

CURRENT TRENDS IN THE DEVELOPMENT OF SODIUM-SULPHUR BATTERIES*

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Summary

The current status of sodium-sulphur technology in CSPL is outlined. 350 W h cells have now been developed with energy densities of 0.36 W h/cc and 0.16 W h/g, and much of the R & D effort is now being directed towards battery design. Because it must be thermally insulated, the shape of the battery and the thickness of the insulation are significant, and it is possible to realise gross battery energy densities of between 0.1 W h/cc and 0.25 W h/cc, volumetric energy density normally being the more critical. These are some three times greater than for conventional lead-acid batteries, and combined with operating characteristics which differ markedly from conventional batteries, they could offer a number of interesting applications in addition to road transport and load levelling.

Introduction

Work on the sodium-sulphur system at CSPL has, over the last four years, mainly been concentrated on the development of cells which are large enough both to be produced economically and to provide a sensible basis for the construction of a battery which is suitable for motive power purposes. In particular, many problems were encountered, such as the development of electrodes which had adequate recharge characteristics and suitably sized electrolyte of sufficient durability for commercial application. These and other development problems have been discussed in some detail elsewhere [1 - 3] and the current position is that a cell design is now available which will store 350 W h of energy. As the target application for the cell is an electric goods delivery vehicle, geometrical factors have determined that the cell must operate horizontally and the design in Fig. 1 has been evolved. Figure 2 shows a photograph of a current motive power cell together with a cell representing the state of the art at the beginning of this R & D programme. Figure 3 shows a test rig which automatically cycles this type of cell. The cells are cycled independently in parallel with automatic data, acquisition,

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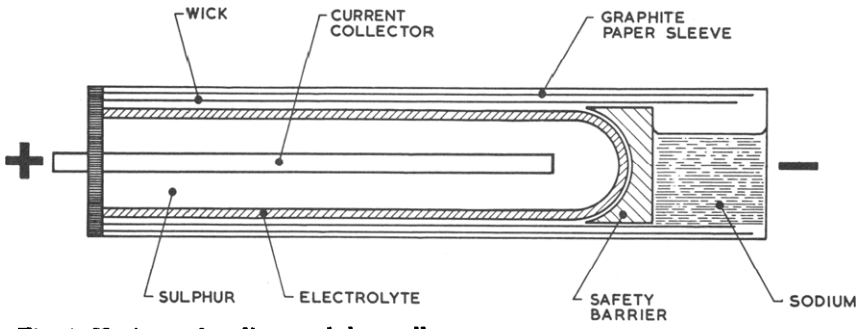


Fig. 1. Horizontal sodium-sulphur cell.

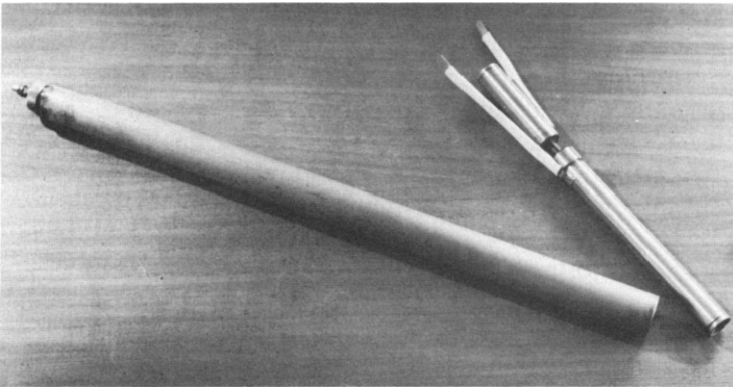


Fig. 2. Sodium-sulphur cells.

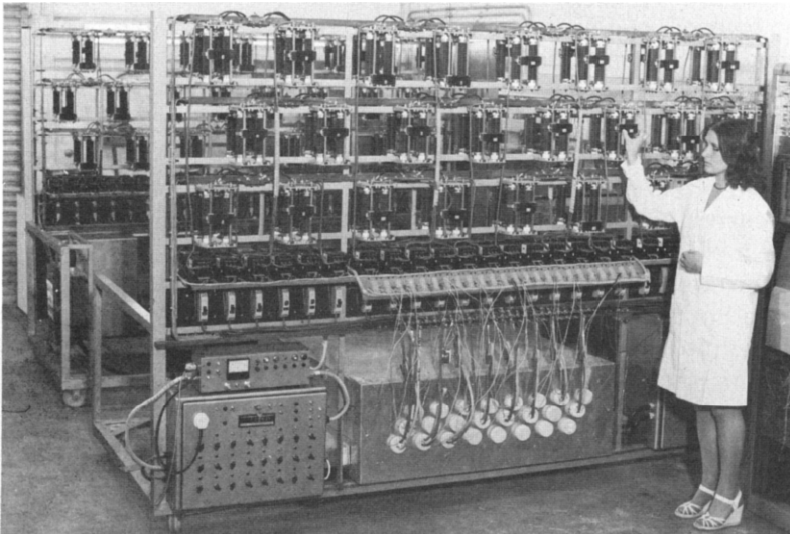


Fig. 3. Automatic test rig.

