

Valve-regulated lead/acid batteries with granular silica

Masaaki Shiomi, Katsuhiko Takahashi and Masaharu Tsubota

Lead-Acid Battery Laboratory, Japan Storage Battery Co., Ltd., Minami-ku, Kyoto (Japan)

Abstract

The performance of tubular, valve-regulated lead/acid (VRLA) cells with granular silica for cycle service application has been investigated and compared with that of conventional gelled-electrolyte counterparts. Laboratory testing shows that the cycle-life performance of granular-silica cells is far superior to that of gelled-electrolyte types, i.e., up to 1600 cycles at 50 °C and 1000 cycles at 70 °C. It is also found that the provision of a gap between the tubes is an effective approach towards increasing the utilization of positive active material in tubular VRLA cells.

Introduction

In recent years, the use of valve-regulated lead/acid (VRLA) batteries that require no water maintenance has rapidly become widespread. For stationary applications, in particular, these designs are replacing conventional, flooded-electrolyte batteries. There is also a strong requirement for VRLA batteries in duties that involve cycle service at high charge and deep discharge.

Nevertheless, the application ratio of VRLA batteries to conventional flooded electrolyte in such operations is still small. The main reason for this is that when conventional VRLA batteries (i.e., starved-electrolyte types where the electrolyte is retained either in fine glass-fibre separators or in electrolyte that is gelled with fine silica powder) are subjected to deep charge/discharge cycling, the capacity decreases at a comparatively early stage compared with flooded-electrolyte batteries.

Accordingly, in order to improve the cycle-life performance of VRLA batteries, we are now proceeding with the development of a tubular type, VRLA battery that differs markedly from conventional VRLA designs [1–3]. This battery employs granular silica as an electrolyte-retaining material, and we call it a 'granular-silica battery'. This paper describes briefly the construction of this new type of battery and provides information on the performance under cycling service. In particular, a cycle-life test has been carried out at high ambient temperatures in anticipation of using the batteries in forklift trucks for which rigorous duties are normally encountered. Finally, an examination has been made of various methods for assessing the virtues of using tubular plates in valve-regulated designs of lead/acid batteries.

Granular-silica battery

Battery structure

Figures 1 and 2 illustrate the design of a granular silica cell. Basically, the construction is the same as that of a conventional VRLA cell, except that granular silica is packed between the positive and negative plates and also around the elements.

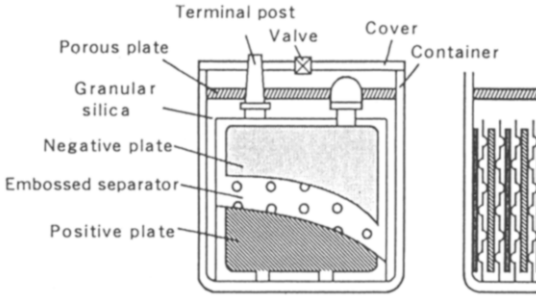


Fig. 1. Construction of granular-silica cell.

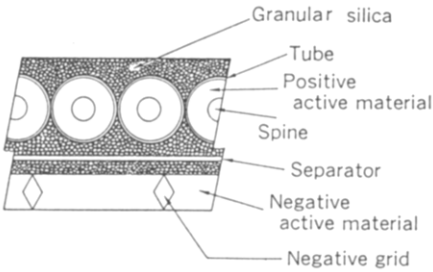


Fig. 2. Cross section of granular-silica cell.

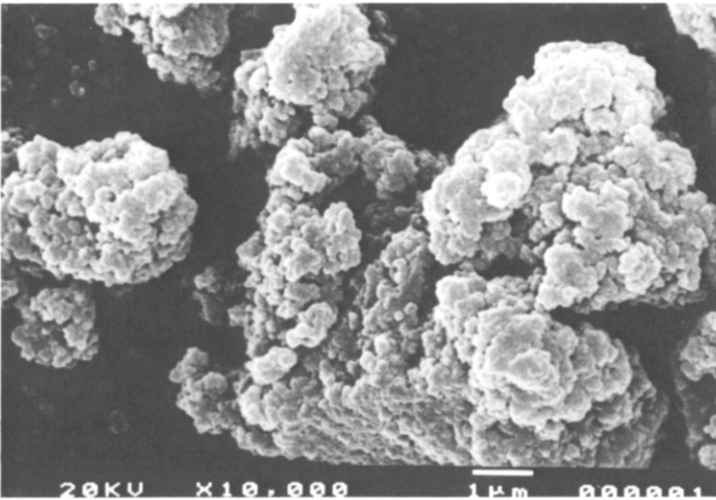


Fig. 3. Scanning electron micrograph of granular silica.

