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# BETA-ALUMINA ELECTROLYTE FOR USE IN SODIUM/SULPHUR BATTERIES
# PART 2 . MANUFACTURE AND USE


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## Summary


Part 1 of this two-part review was concerned with the fundamental chemical and physical properties of sodium beta-alumina. In Part 2 we consider the ceramic science and technology involved in the manufacture of electrolyte tubes and their use in sodium/sulphur batteries.

The specification set for $\beta$-alumina tubes is first outlined, followed by a review of the fabrication procedures which have been employed. The problems of quality control and the elimination of flaws are emphasised. Mechanical and thermal expansion data which have been measured for $\beta$-alumina ceramics are discussed. The surface interaction effects between the electrolyte and the electrode materials (sodium and sulphur) are considered, and it is suggested that wetting effects are important in determining both the cell resistance and the life span of the electrolyte in use.

The failure modes of $\beta$-alumina electrolyte tubes fall into three categories — electrical breakdown, mechanical shock, and thermo-mechanical failure — but in a real situation these may be interactive. Electrical breakdown may be either a result of localised high current densities during recharge or a consequence of too high an imposed voltage at top of charge (dielectric breakdown). Published work on these failure modes is reviewed. Finally, the present state-of-the-art in manufacturing $\beta$-alumina electrolyte tubes is summarised, and the need for further research and development on improving their durability is noted. As one component of a system — the Na/S cell — the electrolyte cannot be viewed in isolation and its durability is a function both of its perfection of manufacture and the conditions of use in the cell.

## Introduction

The first part of this two-part review [1] was devoted to the chemical, crystallographic, and electrical properties of sodium β-alumina. We now turn our attention to the practical aspects of the exploitation of those properties in the use of the material as a high temperature electrolyte-separator in sodium/ sulphur cells.

The principles of the construction of the sodium/sulphur cell are illustrated in Fig. 1. The solid electrolyte, composed of β-alumina ceramic, usually takes the form of a tube, while the electrodes, which are liquids at the temperature of operation, are disposed one inside and one outside the tube. Figure 1 shows the sulphur electrode inside the tube and the sodium electrode outside – the "central sulphur" design. The cell may also be run with the electrodes interchanged, but that configuration gives rise to problems of corrosion of the outer casing by the sulphur electrode material. Most research on the central sulphur design has been carried out in Britain, while other countries have concentrated their efforts on the central sodium design; each concept has its advantages and limitations.
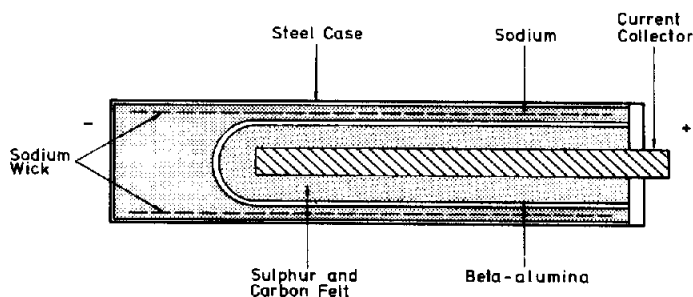


Fig. 1. Schematic of sodium/sulphur cell (central sulphur design).

The sulphur electrode contains a matrix of graphite felt which serves as an electron injector/acceptor. On discharge, sodium metal is ionised, the $Na^+$ ions travel through the electrolyte to the sulphur electrode, electrons pass around the external circuit to the graphite felt where reaction takes place to form sodium polysulphides. Cells are operated at between 595 and 655 K so that the discharge products remain liquid. The elevated temperature increases the conductivity of the β-alumina electrolyte, but it also defines very stringent materials requirements for some of the other components of the cell.

It will be evident that the sustained integrity of the β-alumina ceramic tube is of central importance to the life and performance of the cell. A great deal of effort has been put into developing successful methods of electrolyte fabrication, and the important parallel activity of studying the remaining shortcomings of the material has also been pursued with great vigour. Pro-

cesses for the manufacture of β-alumina electrolyte, and its mechanical properties were reviewed in 1978 [2]. In the present paper we seek to deal with progress in the manufacture, and experience in the use, of the electrolyte, reported in the literature since that time. As in the first part of this review, the literature coverage will be selective rather than comprehensive.

