

Development of advanced electrolyte retainers for improvement of the life cycle of valve-regulated lead–acid batteries

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Abstract

Advanced electrolyte retainers have been developed to improve the life cycle of valve-regulated lead–acid (VRLA) batteries. One of the retainers is a separator mat which contains synthetic wood pulp (SWP), or fine polymer fibre. It shrinks less than conventional absorptive glass mat (AGM) when wetted with acid and is so elastic that the plates are kept well-pressed together when the volume of the plates changes during charge and discharge. The other retainer is granular silica which fills the space between and around the plates instead of the AGM. In a battery using this type of retainer, the plates are tightly compressed from all directions and the compression does not decrease after water loss. The basic characteristics of these new retainers and their influence on battery performance are discussed. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Absorptive glass mat; Compression; Life cycle; Separator; Silica; Valve-regulated lead–acid batteries

1. Introduction

In order to extend the life cycle of valve-regulated lead–acid (VRLA) batteries, it is important for the plates to be kept compressed during operation. Unfortunately, the conventional absorptive glass mat (AGM) separator, widely used as an electrolyte retainer, shrinks when acid is poured into the battery or water is lost from it during operation [1]. This is because the glass fibres are attracted to each other under the action of the surface tension of the acid solution. Shrinkage reduces the compression on the plates which, in turn, shortens the life cycle of the battery. Therefore, two kinds of electrolyte retainers have been developed to sustain the required pressure. One is a separator mat which contains synthetic wood pulp (SWP), or fine polymer fibre [2]. The other is granular silica which is filled between and around the plates instead of the AGM [3]. In this paper, the basic characteristics of the conventional AGM separator and of these new retainers, together with the effect on the battery performance, are compared.

2. Conventional AGM separator

2.1. Experimental

2.1.1. Basic characteristics

The change in compression of a conventional AGM separator with thickness under dry and wet conditions was examined in order to measure its ability as an electrolyte retainer for batteries designed for use in electric vehicles. The apparatus employed to determine the compression of AGM is shown schematically in Fig. 1. The measurement procedure was as follows:

- (i) 10 sheets of AGM were stacked and placed in the cell;

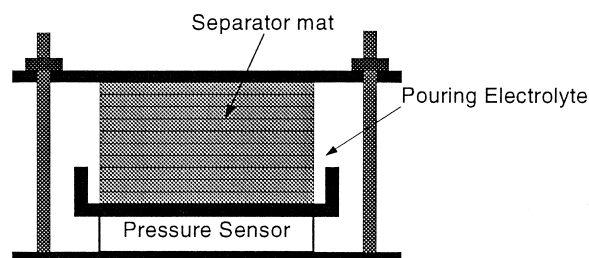


Fig. 1. Schematic diagram of apparatus used to measure the compression of separator mat.

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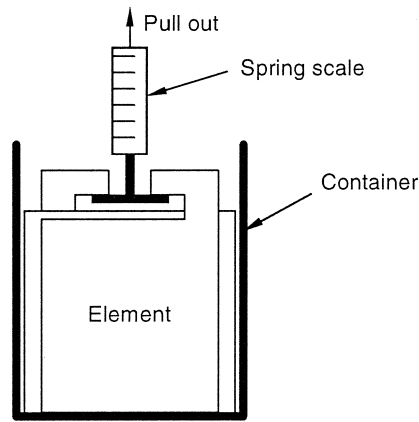


Fig. 2. Schematic diagram of method of compression measurement.

- (ii) the sheets were pressed at 20 kgf dm^{-2} ;
- (iii) the sheets were kept pressed at the same thickness for 1 h;
- (iv) acid was poured on to the sheets and the change in pressure was measured.

The amount of the acid poured on to the mat was varied and the change in compression was measured in each case.

Next, the relationship between the amount of water absorbed in the AGM and the compression on the plates in the cell container was investigated. The force required to pull the element out of the container under dry or wet conditions was measured by means of the apparatus shown in Fig. 2. The procedure was as follows: (i) under dry conditions, the force required to pull the element out of the container was measured by a spring scale; (ii) excess water was poured into the cell which was then left to stand for a day; (iii) surplus water was removed and the force required to pull out the element was determined; (iv) measurement of the force was repeated after a small amount of water was removed from the element by drying the cell at 50°C for a given time; this procedure was repeated until 25% of the water was lost.

