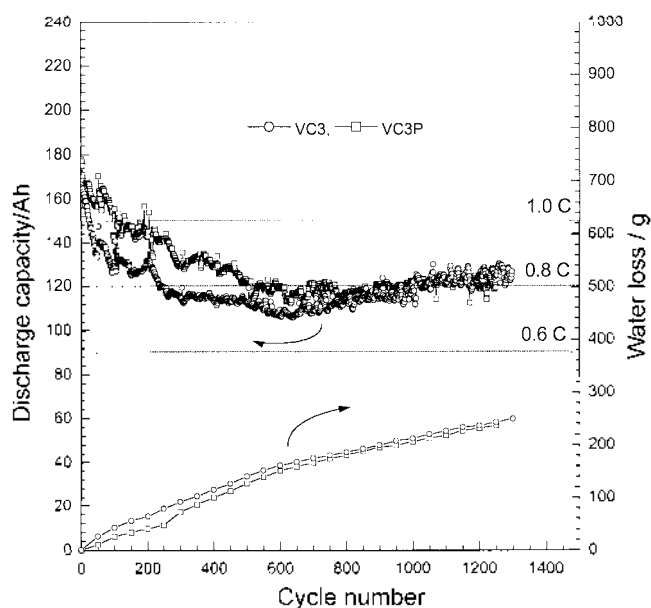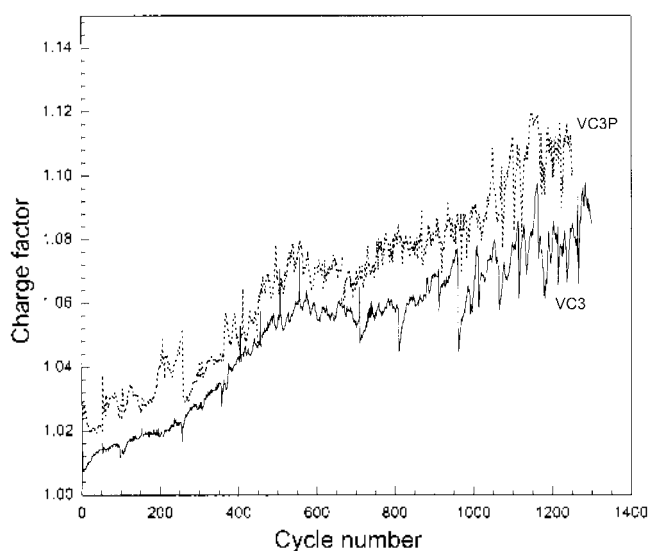

Figure 2. Changes of charge factor on the pressure of safety valve during cycle life test.

cycling. The evidence is shown in a SEM photograph later.

Figure 2 shows the charge factor of the batteries during cycle life tests. The charge factor, the value of the discharged capacity over charged capacity, was bigger than one because the charging efficiency of the positive plate was in the range of 70-90%. The difference in the charge factors at the starting point was about 1%. This was probably caused by the difference in the internal resistance stemming from the manufacturing process. Generally, the charge factor in lead acid batteries is in the range of 1.07 to 1.20, but it varies with internal structure, type of electrolyte and applications. The overcharged electricity play a role in the corrosion of the positive grid and electrolysis of water as follow.

Positive plate : $2H_2O \rightarrow O_2 + 4H^- + 4e^-$
Negative plate : $O_2 + 4H^- + 4e^- \rightarrow 2H_2O$
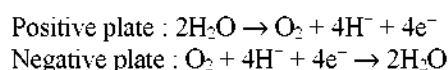
During cycle tests limited by the charging voltage, as in the present study, heat generation and the charge factor increased continuously because the internal resistance of the battery increased with the change of micro structure. The VC3P battery with more discharge capacity showed a higher charge factor in cycle life tests. This might suggest that the test battery with the higher charge factor loses water more. But VC3P lost less water than VC3, as shown in Figure 1. The reason is that the oxygen recombination reaction on the negative plate of the VC3P battery was accelerated with higher oxygen pressure because of the higher setting of the safety valve pressure.

