Characteristics of valve-regulated lead/acid batteries for automotive applications under deep-discharge duty

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Abstract

The performance and discharge characteristics of valve-regulated lead/acid (VRLA) batteries for automotive applications are investigated under various charge–discharge conditions. The influence on cycle-life of factors such as grid structure (cast and expanded) and compression of the element are examined. The possible benefits of adding anisotropic graphite to the positive active material of pasted-type plates are also studied. It is found that optimization of both the structure and the weight of the grids, as well as maintenance of a tight contact between the separators and the plates, are necessary to improve the cycle-life of VRLA batteries at high temperatures. Furthermore, anisotropic graphite is shown to be an effective additive for the enhancement of the high-rate discharge capacity, particularly at low temperatures.

Introduction

Automotive batteries have recently been regarded not only as a means for providing electrical power for the starting, lighting and ignition of automobiles, but also as the basic support for the vehicle's electronic systems. This is because apart from powering accessories (such as audio-visual instruments and air-conditioners), electrical functions have now been incorporated in engine management, driveability and safety systems. As a result, the load on the batteries is continually growing [1, 2]. Moreover, as can be understood from the fact that the surrounding temperature of batteries exceeds 70 °C due to overcrowded engine space and heavy traffic in cities, the conditions under which batteries have to operate are becoming increasingly severe [3].

Valve-regulated lead/acid batteries (recombination type) — VRLA batteries — have been widely used for industrial and consumer applications because they are maintenance free. The development of such batteries for automotive service will bring many advantages, e.g., it will not be necessary to add water during normal lifetime, there will be no spillage of electrolyte and no release of gas or mist, the units can function in any position. These advantages are accompanied by some disadvantages when compared with conventional (flooded type) lead/acid batteries, e.g., poor cycle-life under

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deep discharge, lower resistance to high temperature, and high manufacturing cost. Note, automotive batteries are required to be reliable under severe conditions such as deep discharge and high temperature.

In order to produce VRLA automotive batteries that meet the above demanding requirements, the effects on life performance of the grid structure, the compression of the element, and plate additives have been investigated both under deep-discharge conditions and at high temperatures. The results of these studies are presented in this paper and the problems associated with the development and improvement of VRLA batteries for automotive service are discussed.

Experimental

In order to investigate the effects of the positive grid structure on battery performance, test cells with either cast or expanded grids were constructed. Expanded grids of differing weight but the same design were prepared by changing the thickness of the rolled strips. All negative grids were of the expanded metal type. Table 1 shows the features of the positive and negative plates used in the test cells.

VRLA cells of the starved-electrolyte type consisted of 4 positive and 5 negative plates. The cell capacity was ~ 25 A h at the $C/5$ rate. The electrolyte was absorbed in highly porous microfibre glass separators. A relief valve was fitted to each cell. Metal frames were applied to the outer face of both side walls of each container to provide durability during tests at high temperature.

TABLE 1

Description of test cells[a]

	Cell no.				
	A	B	C	D	E
Positive plates					
Types of grid	expanded	expanded	expanded	cast	expanded
Strip thickness (mm)	0.8	1.0	1.2	1.3[b]	1.2
Grid weight (g)	24.4	30.5	36.6	37.4	36.6
Grid alloy			Pb–0.1 wt.%Ca–0.75 wt.%Sn		
Negative plates					
Type of grid			expanded		
Strip thickness (mm)			0.75		
Grid alloy			Pb–0.06 wt.%Ca–0.5 wt.%Sn		
Remarks		sealed (starved)			conventional (flooded)

[a]2 or 4 V.
[b]Grid thickness.

For comparison, conventional cells containing free electrolyte were also examined. The specific gravity of the electrolyte was 1300 (20 °C) and 1280 (20 °C) for starved and conventional cells, respectively.

In the search for an improvement in battery performance — especially discharge capacity — other test cells in which anisotropic graphite was added to the positive active material were also constructed. Cast grids were used for the positive plates of these cells. Anisotropic graphite (0.5 wt.%) was first mixed with the leady oxide and then made into a paste with dilute sulphuric acid. The graphite had a diameter of 250 to 1250 μm and was of high purity. The elements of these cells were assembled with two kinds of pressure, viz., 5 to 10 and 20 to 30 kg dm^{-2}, to determine the effects of compression on the element.

