

RECENT ADVANCES IN Na/S CELL DEVELOPMENT — A REVIEW

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Summary

This paper describes recent progress in the development of sodium/sulfur batteries. Ceramic beta alumina electrolyte tubes with high conductivity and long life are being fabricated. Sulfur utilization is increased to 80%. Improvements are outlined which have been made in finding corrosion resistant casing materials and in cell design.

Experimental cells with a weight of 1.1 kg and a capacity of 90 Wh have been built and successfully tested. Ninety-six of these cells have been electrically connected and enclosed in a conventional thermal insulation. The energy density of this non-optimized battery was 36 Wh/kg at the 2.5 hour discharge rate. Optimization with respect to weight will result in batteries with an energy density of more than 100 Wh/kg. Further improvements in cycle life are necessary for the practical application of these batteries.

Introduction

Sodium/sulfur batteries, when fully developed, are expected to store about five times more energy per unit of mass, to be cheaper and to have a longer cycle life than lead/acid batteries. Therefore, with respect to energy density the sodium/sulfur system is one of the most promising batteries for motive power applications [1 - 4]. Because of the low cost and expected long cycle life it may also find application in load levelling and peak shaving in electric networks [5 - 8].

Figure 1 shows a schematic of a Na/S-cell. A charged cell contains molten sodium as the negative active material and molten sulfur as the positive active material. The solid sodium ion conducting electrolyte is tubular in most cases. Cell components not shown in the Figure are a carbon felt as current collector in the sulfur compartment and a capillary wick in the sodium compartment causing sodium wetting of the electrolyte and preventing sodium flow into the sulfur compartment in case of electrolyte damage. Discharging the cell results in reaction products Na_2S_x ($3 \leq x \leq 5$) with melting points between 235 and 285 °C. In order to avoid solid reaction products the cell has to be operated at a temperature of 300 - 350 °C. Thus temperature is maintained by insulation surrounding the cells of the battery.

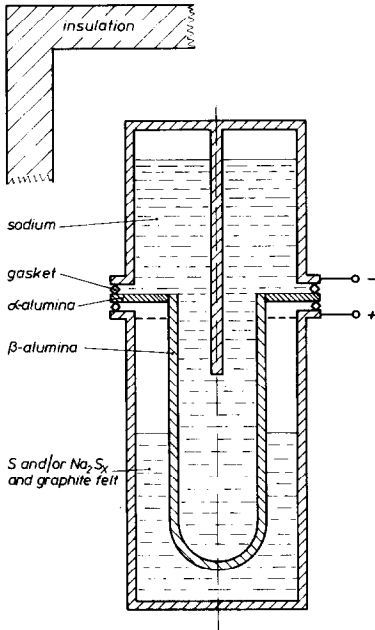


Fig. 1. Cross-section of a sodium/sulfur cell. — charged; ----- discharged.

Problems in the past have involved achieving: high Na^+ conductivity and durability of the solid electrolyte, high sulfur utilization, corrosion resistance for sulfur containment, leak tight sealing, long cycle life, and reproducibility. This paper describes the present status of development in these areas.

Ceramic electrolyte

The majority of sodium/sulfur batteries under development use polycrystalline sodium beta-alumina as the electrolyte. The suitability of beta-alumina as electrolyte for sodium/sulfur cells is due to the high sodium ion conductivity and durability of this material.

Figure 2 compares the conductivity of different alkali and fluor ion conductors. Only two types of electrolyte with a high sodium ion conductivity are known up to now, beta-alumina and electrolytes with the composition $\text{Na}_{1-x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ ($0 \leq x \leq 3$) [9, 10]. No data about the chemical stability in contact with sodium or sulfur and no durability tests have been reported in case of the latter electrolyte. At present beta-alumina remains the only good conducting electrolyte the properties of which are sufficiently known for utilization in sodium/sulfur cells.

Furthermore Fig. 2 shows the conductivity of beta-alumina to be dependent on the chemical composition. Magnesia-doped beta-aluminas with