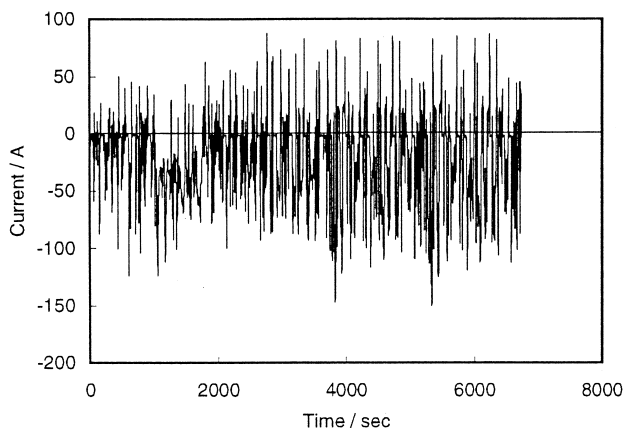


Fig. 3. Current profile of EV load pattern.

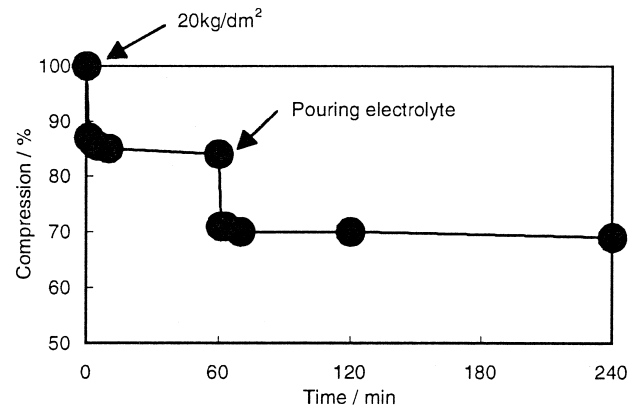


Fig. 4. Compression of conventional AGM when pressed and after adding electrolyte.

The cell containers and elements used in the test were of the 2-V, 6-Ah type. The initial compression in the dry condition was set at 20 kgf dm^{-2} .

2.1.2. Battery performance

Batteries with various levels of AGM compression on the cell elements were constructed and their performance determined. Batteries were constructed with either rough plates or flat plates in order to investigate the effect of differences in compression over a plate surface, i.e., the influence of plate surface roughness. Sufficient acid to fill all of the pores of the AGM was poured into the battery.

The change in discharge capacity was measured before and after loss of water from the cell. Both low rate (0.33 C) and high rate (2 C) capacities were determined. The batteries were overcharged to remove more than 10% of the water from them, and the discharge capacity then re-determined.

Batteries of 60-Ah capacity were cycled under the simulated electric vehicle charge–discharge load pattern shown in Fig. 3. This profile was obtained on a Toyota

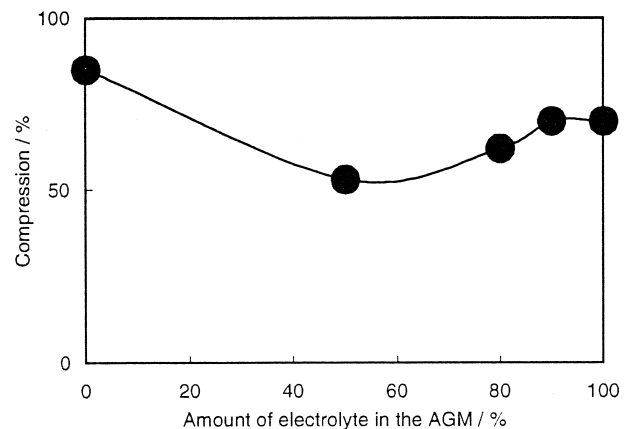


Fig. 5. Relationship between compression of AGM separator and amount of electrolyte.