Characteristics of granular silica

Figure 3 shows the microstructure of granular silica. This material is made by granulating hydrous silicon dioxide. Granulation is required because the bulk density of the material in a primary-particle condition is low and thus it is difficult to pack it densely inside a cell. With loose packing, the silica will shrink on addition of electrolyte.

The granular silica has about the same porosity as the fine glass-fibre separators that are used as the acid-retaining material in conventional starved-electrolyte batteries. On the other hand, since the specific surface area of the granular silica is extremely large, the material exhibits an excellent capability for retaining electrolyte, and thus reduces stratification effects. This property offers a significant advantage for tall batteries used in forklift trucks.

Examination of the pore-size distribution of the granular silica (Fig. 4) reveals that there are two types of pores. The large pores are greater than those in the active material of either the positive or negative plates and are nearly the same size as those in a glass separator. This shows that functions similar to those of a glass separator can be expected from granular silica when it is used as an electrolyte-retaining material.

The transfer rates of sulfuric acid in granular silica, compared with those in either a fine glass-fibre separator or a gel, are given in Fig. 5. The data were obtained from a cell that was composed of two vessels that were separated by a separator, as shown in the Figure. One vessel was filled with an electrolyte-retaining material that contained sulfuric acid of 1.300 (20 °C) sp. gr., and the other with water. The cell was left standing for 48 h, after which the specific gravity was measured at the sampling point, item 5 in the Figure. For granular silica, the difference in the specific gravity of the sulfuric acid before and after the standperiod was smaller than that for a glass separator, but larger than that for a gel. In other words, the transfer of sulfuric acid in granular silica is slower than that in a glass separator, but faster than that in a gel.

When a sheet-like electrolyte-retaining material, such as a glass separator, is used in tubular designs of VRLA cells, there is a problem with ensuring an effective contact with the plates. This difficulty is removed with granular silica since the latter can be easily packed into small gaps (as found between tubes), as shown in Fig. 2. Thus,

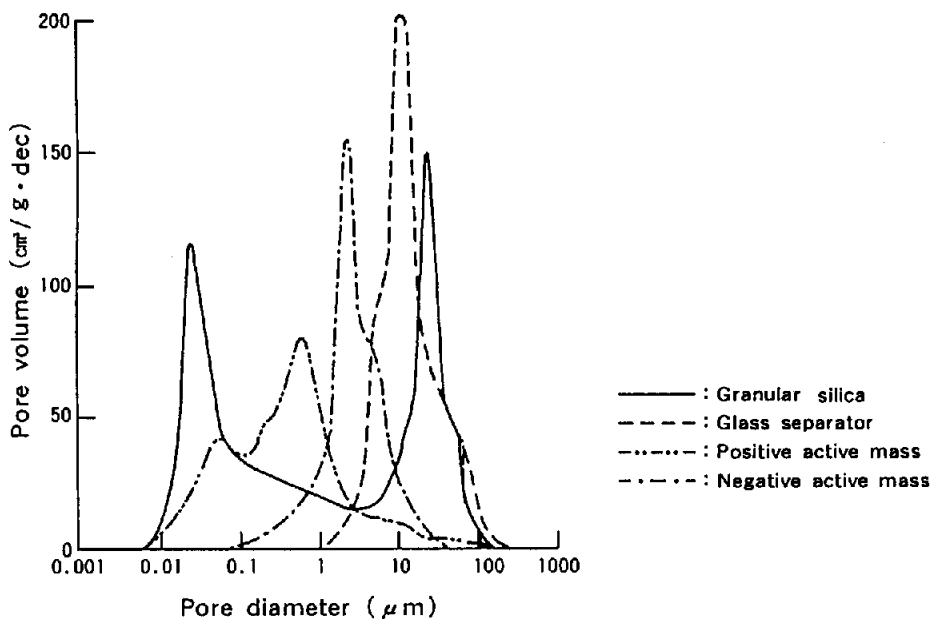


Fig. 4. Comparison of pore-size distribution.