## Fabrication

The specification which has to be met by β-alumina electrolyte (Table 1) is considerably more exacting than is conventional for ceramic tubes.

TABLE 1

β-Alumina tube specification

High ionic conductivity
Impervious at 300 - 400 °C
Stable to moisture
High strength (fine grain size)
High fracture toughness
Straightness and close dimensional tolerances
Good surface finish and closed end
Low interfacial impedance/polarisation
Long life in cells at appropriate current densities
Resistance to electrical breakdown
Reproducible properties and high manufacturing yield
Rapid, low cost production

Several of the properties called for tend to be incompatible with one another; thus the high conductivity $\beta''$ phase is favoured by a high doping level which, in turn, increases moisture sensitivity. Also, the highly doped materials tend to be unstable in liquid sodium and sensitive to breakdown by sodium dendrite penetration. Despite these problems it is possible to devise a formulation and sintering regime which gives rise to a satisfactory ceramic electrolyte. Some of the measures necessary to meet the specification shown in Table 1 are listed in Table 2.

TABLE 2

Prerequisites to meet β-alumina specification

Control of chemical composition and purity
Homogeneity of powder feed
Attention to detail in isostatic pressing
Accurate control of sintering cycle
Development of acceptance tests for sintered tubes
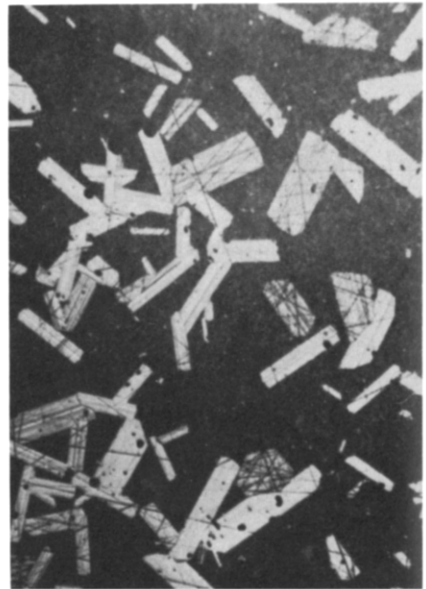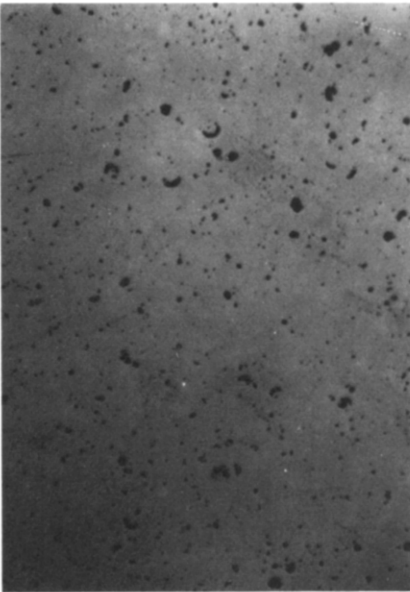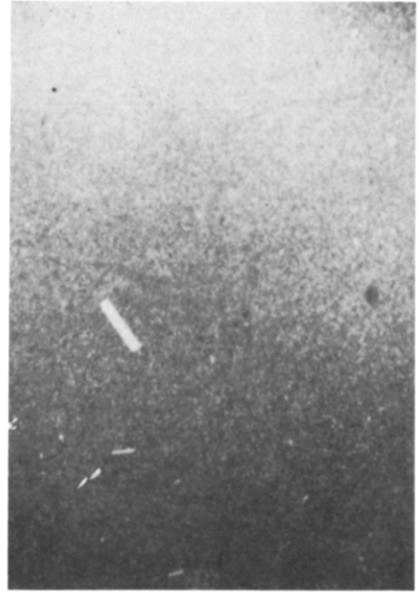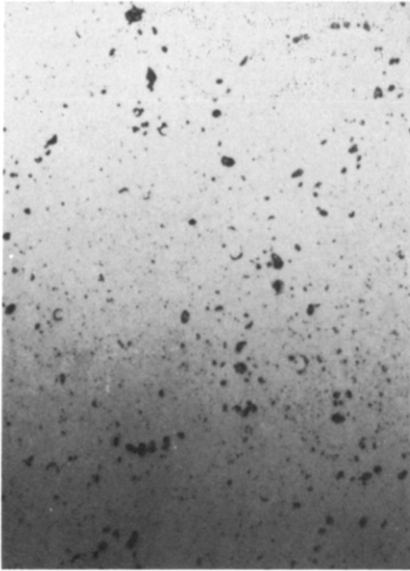Automation of process on industrial scale