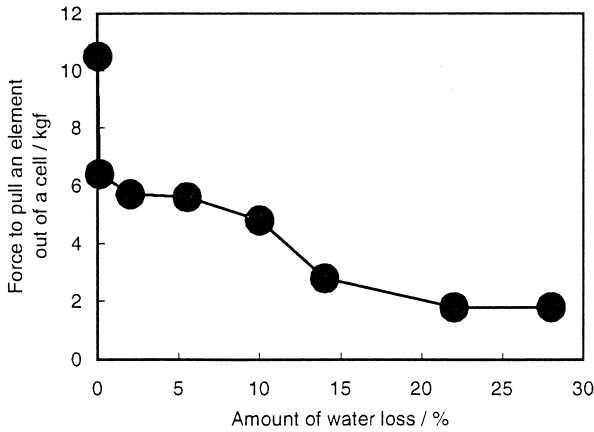


Fig. 6. Effect of water loss on compression in conventional AGM cell (6-Ah, 2-V test batteries).

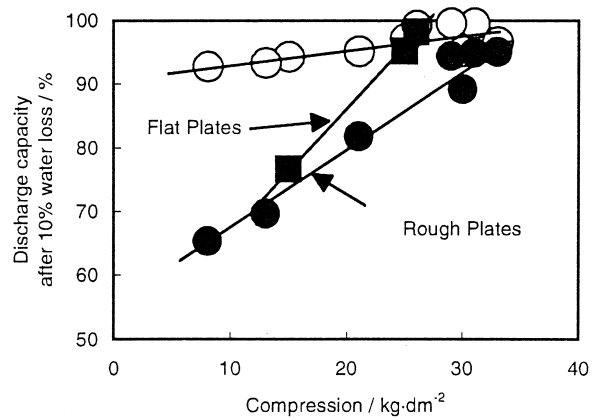


Fig. 8. Relationship between discharge capacity after 10% water loss and initial compression: (○) low rate (0.33 C); (●) high rate (2 C), cell with rough plates; (■) high rate (2 C), cell with flat plates.

Town-Ace electric vehicle. After every 50 cycles, both the 0.33 C and 3 C discharge capacities were measured.

2.2. Results and discussion

2.2.1. Basic characteristics

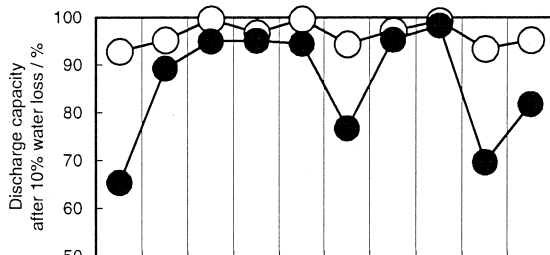
Compression data for AGM in a dry and a wet state are presented in Fig. 4. In this case, 50% of acid that can be retained in the mat was added to the cell. After wetting, the compression of the AGM decreased rapidly. The relationship between the level of compression and the amount of acid in the AGM is shown in Fig. 5. The drop in compression caused by shrinkage of the AGM becomes significant when the amount of the acid is less than 90% of the pore volume in the mat.

The change in the force required to pull the element out of the container with the amount of water loss is given in Fig. 6. The compression rapidly declines after pouring water on to the AGM. This is because the fibres are attracted to each other under the action of water surface

tension and the mat shrinks. The compression decreases further after about 10% water loss. This may be due to the fact that the water surface tension becomes stronger than the binding force of the micro-glass fibre at this water content. Thus, the amount of acid must be kept above 90% in conventional AGM used in VRLA batteries.

2.2.2. Battery performance

The ratio of the discharge capacity after 10% water loss to the initial value is shown in Fig. 7. A battery with high compression maintains its discharge capacity at a higher level than that with low compression, after 10% water loss.



Cell No.	1	2	3	4	5	6	7	8	9	10
Number of separators between plates	1					2				
Surface roughness of positive plates	Large				Small (Flat)			Large		
Surface roughness of negative plates	Large				Small (Flat)			Large		
Compression(kg/dm ²)	8	30	31	33	29	15	25	26	13	21

Fig. 7. Battery discharge capacity after 10% water loss (% initial value): (○) low rate (0.33 C); (●) high rate (2 C).