and processing. Each rig will test 24 cells operating horizontally and four such rigs have been built to date.

The sodium-sulphur cell

The cell is fabricated in the form of a cylinder which contains concentric electrodes. Unlike the lead-acid battery in which the electrodes are solid and the electrolyte is liquid, the electrodes of the sodium-sulphur cell are liquid, and the electrolyte solid. Metallic sodium constitutes the negative electrode and the positive electrode consists of sulphur which has been absorbed onto carbon felt. The latter is necessary to conduct electricity as sulphur is a very poor conductor.

To ensure that the products of the reaction, sodium polysulphides, remain liquid at all states of charge, the cell has to be heated to over 300 °C. The operation of the cell hinges on the β -alumina electrolyte, a ceramic that is impervious to all species except sodium ions. The electrolyte acts, therefore, as a type of sieve which is highly specific to sodium ions.

When the cell is fully charged, the sodium electrode compartment is filled with sodium and the sulphur electrode compartment is filled with pure sulphur. As the cell discharges, sodium is transferred via sodium ions into the sulphur electrode to form sodium polysulphides. A fully discharged cell contains an empty sodium electrode and a sulphur electrode compartment which is filled with sodium polysulphide. When the cell is charged, the process is reversed. A consequence of this process is that the level of sodium in the cell falls during its discharge, which proportionally reduces the area of the electrolyte wetted with sodium and, hence, its effective surface area. This is clearly an unsatisfactory process, as the internal resistance of the cell would slowly rise during its discharge causing an equivalent reduction in available power. To overcome this problem a wick has been developed which ensures that the electrolyte is fully wetted with sodium at all stages of discharge.

Development and design

Safety engineering has played a major role in the development of this cell. If the electrolyte should break for either internal or external reasons the design restricts the rate at which sodium and sulphur can react to a point where there is no emission of active material from the cell case. This is effected by a number of factors. The sodium and sulphur are contained at separate ends of the tube and are separated by a refractory safety barrier which also restricts the rate of flow of sodium to the electrolyte. The close fitting wick further restricts the rate of flow of sodium to the site of the fracture and at the same time helps to support the electrolyte, preserving its mechanical integrity. To prevent any hot reactants from penetrating the cell

case the latter is lined with carbon paper as described by Hames and Tilley [4]. Many tests have been carried out on this type of cell in these laboratories and elsewhere, when the electrolyte has been artificially broken, and on no occasion has the cell case been breached.

Cells of this type have now been cycling for over 10 000 hours and testing is continuing. No maintenance has been carried out on them, or indeed has been possible. As the development policy has always been to design cells which can be produced economically in large quantities, to the point of discarding solutions to problems which would not fit into a framework of a cost effective production unit, these cells now provide a firm foundation on which to develop batteries which will bear a close resemblance to a final commercial product.

Work has now begun in this area and much of it is concentrated in the development of a battery for a 7.5 tonne delivery vehicle. Although battery weight is of obvious importance the critical parameter for electric vehicles is volume, as the battery must fit in the space available under the chassis of the vehicle. After due allowance has been made for transmission and suspension, this space is surprisingly limited. It is feasible, however, to fit a sodium-sulphur battery which will give a range of 120 miles, and this is considerably greater than the daily duty of these vehicles in the UK. Hence, with sodium-sulphur batteries, range would not be the limiting factor in the utilisation of electric, medium weight goods vehicles in the UK.

Because battery volume is, in many applications, more critical than weight, much of the work at CSPL has concentrated on volume reduction. The maintenance free characteristics of the sodium-sulphur battery present a major opportunity in this area. As there is no need to top up the cells, nor to carry out any other form of routine maintenance, there is no need to allow access space and the cells can be packed very tightly indeed to produce batteries of a wide range of sizes and shapes. The volumetric energy density of the sodium-sulphur battery is, however, size dependent. The battery requires an insulating case to maintain its operating temperature and the thickness of this case, which is not primarily dependent on battery size, will degrade the volumetric energy density increasingly as the size is reduced. This is a consequence of the surface area to volume ratio.