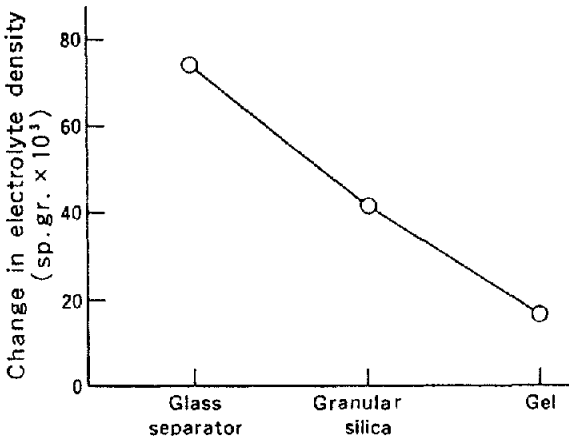
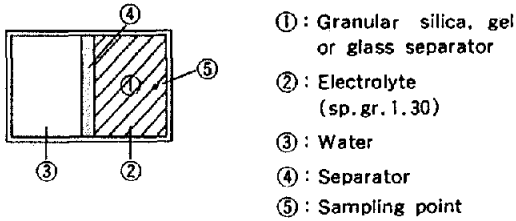


Fig. 5. Comparison of transfer rates of sulfuric acid.

granular silica is eminently suitable as an electrolyte-retaining material for tubular VRLA cells.

Battery performance with granular silica

Experimental

Experiments were performed on tubular VRLA cells, each of which was composed of two tubular positive plates (inside tube diameter: 9 mm) and three pasted negative plates (thickness: 5.0 mm). The capacity was ~ 25 A h at the 5 h rate. The grids for the positive and negative plates were fabricated from a Pb-Ca-Sn alloy. Granular silica was packed into the cells, electrolyte was added, and the cells were charged to the specified level. The specific gravity of the electrolyte was 1.30 (20 °C). For comparison purposes, tubular gelled-electrolyte cells (of the type already in practical use in Germany and other countries) were also prepared.

After examining the discharge capacity and the gas-recombination efficiency at a number of currents, cycle-life tests were conducted under the following conditions: discharge: 0.4 C A for 1.3 h; charge: two-step, constant current (124% of discharge A h), and temperature: 50 and 70 °C (in a water bath).

Results and discussion

A comparison of the discharge capacities of gelled-electrolyte and granular-silica cells is given in Fig. 6. No difference in capacity was observed for a discharge at the

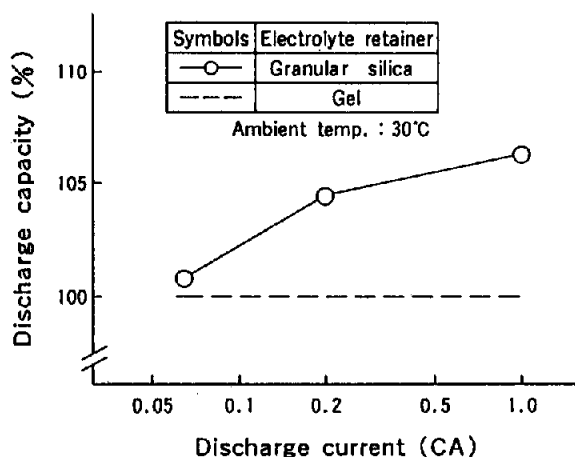


Fig. 6. Dependence of discharge capacity on discharge current.

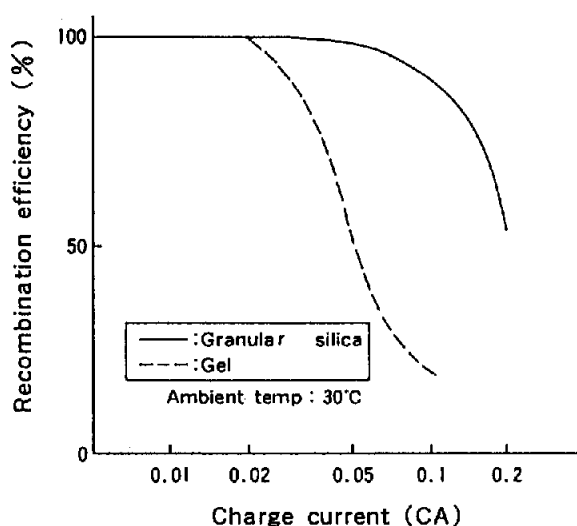


Fig. 7. Dependence of recombination efficiency on charge current.

