DESIGN AND PERFORMANCE OF A SODIUM/SULPHUR MULTITUBE CELL

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Summary

Multiplate or multitube arrangements in battery designs generally result in higher specific energy and power values. Preliminary investigations into the design and operation of a 4-tube Na/S cell with a theoretical capacity of 155 A h showed values of 100 W h/kg for the energy density at the 3 h rate and of 6 mΩ for the cell resistance, corresponding to a maximum power density of 100 W/kg. With further improvements, values of 165 W h/kg and 180 W/kg can be expected to be realized. Another advantage of this design is reduced corrosion problems because the sulphur electrode can be put inside the β-Al$_2$O$_3$ tubes. A more complex fabrication process and a higher probability of failures may be considered as drawbacks of this design.

Introduction

The sodium/sulphur battery being developed at Brown Boveri is one of the most promising candidates for electric vehicle traction and utility load levelling [1, 2]. Modules and batteries consist of an array of single (about 50 A h) cells with series and parallel connections.

Various battery systems, such as lead–acid and LiAl/FeS batteries already use a "multi-cell" array [3]. Such a design will increase the energy and power densities and will simplify and reduce the electric wiring. If the single cells are not prismatic but are tubular in design, however, as is the case with Na/S, multicell arrangements are difficult to realize. Nevertheless, some efforts have also been made to put several single Na/S cells into one common casing [4 - 8]. In all of these designs the β-Al$_2$O$_3$ tubes were placed in a common sulphur compartment, representing the so called sodium core arrangement. Such a design tends to lead to higher cell resistances, however, because the distance of the sulphur electrodes from the casing is not uniform. On the other hand, if sodium is outside ("sulphur core design") in a common sodium compartment [8], no resistance problems will arise, because the

sodium electrode generally has a considerably lower resistance than the sulphur electrode. An additional advantage of such a design is the reduction of corrosion problems, because it is easier to coat the outside of a current collector rod with a corrosion resistant material than it is to coat the inside of a narrow tube.

Experimental

As a first step towards a multicell arrangement a 4-tube cell was designed, built and operated. The four tubes have a common casing which contains the sodium. Inside the tubes are the sulphur electrodes. Calculations showed that the distance between the walls of the four β-Al_2O_3 tubes should be 1 - 1.5 mm. Larger distances were not possible because no advantage in energy and power density would result. Such small distances required that instead of the usual α-Al_2O_3 headers one single α-Al_2O_3 disc was used to locate the four tubes. After drilling four holes in such a disc, the tubes were sealed to it with glass so that the distance between the tube walls was 1 mm (Fig. 3). The tubes were 26 mm in outer diameter and 210 mm long and had a specific ionic resistance of about 8 Ω cm at 330 °C. As the space in the cell was re-stricted, a thermocompression bond seal was applied to connect the α-Al_2O_3 disc to the casing. The bonding procedure (0.5 h at 600 °C) is critical because the disc may crack if the rate of change of temperature is too great.

The optimum design of the casing is a square cross section. For practical purposes, however, we used a cylindrical stainless steel casing of 64 mm dia. (Figs. 1 and 2). This leaves a relatively large volume outside the β-Al_2O_3 tubes for the sodium, which, in turn, affects the safety and the uniform distribution of sodium along the tubes. In order to displace excess sodium, therefore, solid aluminium blocks were placed between part of the casing wall and the tubes (Fig. 2). Additional safety was obtained by putting five steel tubes, which were connected at their base to the bulk of the sodium, between the β-Al_2O_3 tubes. About half the sodium needed was placed in a separate reser-voir at the bottom of the cell (Fig. 1). Sodium was brought to the surface of the tubes by the capillary action of alumina powder which filled the free space between the tubes. Thus, it may be expected that the safety of such a design is sufficient. In order to measure their individual performances each tube was provided with a separate feedthrough (large conventional type, see Fig. 1). With a more advanced design, only one small feedthrough will be needed, thus reducing the cell weight and volume considerably.