Fig. 2. Microstructure of fine grain (above) and duplex (below) β-alumina. The micrographs on the left are polished specimens, while those on the right are etched specimens.

The most characteristic feature of the sintering of β-alumina ceramic is its tendency towards exaggerated grain growth which occurs on over-sintering. Figure 2 shows microstructures of fine-grained β-alumina, such as is desirable for high strength and homogeneous current flow, and over-sintered β-alumina showing exaggerated growth of certain grains leading to a characteristic duplex structure. This effect has been observed by many researchers. The skill of the ceramist lies in achieving high conversion to the desired $\beta''$ phase without over-doping and without over-sintering, and this requires very precise control of the sintering cycle [3, 4].
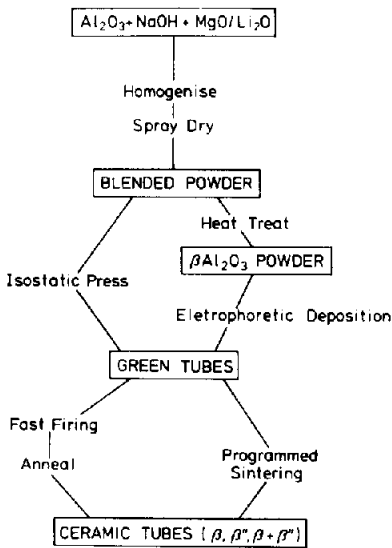


Fig. 3. Plan of manufacturing routes.

A number of different fabrication procedures has been adopted for β-alumina, as summarised in Fig. 3. The starting materials are normally a fine particle size $\alpha$-$Al_2O_3$ powder, with soda added as $Na_2CO_3$, NaOH, $NaNO_3$ or $NaAlO_2$, MgO as $Mg(NO_3)_2$ or MgO, and $Li_2O$ as $Li_2CO_3$ or LiOH. Lithium may also be used in the form of lithium aluminate in order to achieve a homogeneous dispersion [5]. These powders are vibro-milled together, either dry or wet, and sometimes spray-dried [6, 7] to improve homogeneity. Recently, the preparation of β-alumina by thermal decomposition of a single starting material (a sodium ammonium trioxalatoaluminate) through an alumina intermediate has been reported [8], but the process does not appear to have progressed beyond the laboratory as yet.

The dried and blended powder is either isostatically pressed to form "green" tubes or is pre-reacted to β-alumina powder, which may be fabricated by other procedures. Two such procedures are plasma spraying and electrophoretic deposition.

Plasma spraying was investigated for some while at Harwell. Electrolyte tubes could be fabricated satisfactorily, but it was found that at the temperature of the plasma gun there was a significant volatilisation of $Na_2O$ even in the short duration of heating the powder. This fabrication route was therefore abandoned.

Electrophoretic deposition, developed in France [9, 10] and the USA [11 - 14], is apparently a very successful means of forming $\beta$-alumina tubes. The pre-reacted powder is suspended in an organic solvent and electrically charged by adsorption of protons from the dissociation of a dissolved organic acid. It is then deposited onto a metal mandrel. After removal, the $\beta$-tube is densified by sintering in a protected atmosphere. It is also possible to prepare the green shape by extrusion of the ceramic constituents with an organic binder [15].

There are two general approaches to sintering "green" $\beta$-alumina tubes: zone sintering and programmed sintering.