20-h rate. By contrast, as the discharge current was increased, the discharge capacity of the granular-silica cell became greater than that of the gelled-electrolyte type. This is because the transfer of sulfuric acid retained in the granular silica is faster than that in the gel. A granular-silica cell is therefore suitable for applications requiring discharge currents at the 5-h to 1-h rates, e.g., forklift truck service.

The recombination efficiency of a gelled-electrolyte cell begins to decrease when the charging current increases beyond the 50-h rate (i.e., 0.02 C rate), Fig. 7. By comparison, the granular-silica cell has a recombination efficiency of more than 90% at a charging current of 0.1 C amperes. From this, it can be seen that the granular-silica cell has significantly superior gas-recombination characteristics.

Figures 8 and 9 show changes in the discharge capacity during cycle-life tests that were performed at 50 and 70 °C, respectively. The capacity of a gelled-electrolyte cell gradually decreases; the cycle life is 1000 cycles at 50 °C and 300 cycles at 70 °C. On the other hand, a granular-silica cell still retains 86% of its initial capacity even after 1600 cycles at 50 °C. At 70 °C, 91% of the initial capacity is obtained after 1000 cycles.

One each of the two types of cell tested at 50 °C was disassembled after 800 cycles and examined to observe the condition of the positive and negative plates. As noted above, the positive-plate capacity of the granular-silica cell was considerably larger than that of the gelled-electrolyte cell. Examination of a representative cross section of the positive plate after discharge revealed that lead sulfate resided only on the inside of the positive plate of the gelled-electrolyte cell, and that there was very little discharge of the surface zones of the active material (Fig. 10). This suggests that the active material on the surface had deteriorated. On the other hand, for the granular-silica cell, lead sulfate was distributed over the entire positive plate. This indicated that there was less advanced deterioration of the active material. The decrease in the amount of electrolyte during the cycle-life test was 4% at 1600 cycles for the

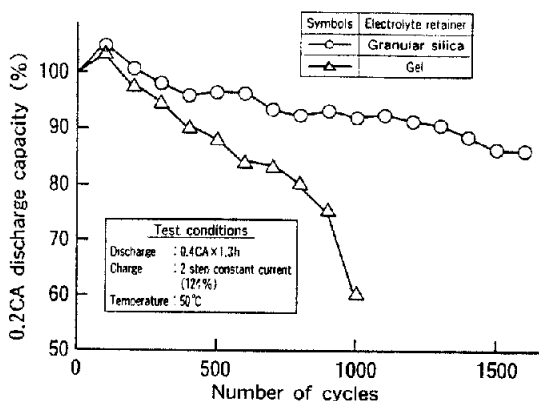


Fig. 8. Changes in discharge capacity of tubular VRLA batteries during cycle-life test at 50 °C.

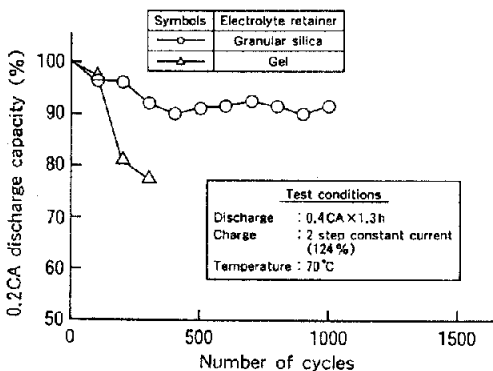


Fig. 9. Changes in discharge capacity of tubular VRLA batteries during cycle-life test at 70 °C.