After capacity tests at various currents, two different life-cycle tests were conducted. The test conditions were as follows.

JIS cycle test
(deep discharge and constant-current charge cycle)
Discharge   20 A × 1 h
Charge   5 A × 5 h
Temperature   40 to 45 °C (in water bath)
Capacity test during cycling   20 A discharge after about every 25 cycles

SAE cycle test
(shallow discharge and constant-voltage charge cycle)
Discharge   25 A × 4 min
Charge   25 A(max.), 2.47 V/cell × 10 min
Temperature   75 °C (in water bath)
Measurement during cycling   30 s voltage at 272 A discharge (every
                                                         500 cycles)

Results and discussion

Effects of grid structure on discharge/life performance
Figures 1 and 2 show the results for discharge at 5.4 A (C/5 rate), 25 A (reserve capacity) and 150 A (at −15 °C), while Figs. 3 and 4 give the discharge characteristics at the C/5 rate (25 °C) and at 150 A (−15 °C). The C/5 capacity of starved-electrolyte cells is about 80% that of flooded-type cells. There appears to be no influence of grid structure or grid weight on either the C/5 capacity or the discharge voltage. As can be seen in Fig. 4, there is a slightly higher voltage at an early stage of discharge for starved-electrolyte cells than for flooded types. This is because the former cells use an electrolyte with a slightly higher specific gravity, i.e., 1300 versus 1280. The reserve capacity exhibits almost the same behaviour as the C/5 capacity. Since the low-discharge-rate capacity, e.g., C/5 rate, is affected by the total amount of electrolyte, it is unavoidable that the capacity of starved-electrolyte cells is less than that of flooded types, even if the former use a slightly
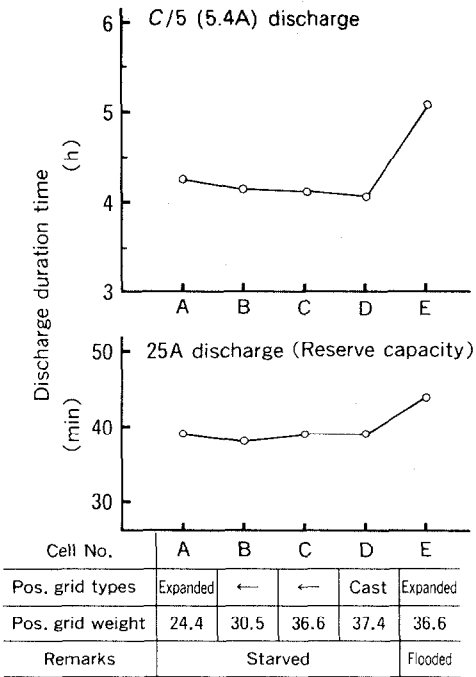
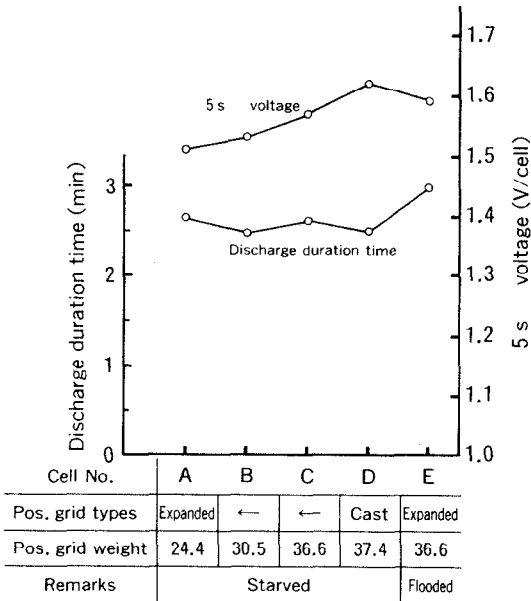Fig. 1. Comparison of C/5 and reserve capacity of test cells (25 °C).

Cell No.	A	B	C	D	E
Pos. grid types	Expanded	←	←	Cast	Expanded
Pos. grid weight	24.4	30.5	36.6	37.4	36.6
Remarks	Starved				Flooded

Fig. 2. Comparison of high-rate discharge performance of test cells (−15 °C).