An interesting note is that the slope of the charge factor changed around 600 cycles, same as the cycle number for water loss in Figure 1. This means that the charge factor and water loss are related very closely with the micro structure of the positive plate. The fluctuations of the charge factor increased gradually during cycle life tests in both test batteries. This suggests that the structure of the positive plate

Figure 1. Changes of discharge capacity and water loss on the pressure of safety valve during cycle life test.
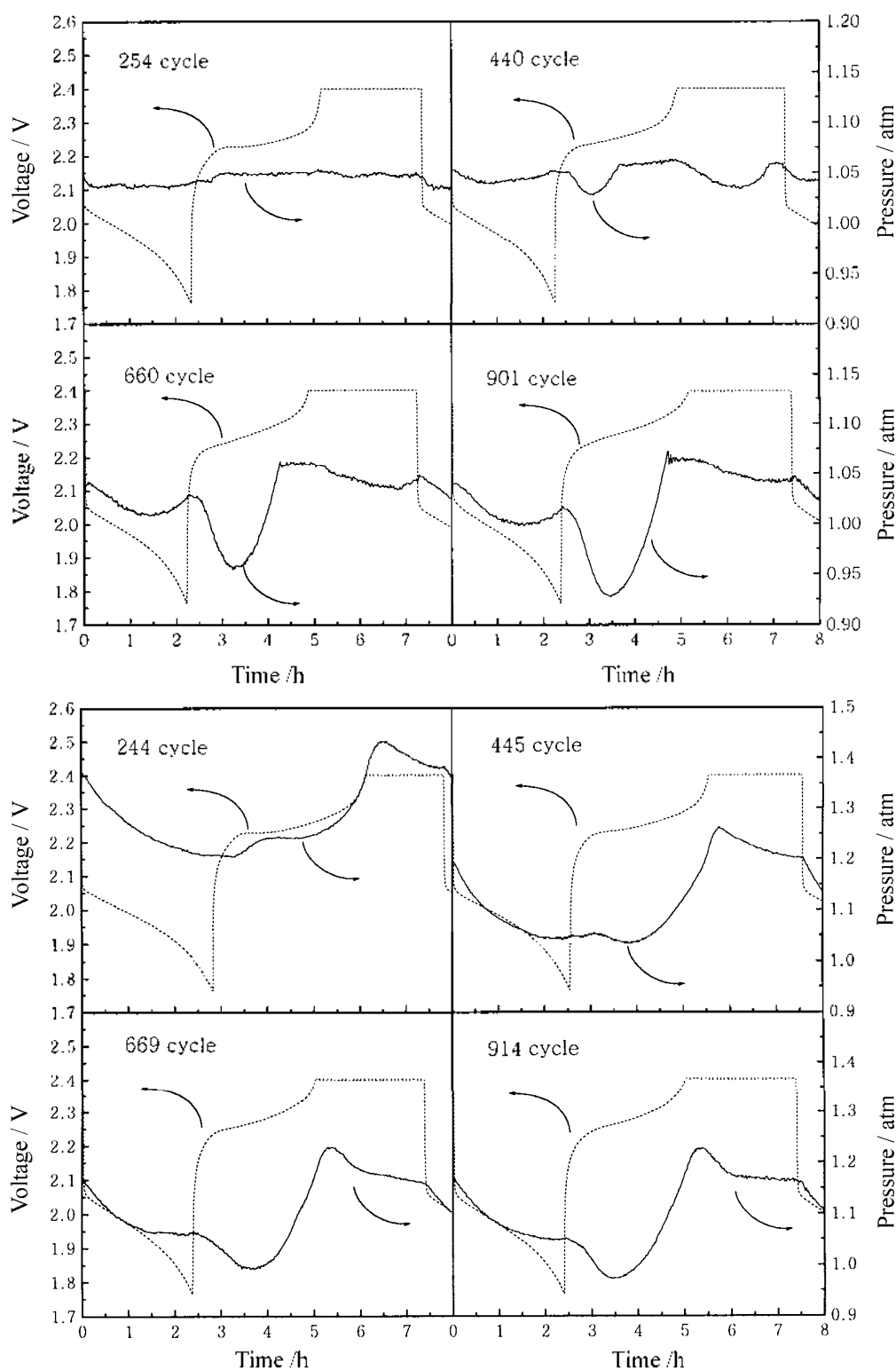
Figure 3. Changes of internal pressure during cycle life test of (a) VC3 and (b) VC3P batteries.

became porous during cycling.

Figure 3 shows the changes in internal pressure and battery voltage during cycle test. The internal pressure of the VC3 battery was not changed during charging and discharging at 254 cycles. Pressure dips appeared at an early and later stage of charging at 440 cycles. These pressure dips

indicate the increase in the oxygen recombination reaction rate at the negative plate.[10-16] During cycling, the pressure dip at an early stage of charging was deeper and broader, and the amount of water loss per one cycle decreased, as shown in Figure 1. In the VC3 battery, the safety valve was opened about 1.06 bar, and internal pressure was decreased to about

0.93 bar during charging at 901 cycles. Pressure fluctuations in the plateau after the pressure dip were caused by opening the safety valve.