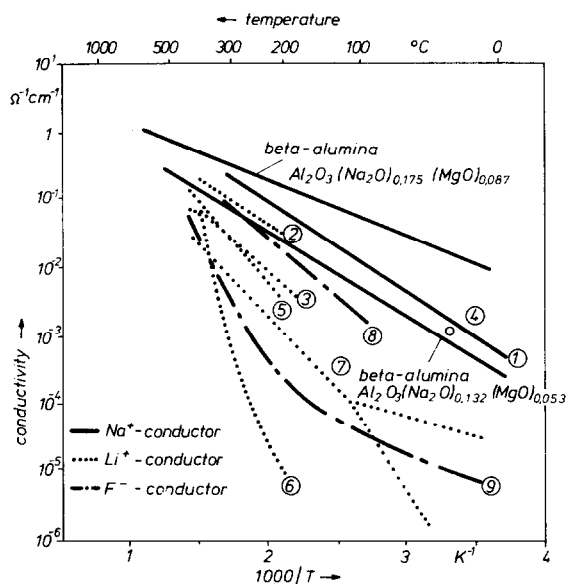


Fig. 2. Conductivity of alkali and F^+ ion conductors. Na^+ -conductors: beta-aluminas of different composition: (1) $Na_3Zr_2P Si_2O_{12}$ [9, 10]. Li^+ -conductors: (2) $Li_{14}Zn (GeO_4)_4$ [11]; (3) $Li_{14}Mg (GeO_4)_4$ [11]; (4) Li^+ -conducting beta-alumina [12]; (5) $Li_2SiO_4 + 60 \text{ m/o } Li_3PO_4$ [13]; (6) $LiAlO_4 + 20 \text{ m/o } Li_2SO_4$ [13]; (7) Li_3N [13]. F^- -conductors: (8) $Pb_{0.75}Bi_{0.25}F_{2.25}$ [14]; (9) $PbF_2 + 0.5 \text{ m/o } AgF$ [15].

a resistivity as low as $3 \Omega \text{ cm}$ at $300 \text{ }^\circ\text{C}$ could be produced by optimization of the composition and the fabrication parameters [16]. Even lower resistivities have been achieved with lithia- or lithia + magnesia-doped beta-aluminas in other laboratories [1, 17]. Electrolytes with lower than optimum conductivity are used, however, since other properties such as non-hygroscopicity and durability can presumably be increased in this way.

While it is relatively easy to optimize beta-alumina electrolytes with respect to conductivity it is difficult to achieve a high durability. The durability is defined as the charge which can be passed through the unit of electrolyte surface with only limited degradation of the electrolyte. It can be measured with $Na/\text{beta-alumina}/Na$ -cells in which sodium is continuously electrolyzed through the electrolyte. Electrolyte degradation, in most cases caused by dendritic sodium penetration, is indicated by decrease of resistance [16] or by deviation from Faradayic behaviour [18].

The electrolyte durability should amount to 500 Ah/cm^2 and 2000 Ah/cm^2 respectively in order to fulfill the demands for motive power and load levelling applications [4]. Experiments by Armstrong [19] showing that by applying current densities of 0.1 to 0.6 A/cm^2 degradation can already occur at 10 Ah/cm^2 , had cast a doubt on whether it would be possible to achieve the high figures necessary for practical applications. In the meantime, however, it has been shown that a durability up to several 1000 Ah/cm^2 can be obtained by choosing an appropriate electrolyte composition [20 - 24]. Our

own experiments in Na/Na-cells at current densities of about 1 A/cm^2 prove that 7000 Ah/cm^2 are achievable with magnesia stabilized beta-aluminas of different composition. The tests show the durability to be very sensitive to the bulk density and microstructure of the electrolyte [16]. Very high densities, up to 99% of theoretical density, and uniform structures with the majority of grains having a diameter of a few μm and with only very few grains up to lengths of $100 \mu\text{m}$ can be fabricated by zone sintering of iso-statically pressed samples. Tubes produced in this way are shown in Fig. 3.

Sulfur utilization

A high utilization of the reactants is one of the pre-requisites for attaining a high energy density. Our measurements with cells of the type shown in Fig. 1 containing sodium polysulfide and graphite felt with a porosity of about 95% within the outer compartment confirm the results of other laboratories, that a high sulfur utilization can be obtained only when low charging current densities are applied. If the charging current density exceeds a threshold value of $30 - 40 \text{ mA/cm}^2$ the electrolyte is blocked by an insulating sulfur layer [17, 21, 23 - 26]. Curve 1 of Fig. 4 illustrates this effect.