Cell No.	A	B	C	D	E
Pos. grid types	Expanded	←	←	Cast	Expanded
Pos. grid weight	24.4	30.5	36.6	37.4	36.6
Remarks	Starved				Flooded
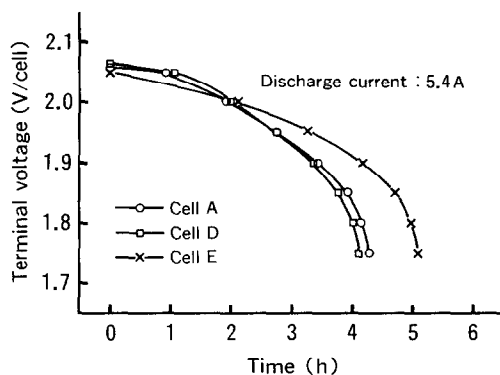
Fig. 3. Discharge characteristics at $C/5$ rate (25 °C).
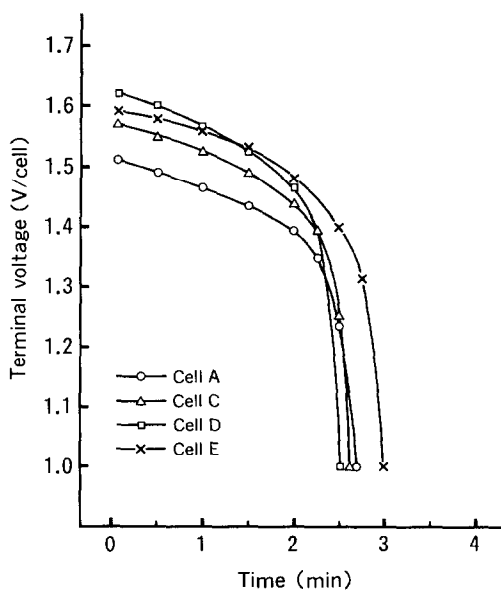
Fig. 4. Discharge characteristics at 150 A (−15 °C).

higher specific gravity of electrolyte. The discharge performance of starved-electrolyte cells when discharged at 150 A and −15 °C is inferior to that of their flooded counterparts. The discharge voltage is affected by the grid weight and the grid structure, i.e., the discharge voltage becomes higher by increasing the grid weight. When the grid weight is the same, the cast grids exhibit higher voltage than the expanded types. This is because cast grids have less ohmic polarization [4]. When flooded- and starved-electrolyte cells with expanded grids of the same weight are compared, the former have a higher discharge voltage. This is considered to result from a difference in concentration polarization due to the delay in supply of electrolyte to the plates.
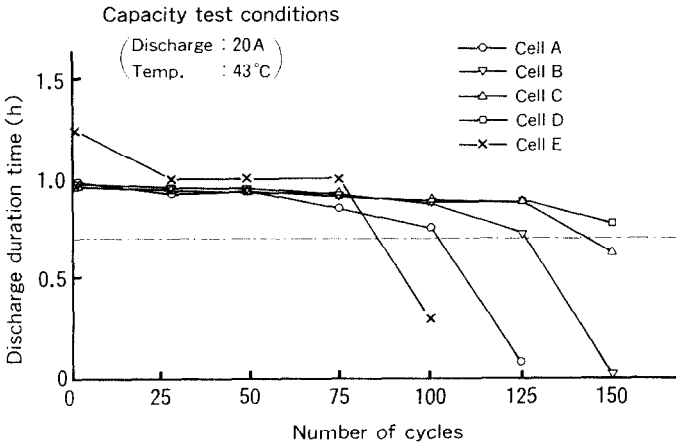
Capacity test conditions

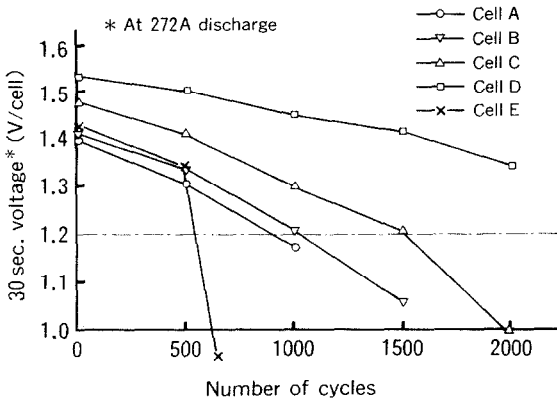Fig. 5. Cycle-life under deep-discharge cycles (JIS D 5301).