Significantly different results was obtained with the VC3P battery as seen in Figure 3(b). In spite of the safety valve being set to 2.0 bar. the peak pressure was about 1.45 bar. and peak pressure decreased to 1.23 bar at 244 cycles. Peak pressure decreased during cycling. and the pressure dip appeared during charging at 669 cycles. The typical shape of the internal pressure was changed by the oxygen recombination reaction when the VRLA battery was charged at constant voltage[15-17] after 669 cycles. From this results, it can be inferred that the VC3P battery was more efficient at oxygen recombination reactions than the VC3 battery and that the increase in the pressure of the safety valve could reduce the water loss of the VRLA battery by improving the oxygen recombination reaction, as shown in Figure 1.

To confirm the dipping effect on pressure, as shown in Figure 3. the composition of gases produced in the VC3 battery was analyzed by a precision gas mass spectrometer. After 700 cycles. 12 samples were taken periodically during discharging and charging by a gas tight syringe and analyzed. Figure 4 shows the results for gas analysis. When a battery was discharging, most of the gas was hydrogen. But during the charging, oxygen content increased initially and finally decreased because of the oxygen recombination process.[10] The identical effect occurred with the VC3P battery. Evolved oxygen recombined on the negative plate to water, therefore the oxygen content was reduced.[15]
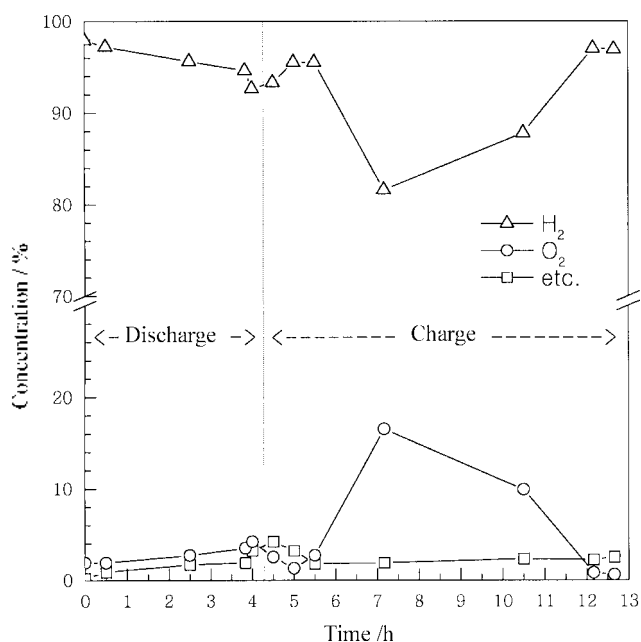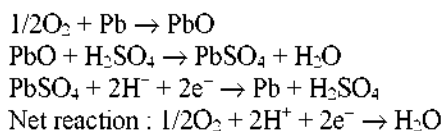
$$1/2O_2 + Pb \rightarrow PbO$$
$$PbO + H_2SO_4 \rightarrow PbSO_4 + H_2O$$
$$PbSO_4 + 2H^- + 2e^- \rightarrow Pb + H_2SO_4$$
$$\text{Net reaction}: 1/2O_2 + 2H^+ + 2e^- \rightarrow H_2O$$

Figure 4. Changes of gas composition at 700 th cycle of VC3 battery.
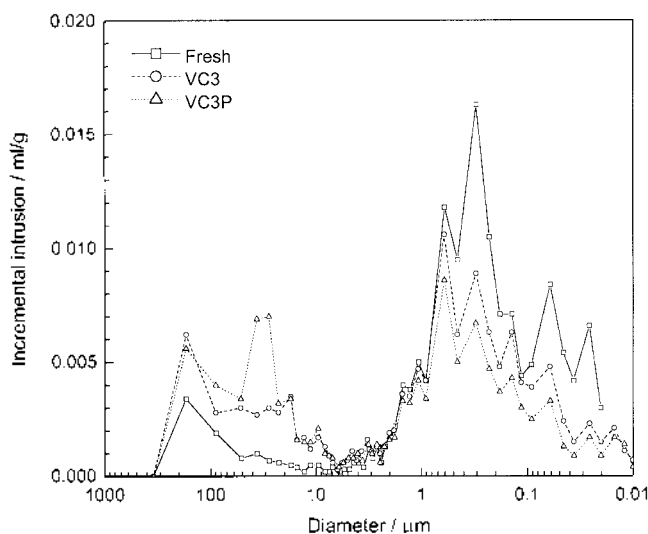

Figure 5. Pore size distributions of the positive plate of a fresh and tested batteries.