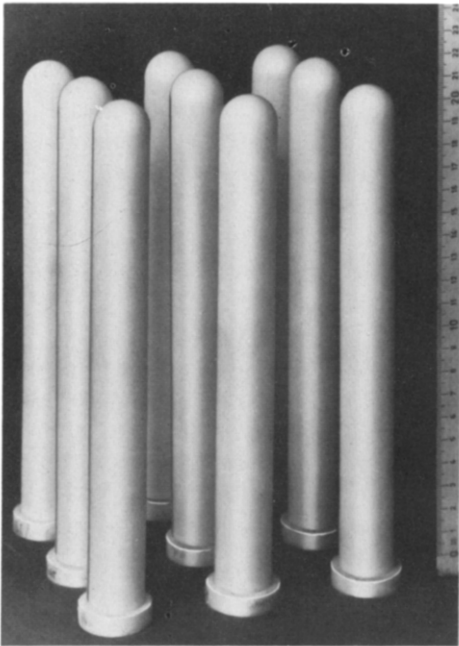


Fig. 3. Zone sintered beta-alumina tubes ready for insertion into sodium/sulfur cells. Length 210 mm, outer diameter 25 mm.

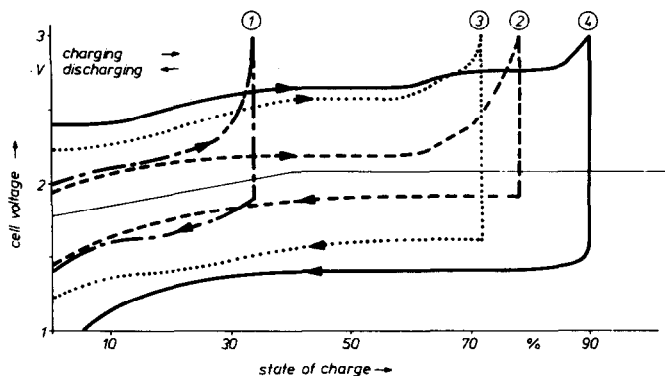


Fig. 4. Voltage of sodium/sulfur cells as a function of state of charge. Current density of cells (1), (2), (3) 80 mA/cm^2 , cell (4) 150 mA/cm^2 . The cathode compartment was filled with: (1) graphite felt and pure sulfur; (2) graphite felt, sulfur and 0.8 mol % C_6N_4 ; (3) graphite felt coated with β -alumina grains in order to create sodium ion concentration cells; (4) same as (3) plus 0.8 mol % C_6N_4 .

We have tried to increase the rechargeability in different ways. One way is to decrease the viscosity of sulfur by the addition of small amounts of selenium and/or boron [25, 26].

Another method is the addition of compounds such as C_6N_4 forming charge transfer complexes with sulfur. In this way the electronic conductivity of sulfur is increased by several orders of magnitude. It has been assumed that sulfur layers are formed at the surface of the graphite fibres if a Na/S cell is charged into the two phase region [21]. These insulating sulfur layers prevent further charging. The blocking effect is offset by the addition of C_6N_4 . Curve 2 of Fig. 4 demonstrates the increased rechargeability obtained by the addition of C_6N_4 [27, 28]. Furthermore, we examined the possibility of using porous graphite systems having large pores in the vicinity of the electrolyte and narrow pores away from it. Sulfur was soaked into the narrow pores by capillary action and the rechargeability was increased [25, 26] in accordance with similar results obtained in the Ford laboratories with cells containing shaped graphite felt electrodes [17]. A rapid decrease of sulfur utilization with cycle life has been observed, however [18, 25]. Finally about half the graphite felt surface has been coated with grains of β -alumina leaving free spaces between the grains. Curve 3 of Fig. 4 illustrates that the rechargeability can be increased by this method. This effect may be due to Na^+ -ion concentration cells formed by the grains with adjacent areas of the melt and/or to the different wetting properties of graphite and β -alumina with respect to sulfur and sodium polysulfide. The combination of the latter effect with the addition of C_6N_4 leads to an even higher sulfur utilization (curve 4 of Fig. 4).

Compatibility of materials

A wide range of metal alloys can be used for the construction of the sodium compartment. More severe material problems arise with the sulfur container, which in cells of the type presented in Fig. 1 is also used as the cathode current collector.

In order to select sufficiently corrosion resistant sulfur container materials the chemical attack on various materials by Na_2S_4 has been studied in static corrosion tests [25, 26] and in experiments where a current was allowed to flow through the surface of the samples [29, 30]. Low carbon steels, cobalt and nickel base alloys, chromium, molybdenum, pure and coated aluminum, nitrides and carbides have been examined by metallographic methods (dimensional changes), scanning electron microscopy and electron microprobe analysis. Stainless steel, cobalt or nickel base alloys and coated aluminum seem to be the most promising materials or material combinations. Some of these materials have been tested in sodium/sulfur cells and have been found to be suitable for at least several months of operation.