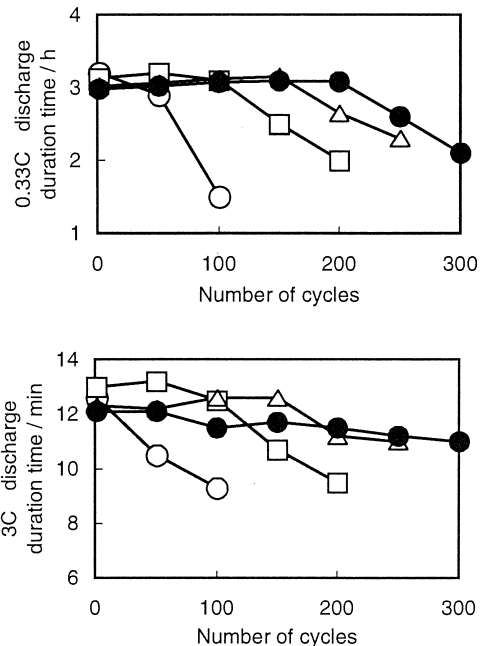


Fig. 9. Changes in discharge capacity during electric-vehicle load pattern life test: plates compressed at: (○) 4 kgf dm⁻²; (■) 18 kgf dm⁻²; (□) 40 kgf dm⁻²; (●) 73 kgf dm⁻².

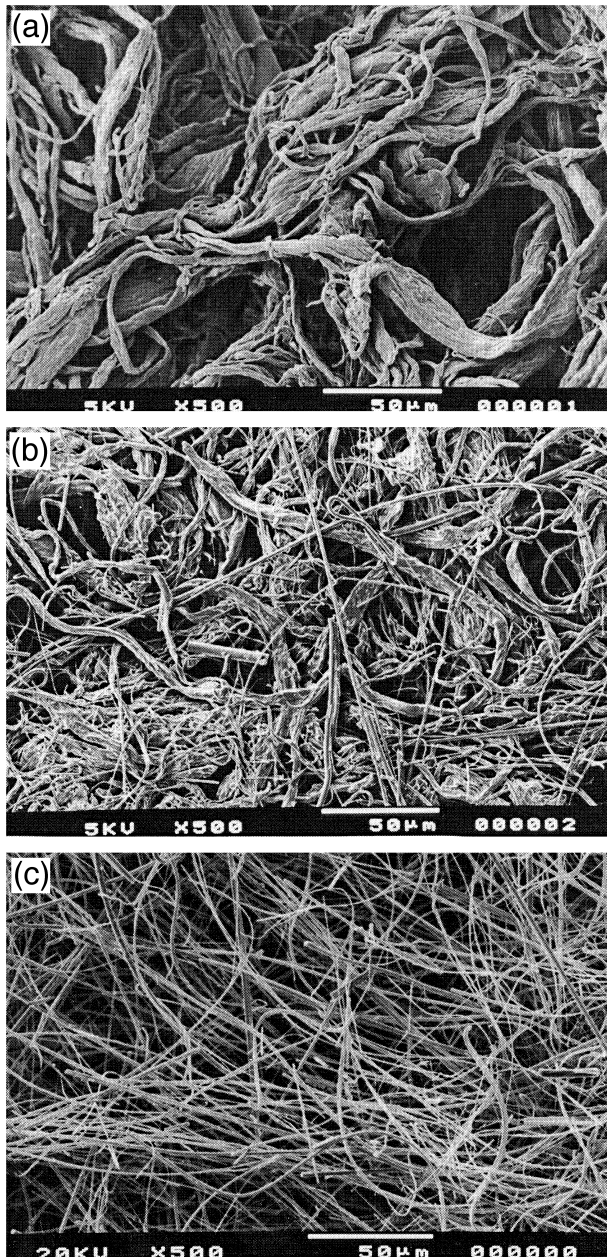


Fig. 10. Scanning electron micrographs of surface of: (a),(b) SWP mats; (c) AGM.

Fig. 8 shows the relationship between the ratio and the initial compression applied to the element. The higher the initial compression, the more the discharge capacity after the water loss. The discharge capacity of batteries with flat plates is greater than that of batteries with rough plates. These results demonstrate that tight and uniform compression to the elements improves battery performance.

The results of the life cycle test (electric vehicle load pattern) of batteries with various compression levels are presented in Fig. 9. The higher the compression, the longer the battery life. Thus, it is found that tight compression to

the plates during charge and discharge improves battery life cycle.