Because the reaction rate of hydrogen recombination on the positive plate is very slow[10,17] and the evolving rate is faster than recombination, the amount of hydrogen increases with cycling. An increasing oxygen recombination rate and decreasing water loss rate were expected with higher safety valve pressure. However, the VC3P battery reveals only an 8 % effect on water loss. as shown in Figure 1.

Figure 5 shows a comparison of pore size distribution of the positive active materials of fresh and cycled batteries. This shows that there are two types of pores. The large pores are larger than 100 μm and the small pores are less than 1
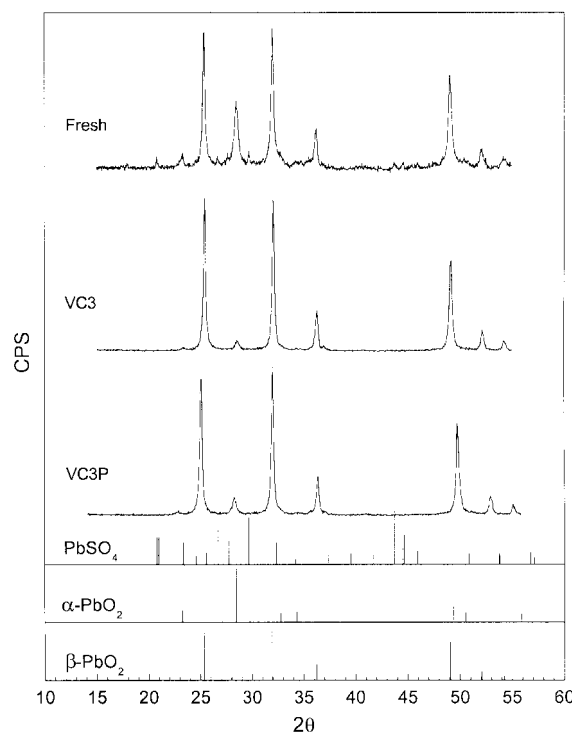

Figure 6. Comparison of XRD patterns of the positive active materials for a fresh and tested batteries.
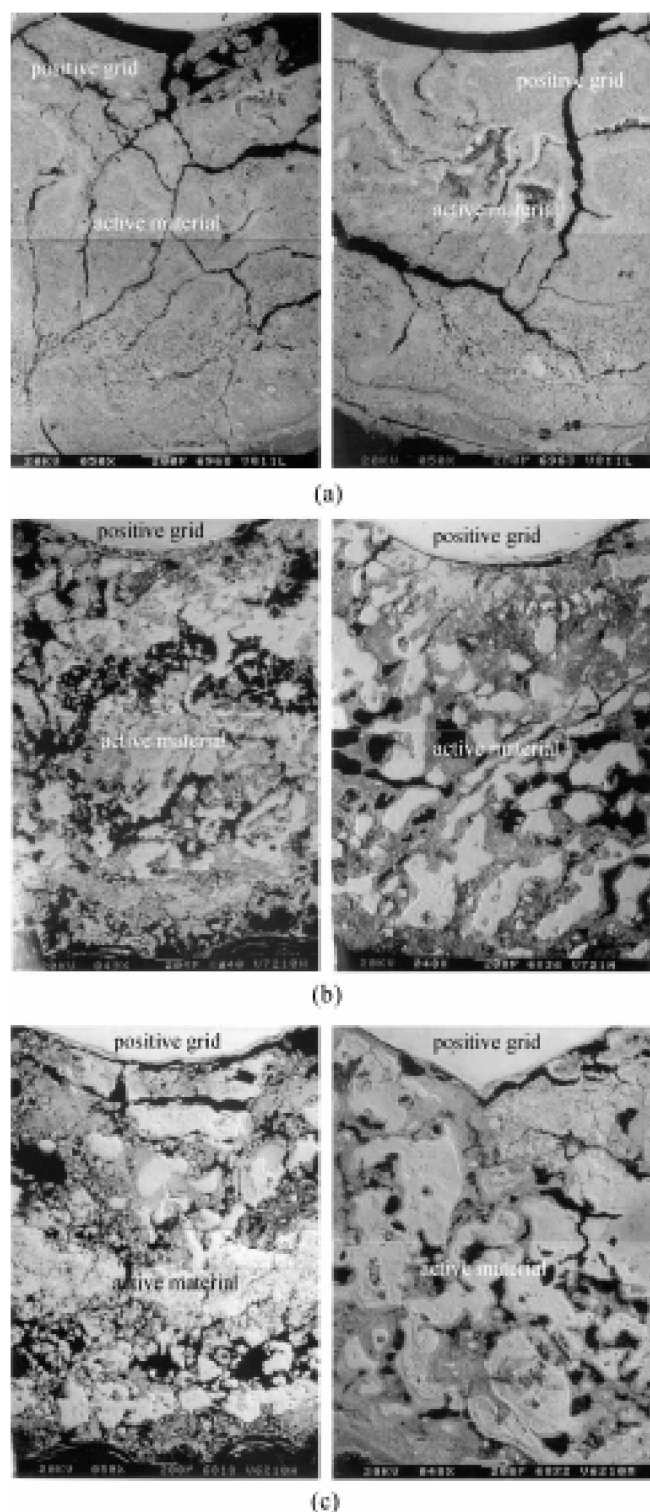
Figure 7. SEM photographs of a cross section of the positive plate. (a) fresh, (b) VC3, and (c) VC3P batteries.