Cell design and battery test

Most of our sodium/sulfur cell experiments have been performed with small cells of 5 - 10 Wh capacity the design of which was similar to that shown in Fig. 1. The beta-alumina tubes of these cells had a length of 5 cm and an outer diameter of 1.1 cm. A glass seal has been used to join the electrolyte tube to the alpha-alumina ring. A leak tight joint between this ring and the metal flanges of the two containers was accomplished by means of a compression seal utilizing aluminum gaskets. Seals of this type have been in operation for more than 5000 hours without failure. Similar joints have been used by other groups [1, 3, 5, 24]. Other hermetic seals are in development.

The sulfur container consisted of stainless steel in most cases. In some cases aluminum or stainless steel coated by plasma spraying with a nickel base alloy layer of 50 - 100 μm thickness have been used. After filling the compartments were evacuated and closed.

Recently experimental cells of larger size have been built and tested. Design and sealing techniques were very similar to those used with the earlier small cells. Beta-alumina tubes of the size shown in Fig. 3 have been inserted into cells having a weight of about 1.1 kg and a capacity of about 90 Wh. Four of these cells are shown in Fig. 5. Single cells of this type have been tested up to 3000 hours without failure of seals. A weight reduction by a factor of 2 leading to a specific energy of 180 Wh/kg is achievable by minimizing the weight of the casing and the flanges and by utilizing the same sealing technique.

Ninety-six cells of the type shown in Fig. 5 have been enclosed in a conventional thermal insulation (Fig. 6). Four parallel connected strings of 8 series connected cells form a block. The battery consists of 3 series con-

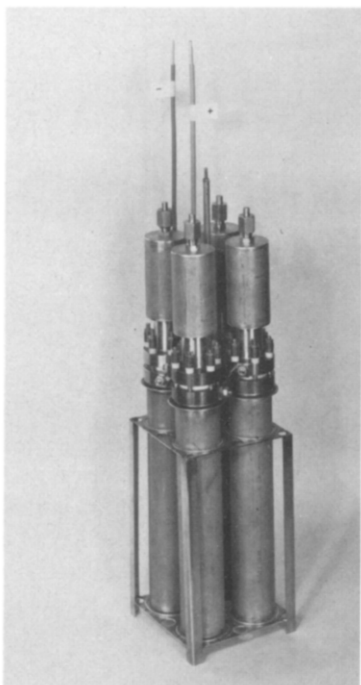


Fig. 5. Series connected experimental Na/S cells each having a capacity of about 90 Wh.

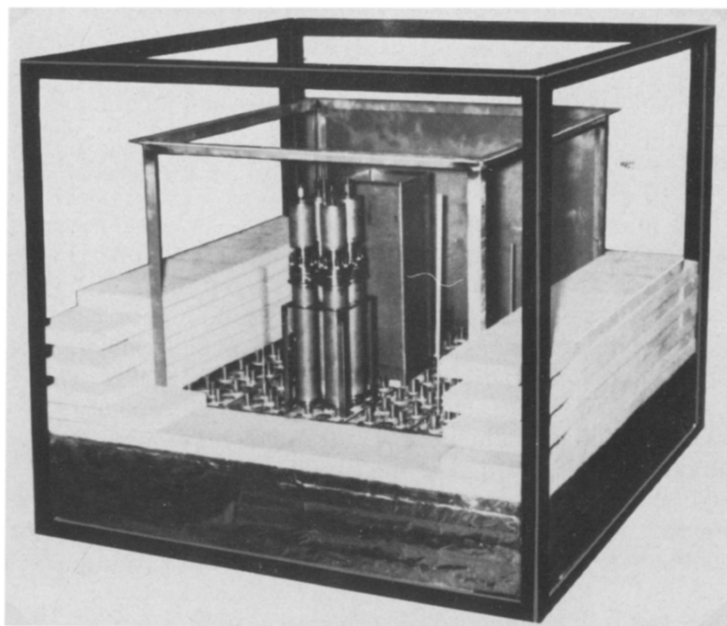


Fig. 6. Partly assembled experimental Na/S-battery. It consists of 96 cells (4 are shown), the heat insulation (white) and an electric heater (cylinder amidst the battery) for setting the battery into operation.

nected blocks. The open circuit voltage amounts to 49.9 V. Neither the cells nor the thermal insulation are optimized with respect to weight. Nevertheless an energy density of 70 Wh/kg for the cells and of 36 Wh/kg for the battery has been achieved by applying a discharging current density of 150 mA/cm² and a charging current density of 75 mA/cm².

The experimental battery has now been on test for several months. The test shows the capacity and resistance to be sufficiently reproducible from cell to cell and to be in accordance with the results obtained with single cells.