Fig. 6. Cycle-life at high temperature (75 °C, SAE J 240).

Figures 5 and 6 display data obtained from cycle-life tests. In these tests, in which deep-discharge and charge are alternately repeated at constant current (Fig. 5). there is an obvious difference in the capacity performance of flooded- and starved-electrolyte cells. The capacity of the former cells decreases during the initial stage of the cycle test. By contrast, starved-electrolyte cells, even those using very light positive grids, exhibit longer life. The cycle-life of these cells is almost in proportion to the weight of the positive grids. Furthermore, *post mortem* examination revealed that the growth of positive grids increases with decreasing grid weight. The SAE cycle test at 75 °C gives the same result as the JIS cycle test (Fig. 6). Flooded-electrolyte cells again have the shortest life, and among starved-electrolyte types, heavier grids tend to yield higher discharge voltage and longer life. Finally, expanded grids provide better performance than cast grids. The difference in

discharge voltage during this cycle test is due to the difference in the electrical resistance of th grids, and this, in turn, influences cycle-life.

Effect of electrolyte quantity on cycle-life

It has been considered that VRLA batteries with lead–calcium alloy grids are unsuitable for use under deep-discharge and at high temperatures. As shown by the above tests, however, starved-electrolyte cells give longer cycle-life than flooded-electrolyte units. Therefore, the effects of the quantity of electrolyte on performance were examined using cell D in Table 1. The discharge current and the cut-off voltage in the cycle test were 20 A (approx. $C/1$) and 1.70 V/cell, respectively. The test results are presented in Fig. 7. This cycle test was first conducted under the starved-electrolyte condition. At the 21st cycle, electrolyte was added to the cells until a flooded state was reached. Thereafter, the discharge capacity started to decrease. At the 44th cycle, the cells were returned to the starved state by drawing off electrolyte. The capacity then started to increase gradually and reached the value recorded at the beginning of the test. These findings suggest that the cycle-life of positive plates with lead–calcium grids is greatly influenced by the amount of electrolyte and that a flooded state results in a decrease in capacity at an early stage. In order to understand this behaviour, each cell was removed from the test circuit at points (a), (b) and (c) shown in Fig. 7. After a discharge at 20 A for 20 min, the interface between the positive grid and the active material was examined. Scanning electron micrographs and the distribution of $PbSO_4$ measured by EPMA (electron probe micro-analyser) are given in Fig. 8. It can be seen that while the corrosion layer on the grids at (a) and (c), discharged in starved electrolyte, contained little $PbSO_4$, the plate at (b) had a large amount of $PbSO_4$ in the corrosion layer. Thus, under flooded conditions, the passivation layer tends to occur on the grid surface at an early
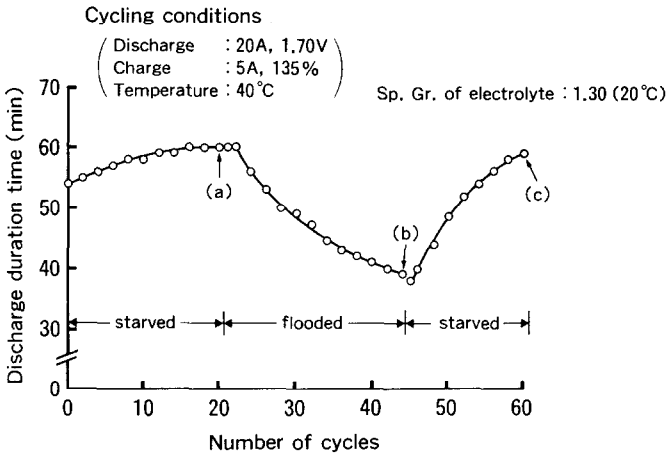