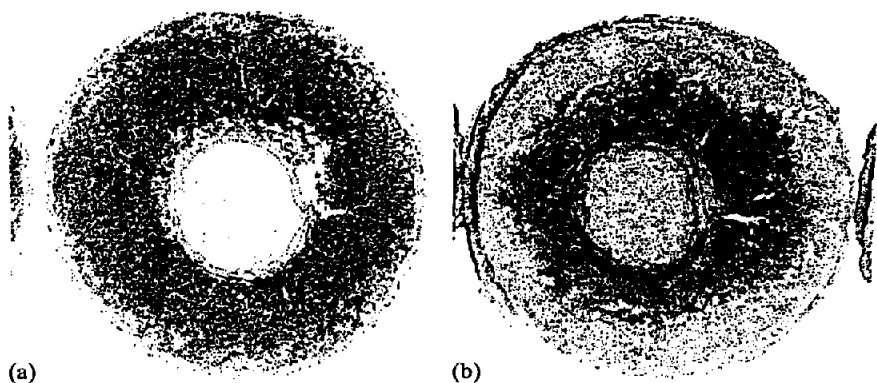


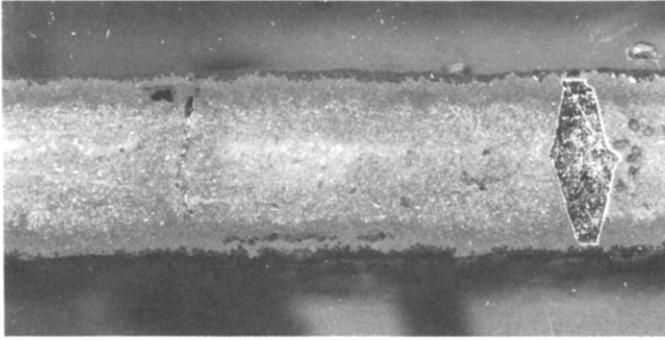
Fig. 10. PbSO_4 distribution in discharged tubular positive plates after 800 cycles: (a) granular silica; (b) gel. Discharge conditions: 0.2 C A to 1.70 V in flooded electrolyte at 30 °C; cycle-life test conditions: discharge: 0.4 C A \times 1.3 h; charge: 2-step constant current (124%); temperature: 50 °C.

granular-silica cell and 10% at 1000 cycles for the gelled-electrolyte cell. This disparity was due to a difference in the recombination efficiencies of the two cells. For the gelled-electrolyte cell, an increase in the specific gravity of the electrolyte caused by an increase in water consumption probably promoted the deterioration of the active material.

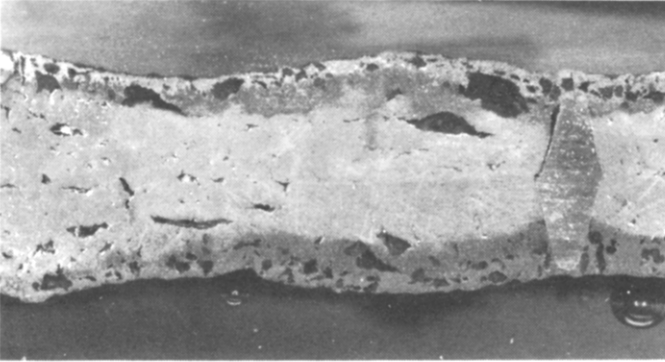
On the other hand, 22% of the lead sulfate accumulated in the negative plate of the gelled-electrolyte cell, while only 4% was in the negative plate of the granular-silica cell. The cross sections of the negative plates from the gelled-electrolyte and granular-silica cells are shown in Fig. 11. It can be seen that the negative plate of the gelled-electrolyte cell has swelled considerably, and has thereby generated some large voids on the surface of the active material. By contrast, this behaviour is not exhibited by the plate in the granular-silica cell; the material is in a good condition. It would appear that granular silica functions to compress the negative plate uniformly, and thereby retards deterioration of the active material [4].

Thus, the performance of granular-silica cells is far better than that of gelled-electrolyte counterparts. Nevertheless, the performance of the former is still behind that of conventional, flooded-electrolyte cells. In particular, the utilization of the positive active material in granular silica cells is low. In order to ascertain the reason for this, an examination was made of the reaction distribution that is available during discharge. Figures 12 and 13 present the distribution of lead sulfate in the cross sections of positive plates after discharge. The analysis reveals that, in flooded-electrolyte cells, the positive plates discharged almost uniformly on the surface side. In granular-silica cells, however, the active material is hardly discharged in those areas where the tubes come in contact with one another. Apparently, this is because the local amount of electrolyte is low and because, in VRLA cells, the electrolyte cannot be supplied sufficiently owing to the much slower rate of electrolyte transfer. Taken together, these factors render it difficult to discharge the active material in the contact areas.

Thus, in order to facilitate the supply of electrolyte to the active material, a gap was established between the tubes, as shown in Fig. 14. Test results showed (Fig. 15) that whereas the flooded-electrolyte cell exhibited hardly any increase in capacity with a gap between the tubes, a significantly enhanced performance was obtained from the



(a)



(b)

Fig. 11. Cross section of negative plates (after 800 cycles): (a) granular silica; (b) gel.

granular-silica cell. It therefore appears that for tubular VRLA cells, in which electrolyte transfer is slow, the provision of a gap between the tubes is an effective method for increasing discharge capacity. Furthermore, by providing a gap between the tubes, the current distribution becomes uniform and, therefore, an improvement in life performance is to be expected.