3. New advanced electrolyte retainer (SWP mat)

It is found that AGM shrinks and relaxes its compression on the cell elements during charge and discharge, and that the reduced compression affects the life cycle of the battery. Reasons for this may be:

- (i) the binding force of the micro-glass fibre in AGM is so loose that the binding is broken when the water surface tension becomes higher than the force;
- (ii) the micro-glass fibre in AGM is not sufficiently elastic to restore the compression once the AGM has shrunk.

Since these two disadvantages are caused by AGM being made of micro-glass fibre, a new separator mat was made of SWP instead of micro-glass fibre. Table 1 shows the composition of the SWP mat produced by GS Kasei Kogyo. The SWP is fine polypropylene or polyethylene fibre. It is sufficiently elastic and is bound tightly by low-melting-point polymer fibre. It is therefore expected to overcome the disadvantage of AGM.

3.1. Basic characteristics

The volume of acid retained in the SWP mat was measured by the apparatus shown in Fig. 1. First, 10 sheets of retainer mat were pressed at 20 kgf dm^{-2} and the thickness was measured. As much acid as possible was then poured on to the sheets, the weight was measured, and volume percentage of the electrolyte in the sheets was calculated.

The change in compression on addition of electrolyte and the elastic properties of the SWP mat were examined

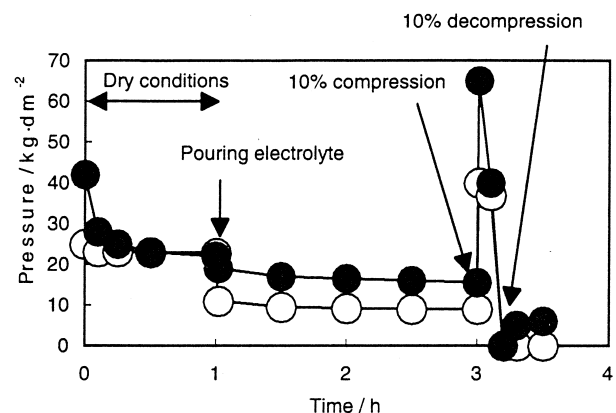


Fig. 11. Compression and decompression changes of (O) AGM and (●) SWP mats with time.

Table 1
Composition (wt.%) of SWP mats

Sample no.	PE-SWP		PP-SWP Thick	Binder				Glass fibres (0.8 μm)	Silica powder
	Fine	Medium		Low m.p. PE-SWP (thick)	Low m.p. fine PET	Low m.p. thick PP	Fine acrylic fibre		
SWP1				34		15	8	27	16
SWP2	70				30				
SWP3		80			20				
SWP4		50	30	20					
SWP5			80	20					
SWP6		60				20		20	
SWP7				40		20		20	20
Silica powder AGM (8)					10			20	70
Conventional AGM (9)								100	

PE = polyethylene; PP = polypropylene; PET = polyethylene terephthalate; m.p. = melting point.

and compared with those of the AGM by means of the apparatus shown in Fig. 1. The procedure was as follows:

- (i) 10 sheets of retainer mat were stacked and put into the cell;
- (ii) the sheets were pressed at more than 20 kgf dm^{-2} in order to set the pressure to 20 kgf dm^{-2} just before pouring acid;
- (iii) the sheets were kept pressed at the same thickness for 1 h;
- (iv) acid was poured on to the sheets and the pressure changes were measured for 2 h;
- (v) the sheets were pressed tighter until the thickness was decreased by 20%;
- (vi) the pressure was slackened until the thickness of the sheets returned to that in (iv).

These changes in pressure on the retainer mat are considered to be equivalent to those that occur in a battery as a result of the volume changes which occur in the positive and negative plates during charge and discharge.

The change in the force required to pull the element out of the container with the amount of water loss was also

measured by means of the same method used above for AGM.

3.2. Battery performance

The 10% water-loss test was performed using the same technique employed for AGM.

3.3. Results and discussion

3.3.1. Basic characteristics

Scanning electron micrographs of the SWP mat are shown in Fig. 10. These show that the mat is composed of twisted and branched fine fibres. The SWP 1 and 7 mats were made from a finer fibre than the other SWP mats, in order to render them more porous.