Zone sintering [16] is a continuous production process. Tubes are passed rapidly and sequentially through a furnace at comparatively high temperatures. Typical conditions to obtain fine grained, high strength ceramic are 1700 °C and a tube speed of 40 - 50 mm/min. Under these conditions densification is very rapid ($\sim 1$ min) and exaggerated grain growth is repressed. Loss of $Na_2O$ through volatilisation is prevented by means of an $Na_2O$-rich atmosphere in the furnace. The conversion of the precursor oxides to $\beta$-alumina occurs in the warm-up period (at 1600 - 1700 °C), but it is possible that a small proportion of liquid $NaAlO_2$, formed transitorily at grain boundaries, facilitates the rapid densification at 1700 °C. The tubes undergo a large contraction in diameter during sintering and this "necking" moves progressively along the tube as it passes through the furnace. Conversion to the $\beta''$ phase tends to lag behind densification and the conductivity can often be improved by a post-sintering anneal at 1350 - 1500 °C [2]. If this anneal is accompanied by the simultaneous application of isostatic pressure, then the residual porosity is reduced to almost zero and improvements in the mechanical properties of the tube are also found [17]; however, the capital and operating costs impose a severe penalty.

Programmed sintering [2, 18] is a conventional "batch" process as normally employed in sintering ceramics. The "green" tubes are stacked in a furnace, heated to sintering temperature and cooled according to a pre-arranged temperature/time cycle. The tubes must be enclosed in a ceramic container to prevent $Na_2O$ loss [19]. Typically, a firing cycle will take 16 - 24 h, with a top temperature of 1600 - 1650 °C according to composition. Accurate control of the peak temperature and dwell time is essential to ensure electrolyte tubes of reproducible conductivity and strength. Recently, it has been reported [20] that a "double-peak" firing routine yields ceramic with higher strength and lower resistivity.

Both zone sintering and programmed sintering of $\beta$-alumina have been satisfactorily developed at different laboratories in the United Kingdom, and each is used routinely for the manufacture of electrolyte tubes. There are some differences as regards physical and mechanical properties of the product,

convenience and cost of manufacture, reject rates, and life of the electrolyte in Na/S cells. Sufficient experience has yet to be gained to make a final choice between these two sintering routes.

A technique which has shown some promise is that of "seeding" the oxide mix with pre-reacted $\beta''$-$Al_2O_3$ powder before isostatic pressing [21]. A small proportion of this phase, present as nucleating agent, facilitates the conversion of the bulk oxide to $\beta''$-$Al_2O_3$ within the short period of zone sintering. In the experiments reported, the addition of 10% $\beta''$-$Al_2O_3$ to the oxide powder led to a marked reduction in electrical resistivity at 300 °C (5.3 ohm cm, compared with 12.2 ohm cm for the unseeded material). On the other hand, the crystallite size of the ceramic was larger (20 - 60 $\mu$m compared with 0.5 - 2 $\mu$m), with an associated reduction in tensile strength (from 250 ± 25 MN m$^{-2}$ to 170 ± 40 MN m$^{-2}$). Further work is necessary to establish whether it is possible to attain the improved conductivity without grain growth occurring.

During the past five years there has been a progressive increase in the size of $\beta$-alumina tubes which have been satisfactorily fabricated, associated with an improvement in quality and reduction in rejection rate. Part of the stimulus for larger tubes has been the adoption in the UK of the central-sulphur design of cell (Fig. 1) which necessitates a larger diameter electrolyte tube. For these cells, tubes of 33 mm dia., in varying lengths up to 650 mm, have been developed [22].

Quality control checking remains a problem. Dye tests can reveal flaws with a radius of 50 $\mu$m, but theory indicates that the key flaws are much finer than this.


## Mechanical and thermal properties

The mechanical properties of $\beta$-alumina (tensile strength, fracture energy, hardness, elastic moduli, etc.) and its thermal properties (expansion coefficients, thermal diffusivity, specific heat, and thermal conductivity) have all been determined. These parameters are tabulated in the review by May [2], and only brief mention will be made of them here. Nevertheless, it should be emphasised that thermomechanical properties are of vital concern in regard to the useful life of $\beta$-alumina, as they control crack initiation and propagation in the ceramic.

A recent addition to the mechanical data reported for $\beta$-alumina is the delayed fracture behaviour which has been measured both in air at 20 °C and in sodium at 300 °C [23]. Compared with other oxide ceramics, $\beta$-alumina shows an abnormally low time dependence of strength under stress (Fig. 4). The strength of $\beta$-alumina measured in sodium at 300 °C shows a 25% reduction from that measured in air at 20 °C. The lack of stress corrosion cracking in $\beta$-alumina has implications for the various failure modes proposed for $\beta$-alumina which are discussed below.