Details of the cell can be seen in Fig. 1. The current collectors (6 mm dia. each) consist of aluminium, plasma-sprayed with molybdenum. The sulphur electrode is a structured type, i.e., graphite and alumina felt rings are piled alternately. In order to prevent sulphur vapor penetrating the compart-ment above the alumina disc, each tube was closed by placing a close fitting aluminium ring between the current collector and the tube wall. The com-plete cell has a theoretical capacity of 155 A h (limited by the sulphur elec-trodes) and has a weight of 1.8 kg and a volume of 1.1 l.
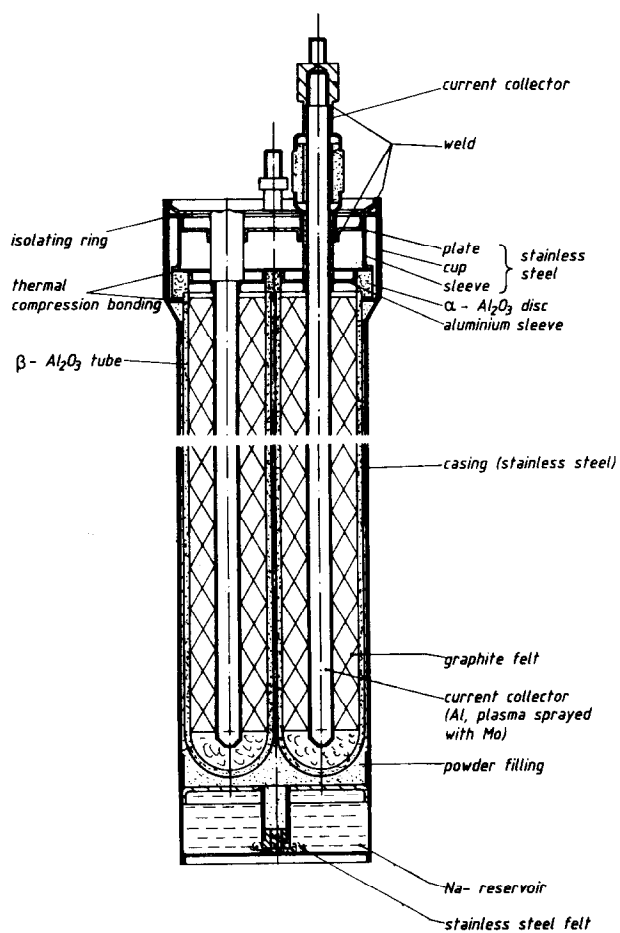
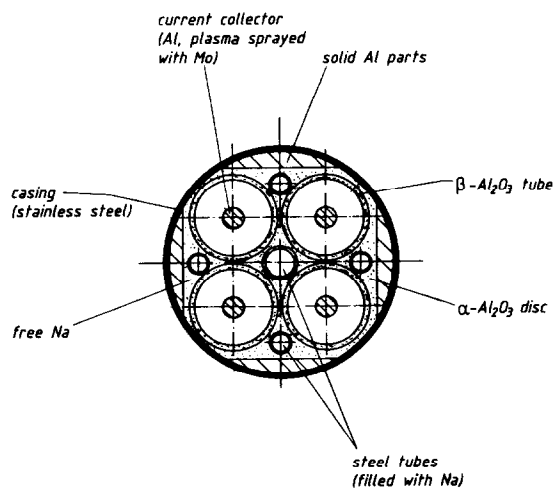Fig. 1. Design of a 4-tube Na/S cell with sulphur cores (longitudinal section).

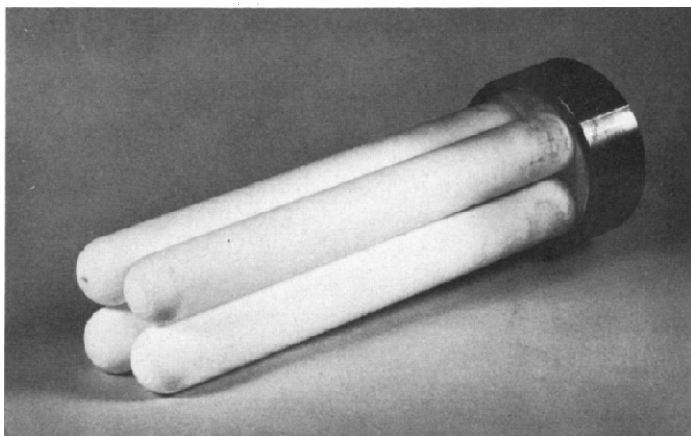Fig. 2. Design of a 4-tube Na/S cell with sulphur cores (cross section).

Fig. 3. Four β-Al$_2$O$_3$ tubes sealed onto a common α-Al$_2$O$_3$ disc and bonded to a steel cup.

Results

Two cells were built and both performed equally well. They were operated at 330 °C, with a discharge current of 45 A and a charge current of 30 A. The voltage and current of each tube were monitored separately. Figure 4 shows the individual voltages and currents for the four tubes, labelled A, B, C and D, during discharge. It can be seen that the voltages differ by about ± 50 mV and the currents by about ± 1 A. These variations showed that the utilizations of the tubes were also different, between 25 and 28 A h. Differences in the electrical resistances of the four tubes account for this and measurements showed that they vary between 22 and 25 mΩ (d.c. values).