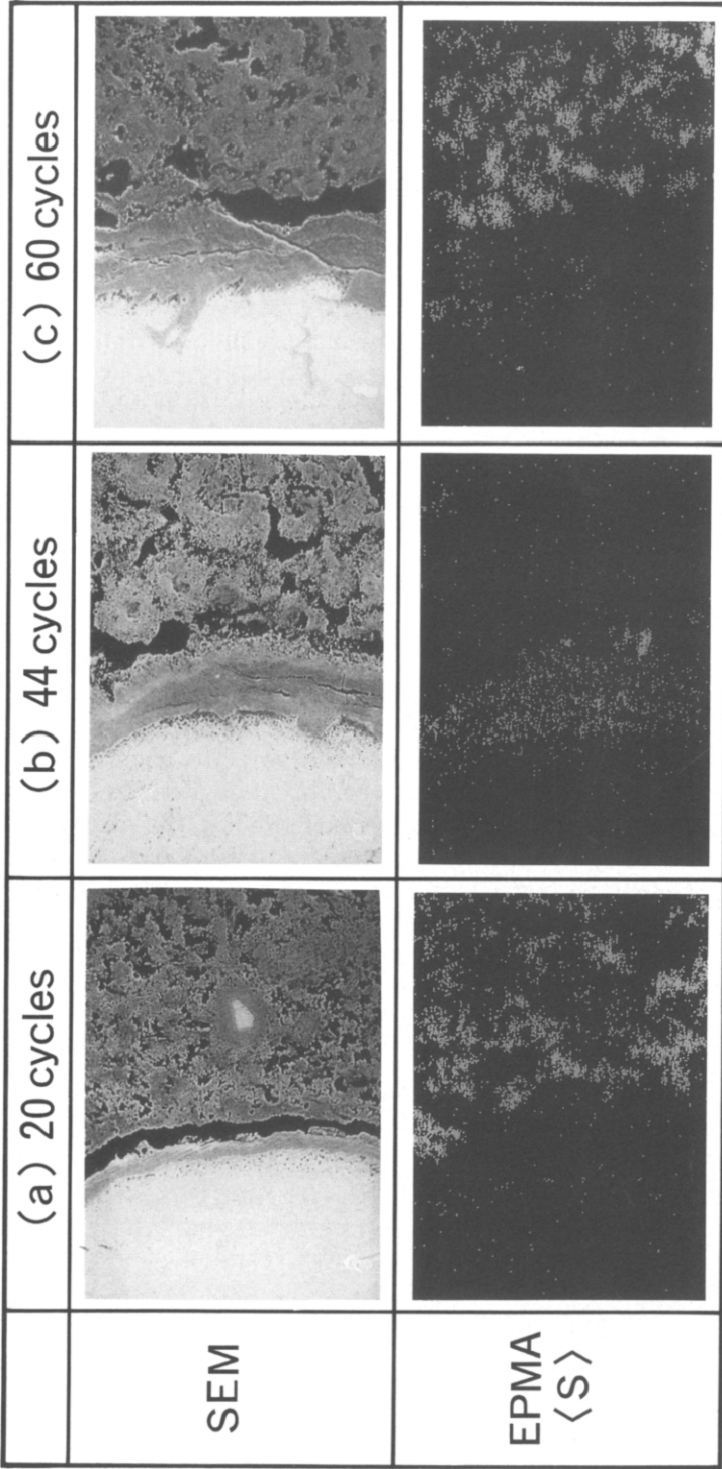Fig. 7. Results of cycle tests.

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Fig. 8. Grid/active-material interface of positive plates (after discharge at 20 A for 20 min).

stage of discharge. This can be taken as the cause for the decrease in the discharge capacity. It appears that the amount of electrolyte changes the pH at the positive grid/active-material interface and, correspondingly, the chemical composition and properties of the corrosion layer are changed. This may give rise to the difference in reactivity of the corrosion layer.

Effect of mechanical strength of container

The cycle-life of VRLA cells, especially at high temperature, depends markedly on whether the compression of the element is kept sufficiently large for the glass-fibre separators to have tight contact with the plates. At high temperatures, the containers tend to be deformed and the contact of plates with separators may not be adequate. Figure 9 shows results at 75 °C for cells using conventional (flooded-electrolyte) automotive battery containers. In one of these cells, the outer face of both side walls of the container was reinforced with metal frames to prevent the deformation. This cell could withstand charge and discharge cycles in a high-temperature environment. By contrast a similar cell, but without reinforcement, exhibited a decrease in capacity at an early stage due to deformation of the side walls.