The basic properties of the SWP mat are shown in Table 2. As an electrolyte retainer, the most serious problem is the low porosity: the porosity of SWP mat is smaller than that of conventional AGM. The SWP 1 and 7 mats were found to be the most porous. The other problem

Table 2
Basic properties of SWP mats (thickness of all sheets = 1.7 mm)

Sample no.	Apparent density (g cm^{-3})	Average pore diameter (μm)	Resistance (Ω 100 cm^2 per sheet)	Porosity calculated (%)	Amount of electrolyte retained (%)	Wetting time (s)
SWP1	0.16	10	0.00200	90	84	3
SWP2	0.13	18	0.00133	88	78	5.4
SWP3	0.15	15	0.00127	85	78	< 1
SWP4	0.13	21	0.00187	86	72	1
SWP5	0.12	27	0.00267	87	75	15
SWP6	0.17	10	0.00153	85	81	2
SWP7	0.19	13	0.00233	87	78	2
Silica powder AGM (8)	0.20	17	0.00048	88	88	3
Conventional AGM (9)	0.14	15	0.00030	93	94	< 1

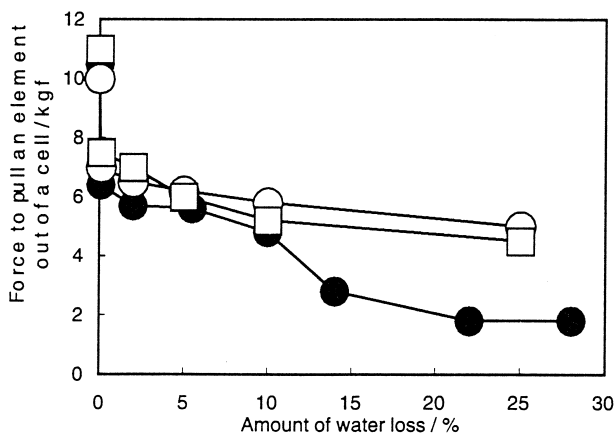


Fig. 12. Effect of water loss on plate compression. Batteries are 6-Ah, 2-V types with: (●) AGM; (○) SWP 2; (□) SWP 7.

is the high resistance: the resistance of the SWP mat is almost 3 to 5 times higher than that of conventional AGM.

Compression changes are shown in Fig. 11. In a dry condition, the SWP mat loses compression faster than the AGM, and thus has to be compressed at about 40 kgf dm⁻² to keep the pressure at 20 kgf dm⁻² after an hour. When acid is added, however, the SWP mat loses less compression than the AGM counterpart, i.e., the performance of the battery with the SWP mat will be less affected by introducing acid. In the compression–decompression test, the SWP mat exhibited another unique property. When the SWP mat was pressed more tightly and then decompressed again, the compression recovered to 6 kgf dm⁻² in 20 min. This behaviour is probably due to the fact that the SWP mat is made of elastic polymer fibres and these are bound by low-melting-point fibres. Meanwhile, once the AGM, made of less elastic glass fibre, is pressed tightly, it does not recover the compression when the pressure is relaxed, i.e., the pressure after decompression is 0 kgf dm⁻². These results indicate that compression will be maintained in a battery with SWP mat during