Cycle life studies

Several effects may cause sodium/sulfur cells to become inoperable. A first important reason is an abrupt decrease of cell performance which in most cases is caused by an electrolyte rupture. A second essential limit is the time to reach an uneconomical capacity or resistance. Since the capacity of a battery with series connected cells is determined by the cell with the lowest capacity the capacity decrease of the cells should be small and reproducible from cell to cell.

Most of the early sodium/sulfur cell tests have been terminated because of electrolyte rupture. With progress in electrolyte fabrication sodium/sulfur cells could be cycled for an increasing period of time. Curve 1 of Fig. 7 illustrates that a long cycle life (1500 cycles $\hat{=}$ 11 months) can be obtained with cells containing only materials which are not corroded. The effective capacity, however, is low in this case. The effective capacity is the ratio of the measured capacity to the capacity obtained when the composition of the melt within the positive compartment changes from Na₂S₃ to pure sulfur. Even higher cycle numbers with similar cells have been obtained at other laboratories [3, 17, 20].

Curve 2 of Fig. 7 refers to a cell with an initially high capacity obtained by a gradient of pore size within the felt. The rapid decrease in capacity is due to narrowing of the wide pores. Curve 3 represents a cell in which C₆N₄ was added to the sulfur. Loss of capacity was caused by incomplete leak tightness of the sulfur compartment. Curve 4 represents a cell which was provided with an aluminum container coated with a nickel base alloy. The sulfur contained C₆N₄ as an additive. The slow decrease in cell capacity is most probably due to loosening of the nickel base alloy layer as a result of corrosion. It is assumed from the results of the corrosion experiments that loosening of the layer can be avoided by applying a compact layer which was presumably not the case in the cell mentioned above. Curve 5 refers to a cell with a steel case coated with a nickel base alloy and filled with sulfur and C₆N₄ as additive.

Figure 7 demonstrates that a high sulfur utilization or generally speaking a high performance can be maintained over extended periods of time. The same conclusion can be drawn from results of other laboratories [1, 31].

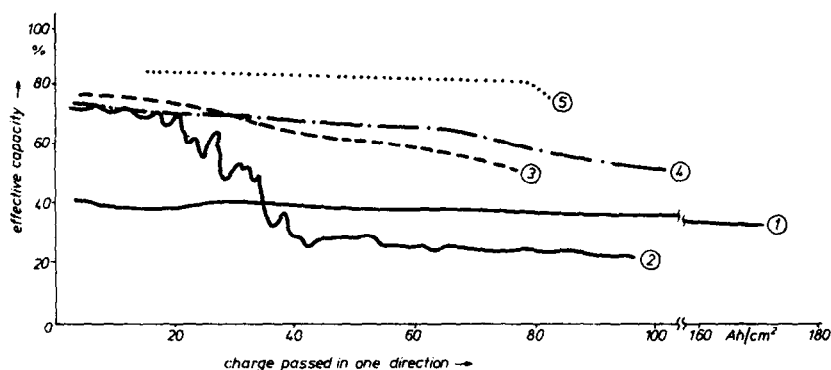


Fig. 7. Effective capacity of laboratory Na/S cells us. total charge passed in one direction.

Curve in Fig. 7	Size of electrolyte		Material of positive current collector	Preparation of graphite felt/additive	Reason for termination of test
	l (cm)	ϕ (cm)			
1	5	1.1	graphite	-/-	power failure
2	5	1.1	stainless steel	large pores at electrolyte/-	low capacity
3	5	1.1	stainless steel	-/C ₆ N ₄	cracked electrolyte leak at sulfur container
4	5	1.1	Al coated with Ni base alloy	-/C ₆ N ₄	
5	21	2.5	stainless steel coated with Ni base alloy	-/C ₆ N ₄	cracked electrolyte

Conclusions

It can be concluded that some of the principal problems of sodium/sulfur cells are solved. Beta-alumina electrolytes with high conductivity, high durability in Na/Na cells and sizes appropriate for application in technical cells have been developed. The utilization of sulfur could be increased to about 80% at charging currents corresponding to a 5 hour charging time and to a 2.5 hour discharging time. Sealing techniques have been tested which allow the construction of cells with a specific energy of about 180 Wh/kg and batteries of more than 100 Wh/kg. These figures can be further improved. With respect to corrosion of container materials a high cycle life of Na/S cells should be achieved. Up to now a charge of 100 Ah/cm² could be passed through the electrolyte of 90 Wh experimental cells maintaining a high performance. The lifetime achieved should be compared with the demand of about 500 Ah/cm² for automotive application. Further experiments, which will be performed within the next years, are necessary to improve the cycle life.

Acknowledgement

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