Effects of anisotropic graphite in positive plates and compression for element

When anisotropic graphite is oxidized anodically in sulphuric acid, a graphite intercalation compound is formed and expands anomalously [5]. Success has already been achieved in improving the discharge performance by applying anisotropic graphite to positive plates [6, 7]. In order to lift the cycling performance of flooded-electrolyte batteries, it has also been found that it is important to prevent the disintegration of positive active material. The latter is caused by stresses that are brought about by expansion and shrinkage of the material during charging and discharging. Because of this,
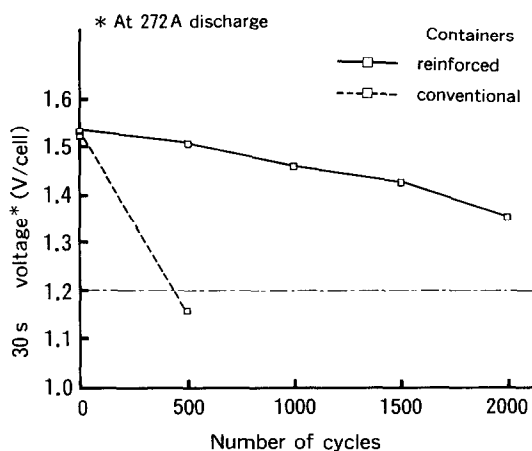

Fig. 9. Cycle-life at high temperature of cell with reinforced container (75 °C, SAE J 240).

it is beneficial if glass-fibre mats exert a tight pressing on the positive plates [8]. These two new technologies have already been introduced into pasted-type lead/acid batteries and are put to practical use in golf carts and electric vehicles in Japan.

As described previously, the discharge performance of starved-electrolyte cells is inferior to that of flooded types. Moreover, the deep-discharge cycling performance of starved-electrolyte cells is below that of flooded-electrolyte units using lead–antimony alloys in the positive grids [9, 10]. To lessen these drawbacks an examination was made of the effects of (i) adding anisotropic graphite to the positive plates and (ii) compressing the element in starved-electrolyte cells.

Figures 10 and 11 present the characteristics at $C/5$ and 150 A discharge, respectively. For $C/5$ capacity, the cells with anisotropic graphite show an increasing discharge time of about 10 min (5%), but are not quite up to the performance of flooded-electrolyte cells. On the other hand, when discharged at 150 A and -150 °C, starved-electrolyte cells with anisotropic graphite exhibit an increased discharge time of about 10 to 30% compared with untreated cells, and also show a slightly higher discharge voltage than that of flooded-electrolyte types. At a comparatively low rate discharge, such as $C/5$, the total amount of electrolyte influences the discharge capacity. When discharged at high current and low temperature, such as 150 A and -15 °C, however, the electrolyte in, and adjacent to, the plates will participate more in the discharge reaction than the total amount of electrolyte. The increase of large pores and porosity brought about by the formation of graphite intercalation compounds in the active material would be expected to facilitate the transfer and diffusion of sulphuric acid into the plates. Therefore, when the temperature is lower and the discharge rate is higher, the addition of anisotropic graphite is more effective. It has also been suggested
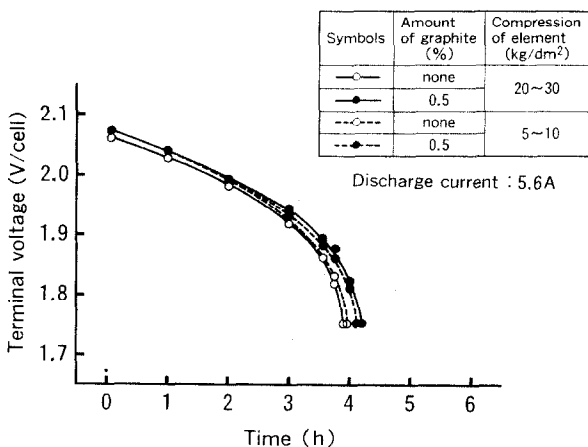
Symbols	Amount of graphite (%)	Compression of element (kg/dm^2)
—○—	none	20~30
—●—	0.5	
--○--	none	5~10
--◆--	0.5	

Discharge current : 5.6A

Fig. 10. Discharge characteristics at $C/5$ rate (25 °C).