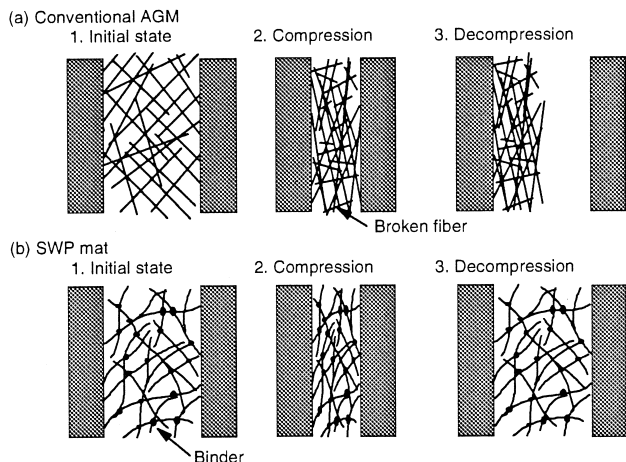
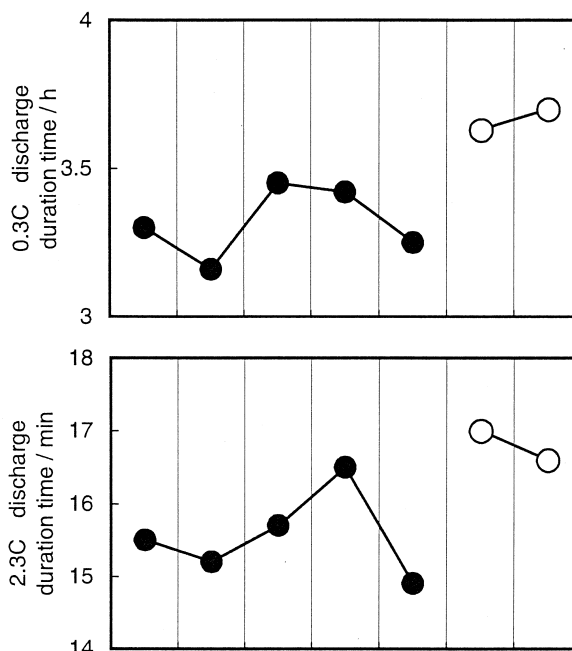


Fig. 13. Schematic representation of the response of (a) AGM and (b) SWP mat to compression and decompression of the cell.



Cell No.	S-2	S-4	S-5	S-6	S-7	SP-AGM	C-AGM
Separator	SWP2	SWP4	SWP5	SWP6	SWP7	Silica Powder AGM	Conventional AGM
	Fine PE-SWP	Medium PE-SWP	Thick PP-SWP	Glass Fiber 20%	Silica Powder 20%	Silica Powder 70%	Glass Fiber 100%

Fig. 14. Initial discharge capacity of battery with (○) AGM; (●) SWP mat.

charging and discharging, while the compression of AGM on the battery element will be reduced.

The change in the force required to pull the element out of the container with the amount of water loss is shown in Fig. 12. As with AGM, the compression decreases rapidly after pouring water on to the SWP mat, but to a lesser degree. This is probably because the SWP fibre is so elastic that it does not lose tension entirely against the surface tension of the water.

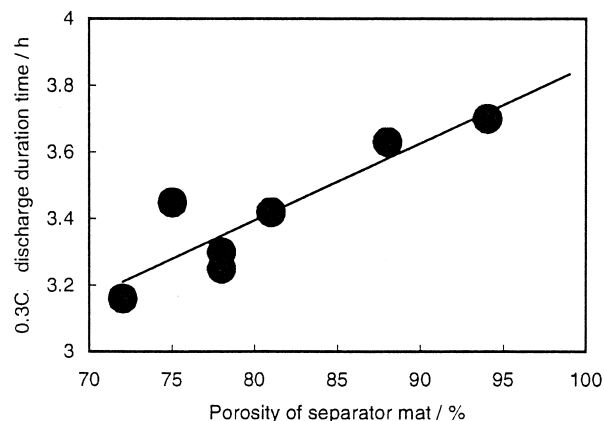


Fig. 15. Relationship between porosity of separator mat and discharge capacity.

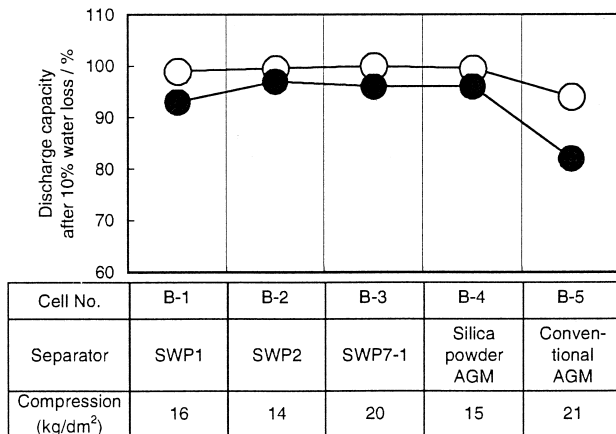


Fig. 16. Discharge capacity after 10% water loss (% initial value): (○) low rate (0.4 C); (●) high rate (2 C).