When the cell was left on open circuit after discharge, equalizing currents flow. Figure 5 shows that tubes A and C were being discharged, thereby charging tubes B and D. This behaviour was also reflected by the open circuit voltages. The time of 1 h, during which the cell was left on open circuit, however, was not sufficient to obtain a fully equilibrated cell. Figure 5 also shows that one of the tubes was fully discharged to Na$_2$S$_3$, which would mean an open circuit voltage of 1.78 V. The reason for this may be a sodium shortage due to poor capillary action of the powder. This explanation is supported by the abrupt decrease of the cell voltage at the end of discharge in Fig. 4.

At the beginning of operation the cells showed a utilization of about 80%, which dropped after a few cycles to an almost constant 65% (Fig. 6). The cells were not developed for long term operation (conventional feedthrough) and, therefore, lifetimes of 55 and 21 cycles, respectively, seem to be encouraging for these first experiments. Failure was due to severe corrosion of the feedthrough and this, in turn, led to a leakage and sulphur losses which caused the observed capacity decline at the end of operation (Fig. 6). By developing special feedthroughs containing no copper this problem can
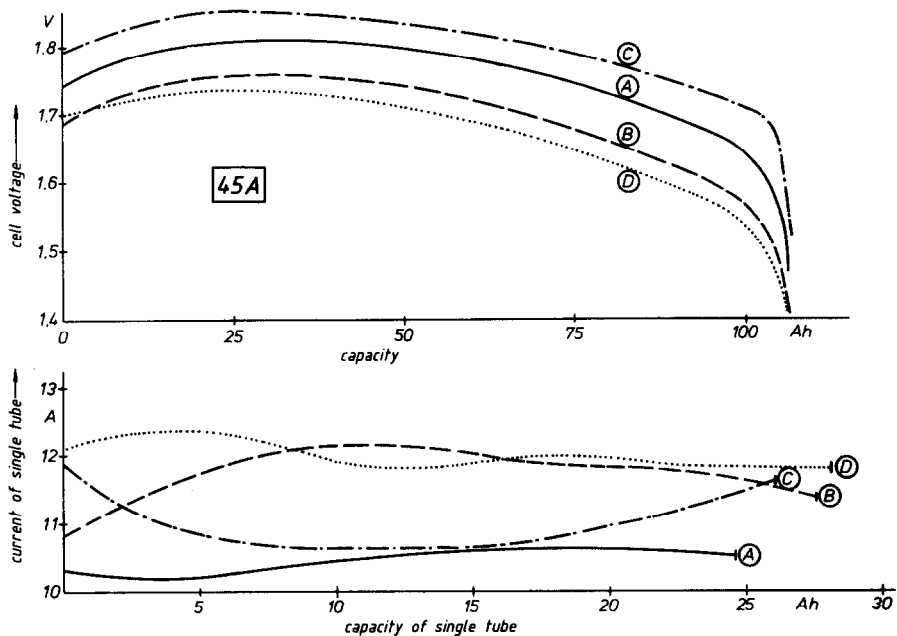
Fig. 4. Cell voltages and cell currents of a 155 A h cell during discharge at 45 A.
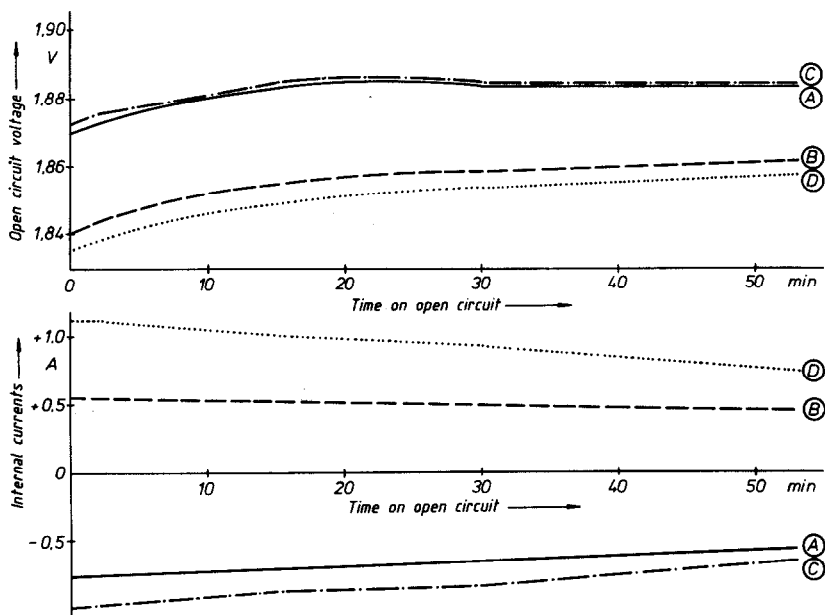