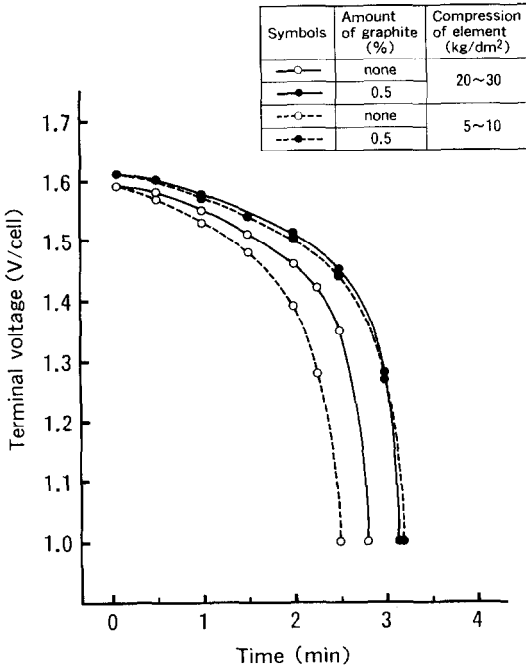| Symbols	Amount of graphite (%)	Compression of element (kg/dm²)
—○—	none	20~30
—●—	0.5	
--○--	none	5~10
--●--	0.5	

Fig. 11. Discharge characteristics at 150 A (−15 °C).

[11] that a further reason for the increase in the discharge capacity caused by adding anisotropic graphite is the action of electro-osmotic pumping.

Figures 12 and 13 provide the results from the deep-discharge cycle test and SAE cycle test at 75 °C. In both cases, anisotropic graphite does not greatly influence the life performance. The latter, however, improves by

Symbols	Amount of graphite (%)	Compression of element (kg/dm²)
—○—	none	20~30
—●—	0.5	
--○--	none	5~10
--●--	0.5	

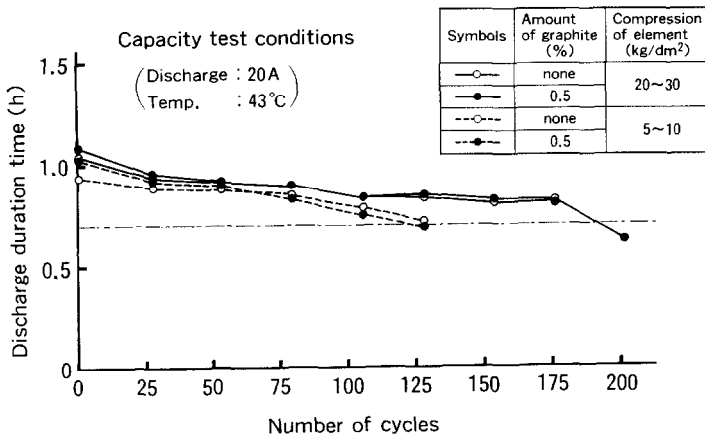Capacity test conditions
(Discharge : 20 A
Temp.   : 43 °C)

Fig. 12. Cycle-life under deep-discharge cycling (JIS D 5301).
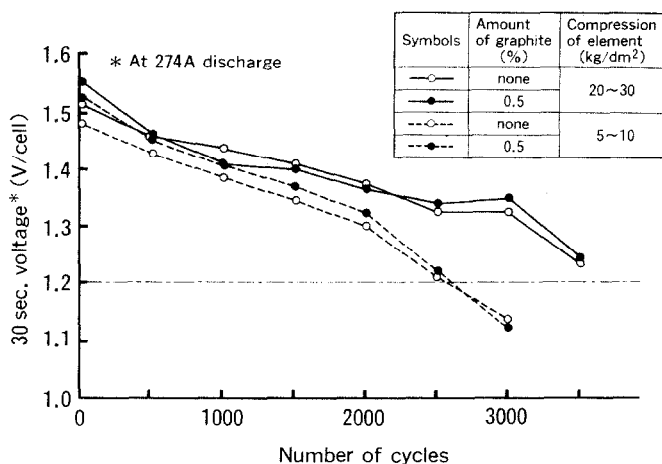
Fig. 13. Cycle-life at high temperature (75 °C, SAE J 240).

increasing the compression of the element. This finding highlights the importance of applying pressure to positive plates.

Conclusions

The structure and weight of positive grids both greatly affect the cycle-life performance of starved-electrolyte cells. Keeping the plates and separators in tight contact by compression of the element was also remarkably effective in increasing the cycle-life at high temperatures. Finally, the addition of anisotropic graphite to the positive active material raised the high-rate discharge performance at low temperature, thus allowing the same performance as that of flooded-electrolyte cells to be achieved.

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