The above characteristics can be explained by the elasticity and binding force of SWP in the mat, as shown schematically in Fig. 13. These two properties allow SWP to recover the compression when it is decompressed. When AGM is compressed, however, some of the less elastic, micro-glass fibres are broken into short pieces and the binding force of the fibre is too weak to recover the compression.

3.3.2. Battery performance

The initial discharge capacities of batteries with SWP mat or with AGM are compared in Fig. 14. The capacities of the former batteries are lower. The relationship between the discharge capacity of the battery and the porosity of the mat is shown in Fig. 15. The lower discharge capacities of batteries with SWP mat is due to their lower porosity.

The ratio of discharge capacity after 10% water loss to initial discharge capacity is shown in Fig. 16. The batteries with SWP mat retain capacity more than those with con-

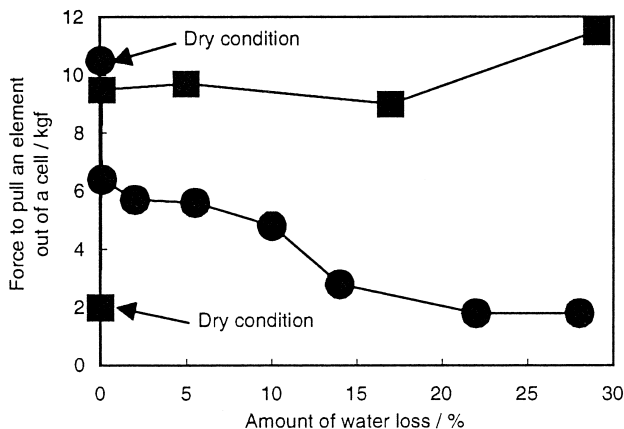


Fig. 17. Effect of water loss on compression. 6-Ah, 2-V batteries with: (●) conventional AGM; (■) granular silica.

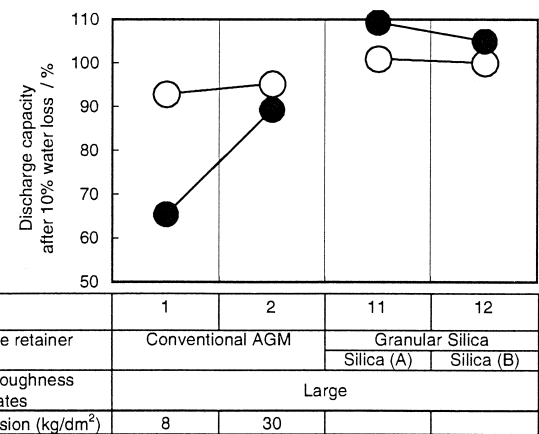


Fig. 18. Discharge capacity of granular silica cell after 10% water loss (% initial value): (○) low rate (0.4 C); (●) high rate (2 C).

ventional AGM. Thus, using SWP mat as an acid retainer is expected to improve the life cycle of VRLA batteries.

3.4. Granular silica

In a battery of this type, the plates are tightly compressed from all directions by granular silica.

The change in the force required to pull the element out of the container with the amount of water loss is shown in Fig. 17. The battery does not lose tension, either after adding water or after 10% water loss. Thus, it is found that granular silica does not shrink or lose compression, even in wet conditions.

The discharge performance after 10% water loss was investigated by the same method as used for SWP mat and AGM. The ratio of the discharge capacity after 10% water loss to the initial value is shown in Fig. 18. The discharge capacity of the battery with granular silica increases after 10% water loss. This is because granular silica does not shrink or lose compression after water loss, and the acid concentration is increased by water loss. From these results, an electrolyte retainer of granular silica is expected to improve the life cycle of VRLA batteries.

4. Conclusions

The following conclusions can be drawn from the experimental results obtained in this investigation.

- (i) The conventional AGM separator shrinks when wetted with acid and when more than 10% of water is lost.
- (ii) Useful SWP mats have been developed.
- (iii) The compression is not decreased when more than 10% of water is lost from the SWP mat. In addition, the mat is so elastic that it sustains compression during changes in the pressure to the mat that are caused by charging and discharging the battery. Accordingly, this separator is expected to improve battery life in electric vehicle applications.

(iv) The granular silica type of battery does not lose compression and, hence, this retainer will also improve battery life in electric vehicle use.

Acknowledgements

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