μm. With cycling, the proportion of small pores decreased, and the proportion of large pores increased with violent gassing on charging. But safety valve pressure had little effect on the structure of positive active materials.

A comparison of the XRD patterns of the positive active materials in the charged state is given in Figure 6. The α-

PbO_2, residing on the inside of the plate decreased with cycling,[19,20] and $PbSO_4$ was not observed after cycle life tests. There was no change in XRD patterns of the battery's positive active materials with change in safety valve pressure. We concluded, the mechanical structure and chemical composition of the plate do not change with higher safety valve pressure.

To observe changes in the micro structure of the positive active materials, fresh, VC3 and VC3P batteries were disassembled and examined by SEM. VC3 and VC3P batteries, 1,300 cycled and 1,250 cycled, respectively, were used. The comparison of the micro structures of fresh and cycled batteries is shown in Figure 7. Active materials (gray color in the SEM photographs) consist of micro porous structures and there were many cracks (black color) formed during production. The active material was partly separated with a grid (Figure 7(a)).

The left and right SEM photographs in Figure 7(b) and (c) show the upper and middle part of the positive active materials of the tested batteries, respectively. Separated interfaces and cracks disappeared because of the swelling of the active materials,[21,22] and there was severe deterioration in the active materials, which appeared as a colloidal structure.[5,23,24] Pores larger than 100 μm and agglomerated active material (white color in SEM photograph) are shown in Figure 7(b) and (c). The many big pores and agglomerations on the plate is related to the rearranging of the active materials by evolved oxygen during charging. Since there was a difference in electrical conductivity with grid height under deep cycling application, the upper part of the positive plate deteriorated more rapidly than the middle and bottom parts.

In spite of the deep cycling application, positive grids were corroded slightly, and the corrosion layer was about 50 μm thick and distinguishable from the active materials. Therefore, porous active materials were shedded by violent gassing under high current charging.[4,5,10] But, there was no significant difference in the mode of deterioration of the positive active materials from safety valve pressure.

Conclusion

An investigation on the effect of safety valve pressure on the gelled tubular VRLA battery under deep cycling application was carried. Safety valve pressure was set to 1.08 and 2.00 bar, respectively. Compared with a normal battery set to 1.08 bar, the battery set to 2.00 bar revealed some beneficial effects on the discharge capacity and water loss in the early stage of the cycle life test. These results suggest that the oxygen recombination reaction was improved due to the high partial pressure of oxygen at charging. But the amount of water loss was similar and discharge capacity was recovered to 0.8 C after 1,200 cycles in both batteries.

Although, big pores, shedding and agglomerated active material were formed during cycle life tests, gelled electrolyte batteries exhibited excellent cyclic characteristics under deep cycling application regardless of the pressure of the

safety valve. We conclude that there was no significant effect of the safety valve pressure on the cyclic performance of the VRLA battery because the mode of deterioration of the positive active materials and discharge capacity of the tested batteries were similar, and the difference in water loss was small during cycle life tests.

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