Conclusions

A study has been made of the performance obtained when granular silica is used in a tubular VRLA cell as an electrolyte-retaining material. Compared with a gelled-electrolyte cell, the granular silica cell excelled not only in discharge capacity but also in cycle-life performance. Furthermore, it has been found that the inclusion of a gap between the tubes is an effective means of improving the utilization of the positive active material in a granular silica cell.

Commercialization of this new type of tubular VRLA battery requires some further problems to be solved. Despite these, granular-silica batteries exhibit excellent features compared with conventional VRLA batteries, and they are considered to be promising

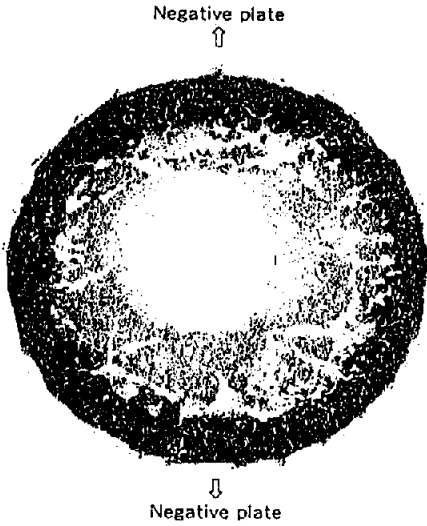


Fig. 12. $PbSO_4$ distribution in positive plate discharged in flooded electrolyte; discharge: 0.2 C A to 1.70 V; sp. gr. of electrolyte: 1.30 (20 °C); temperature: 25 °C.

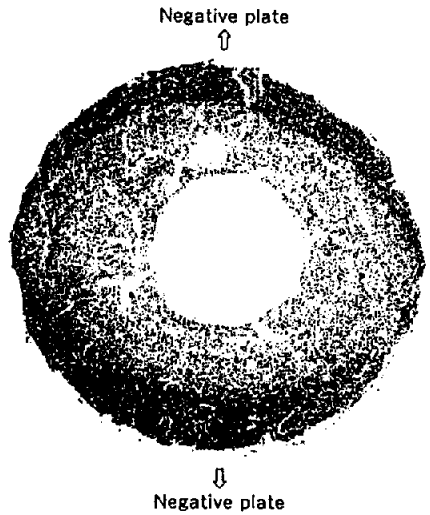


Fig. 13. $PbSO_4$ distribution in positive plate discharged in granular silica cell; discharge: 0.2 C A to 1.70 V; sp. gr. of electrolyte: 1.30 (20 °C); temperature: 25 °C.

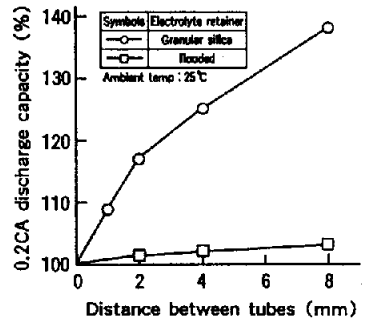
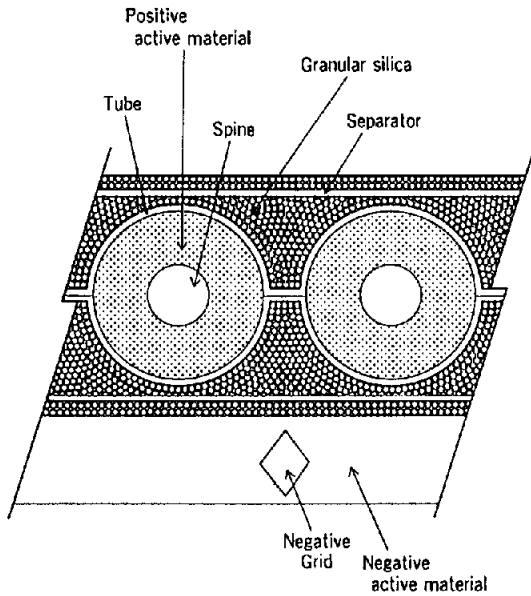


Fig. 14. Cross section of granular-silica cell using a new tube for the positive plate.

Fig. 15. Relation between discharge capacity and distance between tubes.

technology for cycling duties such as those required in the operation of forklift trucks.

References

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