The aspect ratio of the battery box will also affect the energy density in the same way, the optimum arrangement for any given capacity being a cube, but in most cases this will be a second order effect; reducing the energy density by less than 10%.

The volumetric energy density of batteries containing the type of cell currently being developed can be calculated by considering a typical sodium-sulphur cell of 38 mm diameter and 82.6 cm long. Current tests on cells of this size in our laboratories indicate that a mean capacity of 185 A h can be obtained reproducibly. At a mean working voltage of 1.9 V the cell will deliver 350 W h. Making allowance for safety engineering and terminals, etc., when mounted in a battery, the cell can be regarded as occupying the space defined by a right rectangular prism, 4 cm square by 85 cm long. These

prismatic "cells" can then be used to build a battery of n^2 cells. The cells are stacked to produce a square cross section. The battery would then be covered with an insulating layer, t cm thick (Fig. 4).

The battery contains n^2 cells, hence, its energy will be $350 n^2$ W h. The volume of the battery will be given by $(85 + 2t)(4n + 2t)^2$. Thus, the energy to volume ratio is given by the expression:

$$\text{Energy/Volume} = \frac{350 n^2 \times 10^3}{(85 + 2t)(4n + 2t)^2} \text{ kW h m}^{-3}$$

This expression is plotted against energy stored for insulation thicknesses of 20 cm to 1 cm in Fig. 5. The energy density of lead-acid traction batteries, 66 kW h m^{-3} is also plotted for comparative purposes, and is assumed to be constant, as variations in the energy density of lead-acid batteries with battery size are negligible. Although the energy density of sodium-sulphur batteries varies somewhat with cell length and aspect ratio, the above expression is accurate to within 10% for cell lengths between 35 mm and 100 cm and for a battery aspect ratio of up to 2:1, *i.e.*, cells packed in configurations of $2n$ by n .

It can be seen that the bigger the battery, the better the volumetric energy density, and that reducing the thickness of the thermal insulation will make a considerable improvement in energy density, the improvement being more dramatic for smaller batteries. Batteries are currently being designed with 5 cm of thermal insulation for motive power purposes and it is considered that this degree of thermal insulation will keep the battery at a satisfactory working temperature for daily use. The high thermal capacity of the battery will buffer most transient emissions and losses of heat and external heating and cooling should only be necessary under abnormal conditions.

As the size of the battery is reduced the ratio of surface area to bulk and, hence, thermal capacity, will decrease and the thermal insulation will become more critical. Figure 5 shows that the energy density approaches the energy density of lead-acid batteries with 5 cm of insulation at a stored energy of 3 kW h. However, reducing the insulation thickness to 1 cm immediately gives more than double this energy density. Because a sodium-sulphur battery must be part of a thermal as well as an electrical system it is unlikely that it will show many advantages over conventional batteries for stored energies of 10 kW h or less. At this energy an insulation of 1 cm still shows a twofold increase on the currently adopted 5 cm. Satisfactory insulation of much less than 5 cm is not currently available in a practical form and it would appear that some form of vacuum insulation system would be required significantly to reduce heat losses in thicknesses of only 1 cm. Figure 5 does, however, illustrate the potential available and it could well be that further improvements in energy density of relatively small sodium-sulphur cells will be gained by developing insulants rather than cells.

Although significant improvements in energy density can be achieved by substituting relatively small sodium-sulphur batteries for lead-acid

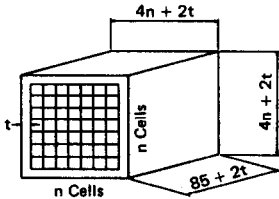


Fig. 4. Sodium-sulphur cells stacked to produce a battery of square cross section and covered with an insulating layer of t cm.

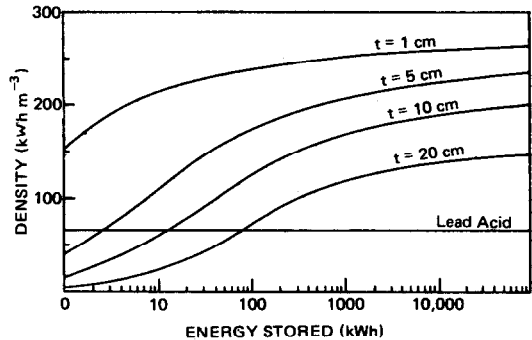


Fig. 5. Effect of insulation thickness on energy density.