Fig. 5. Open circuit voltage and internal currents of a 155 A h cell during a break after discharge.
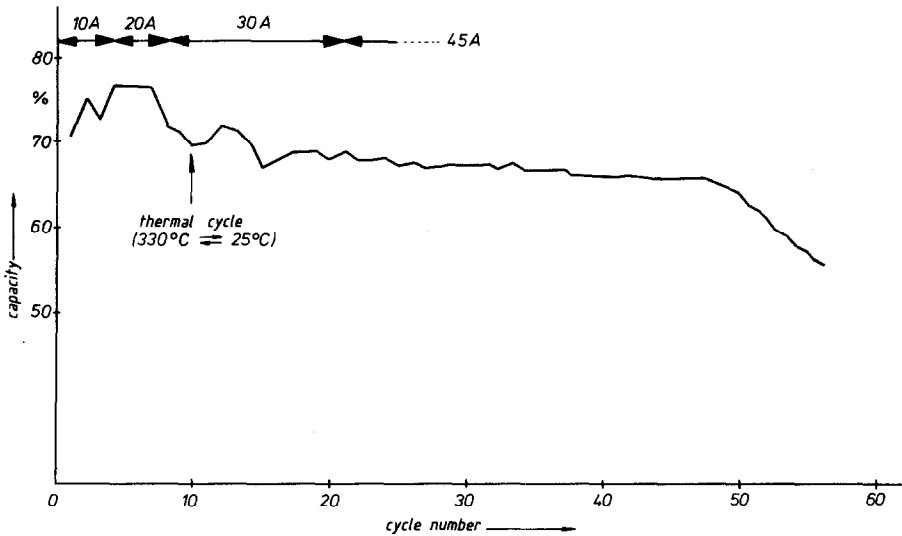
Fig. 6. Capacity of a 155 A h cell as a function of cycle number.

TABLE 1

Performance data and projected data of 4-tube Na/S cells

	Test cell	Projected data (second generation cell)
Capacity (A h)	155	155
Utilization (%)	65	80
Weight (kg)	1.8	1.3
Volume (l)	1.1	0.85
d.c. resistance at 330 °C (mΩ)	6.0	4.5
Specific energy (2 h) (W h/kg)	100	165
(W h/l)	160	250
Specific max. power (W/kg)	100	180
(W/l)	160	280

be overcome. The sturdiness of the cell was also demonstrated by its ability to undergo thermal cycling (330 °C to room temperature) without decrease in performance. Table 1 summarises the experimental data, together with a set of data which can be expected following some relatively simple improvements.

Discussion

The experiments showed that it is possible to build multitube Na/S cells with a similar technique to that used for single cells. The performance of the

4-tube cells operated so far can be improved by the following measures which should pose no problems in application:

— reduction of cell weight: by using only one light feedthrough, making the casing from aluminium, making the aluminium blocks hollow and placing the sodium in them;

— reduction of volume: by removal of the sodium reservoir (Na in hollow Al-blocks);

— increase of capacity: by improving the wetting characteristics of the Na electrode and optimization of the structured sulphur electrode;

— decrease of cell resistance: by using β-Al$_2$O$_3$ tubes with thinner walls (now: 1.7 mm, possible: 1.3 mm), and by increasing the temperature to 350 °C.

Using the projected data in Table 1 (upper part) future values of 165 W h/kg and 180 W/kg will result. Further improvements can be achieved if the casing has a square cross section, thus enabling a higher packing density.

The experiments and the extrapolated data showed that 4-tube cells of the design described above have a high potential for reaching better values of the specific maximum power than single cells (of the sodium core design). This is an important finding because single cells of the sulphur core design (as used in the 4-tube cell) usually show lower values than those of the sodium core design. Therefore, by using 4-tube cells the advantage of reduced corrosion (the casing can be of aluminium or mild steel) is combined with good performance data. It is not yet clear, however, how economical such a cell will be, because the cost of the α-Al$_2$O$_3$ disc is probably rather high and the requirements for the straightness of the β-Al$_2$O$_3$ tubes are very severe. Another point which has not yet been examined is the safety of the design. As already mentioned, putting most of the sodium in a reservoir and in steel tubes will help to establish a high safety standard. Tests have to be carried out, however, to decide whether further safety measures are necessary. Problems with the sodium electrode of this design may also arise. Although we had no problems, it is possible that after more than a hundred cycles or so the capability of the powder to deliver the sodium uniformly to the surface of the β-Al$_2$O$_3$ could decrease. In this case it may be necessary to operate the cell upside down, for example. These potential problems show that further work is needed to decide whether such cells could be used effectively in a battery.

Acknowledgements

References

1 W. Fischer, *Solid State Ionics, 3* (4) (1981) 413.
2 R. Knödler, *Proc. 17th IECEC Conf., Los Angeles, Aug. 1982*, p. 552.