batteries, say between 10 kWh and 20 kWh, the actual volume of free space released is, of course, small. For example, a 15 kWh sodium-sulphur battery with 5 cm insulation would occupy 0.13 m^3 whereas the equivalent lead-acid battery would occupy 0.23 m^3 , almost twice the volume. But the volume saved would be 0.10 m^3 , which may be only a small proportion of the total system volume of which the power source may be a small part. The situation is very much different for large batteries where considerable quantities of space can be saved. Hence the current interest in this system for load levelling. Figure 6 shows energy stored plotted against storage volume where the volumetric advantages of large sodium-sulphur batteries can be clearly seen. This graph is a useful guide for assessing the applications of sodium-sulphur batteries. It shows that little volumetric advantage can be gained by producing unit batteries of more than ten cubic metres. Indeed, engineering considerations would, in any case, require that large batteries were split up into smaller units.

Design studies have now begun on methods of constructing batteries, and it is evident that these batteries will exhibit significantly different properties from conventional batteries, and it is worthwhile at this stage considering how they differ from the lead-acid battery and how these properties will affect their applications.

Gravimetric energy densities of 100 Wh kg^{-1} are attainable compared with 25 Wh kg^{-1} for standard lead-acid batteries and $35 - 40 \text{ Wh kg}^{-1}$ for advanced lead-acid batteries. Although a reduction in weight is desirable, the improvements in volumetric energy density are far more useful, as most applications are constrained by space rather than weight. In this case, as already outlined, the realisable performance is determined by size and degree of thermal insulation required. The volumetric efficiency of the battery

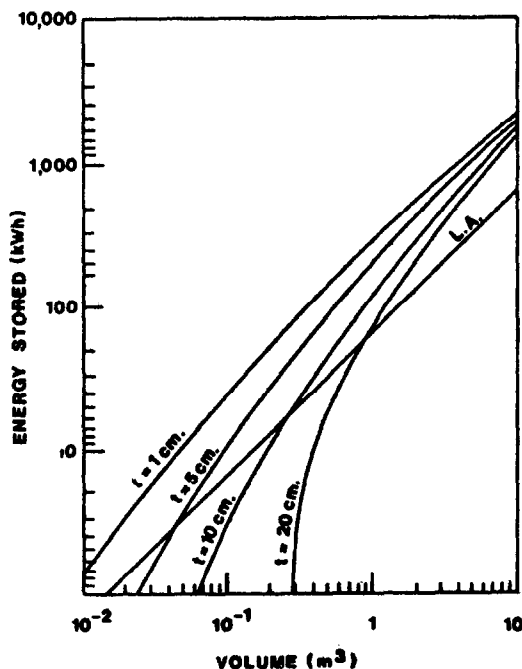


Fig. 6. Energy storage of sodium-sulphur batteries.

improves with size and shows real advantages over the lead-acid battery in sizes about 20 kW h.

Production costs are yet to be determined but they are known to be labour intensive and are sensitive to cell size and particularly to production rate. Unlike the lead-acid battery, it is improbable at this stage that small production runs of specialised cells will be economic. Costs will, however, not be sensitive to the costs of raw materials which are highly abundant.

Conclusions

Sodium-sulphur cells are hermetically sealed. They do not gas on charge and they do not require, nor can they be given, any maintenance. As a consequence, they can be operated in environments where gas evolution will be undesirable or even unacceptable such as at coal faces. Further consequences of their lack of gassing is the absence of hydrogen, which can be hazardous in enclosed environments, and the absence of spray, which can degrade the electrical insulation of the top of the cell. The high operating temperature is, in this case, an advantage giving very high top of cell insulation levels, which make it ideal for the large installations which are necessary for duties such as load levelling.

Because the active materials are separated by a β -alumina membrane which is impervious to non ionised species there can be no self discharge and full capacity is maintained indefinitely. No long term open circuit tests have yet been carried out, but there is no known mechanism which can allow thermochemical reaction between the active species.

A major disadvantage of this battery is that it must be heated to 300 °C before it can be used, and this restricts its applications to situations where it is used continuously. For motive power applications it will be restricted to fleet operators although its non gassing nature, complete with its high energy density, makes it suitable for some mining applications. It can be kept warm by internal heaters on an independent circuit which, with good thermal insulation, can consume little energy, and its lack of self discharge and routine maintenance could well make it suitable for long term stand applications. Much will depend upon the economics arising out of the interaction between production rates, market size, and the degree of reliability which can be attained. These areas will receive particular emphasis in the forthcoming years.

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