The role of macro-defects in $\beta$-alumina in determining its strength has been studied in some detail [24]. It has been shown that the strength-
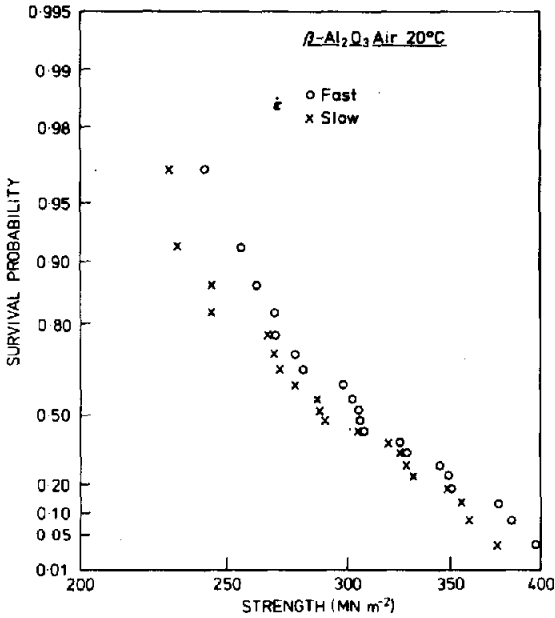
Fig. 4. Variation of strength of $\beta$-alumina with strain rate.

controlling flaws in tubes include very large grains, porous regions of various types, and localised regions of high impurity content. Typically, tubes showed a mean fracture strength of ~90 MPa, whereas small specimens cut from the tube and free from major flaws had mean strengths as high as ~250 MPa. This illustrates the major incentive for the elimination of macro imperfections.

The thermal expansion coefficients of $\beta$-alumina have been remeasured recently [25], with care being taken to avoid distortion of the results by moisture pick-up or sodium loss. The measured values (Table 3) indicate that internal stress as a result of anisotropy in the thermal expansion of the two phases should have little adverse effect on the application of $\beta$-alumina in electrochemical cells.

TABLE 3

Thermal expansion coefficients of $\beta$-alumina [25] measured over the range 293 - 1178 K

| $\beta$-alumina | $a$ axis | $8.0 \pm 0.2 \times 10^{-6} \ K^{-1}$ |
|---|---|---|
| | $c$ axis | $8.1 \pm 0.3 \times 10^{-6} \ K^{-1}$ |
| $\beta''$-alumina | $a$ axis | $8.1 \pm 0.3 \times 10^{-6} \ K^{-1}$ |
| | $c$ axis | $7.0 \pm 0.4 \times 10^{-6} \ K^{-1}$ |

## Interaction with electrode materials

Ideally there should be no interaction between the electrolyte and the electrode materials apart from the transfer of sodium ions. Any other interactions taking place at the surface of the electrolyte will probably lead to an increase in interfacial resistivity or to electrolyte degradation, either of which will be detrimental to cell performance.

In order to function efficiently, the surface of the electrolyte must be completely wetted by sodium. The sodium metal/$\beta$-alumina interface has been studied by means of impedance measurements and also by contact angle measurements [26, 27]. The a.c. impedance measurements showed that with a smooth $\beta$-A$l_2$O$_3$ surface good contact with liquid sodium was rapidly established at 150 °C, whereas with coarse surfaces wetting occurred only above 250 °C [26]. The more detailed investigation of Gibson [27], using both d.c. resistivity and contact angle measurements, showed that only limited surface wetting takes place below 300 °C. However, wetting is complete at 350 °C and, once initiated, it is maintained on cooling. The conclusion is that a properly constructed sodium/sulphur cell shows no interfacial polarisation at either surface of the $\beta$-alumina electrolyte and that the measured cell resistance is that of the electrolyte and the electrodes together.

It has been stressed [28] that wetting is of great importance for cell longevity, as well as for reasons of cell resistance, since the presence of even small, non-wetted areas gives rise to high local current concentrations and premature electrolyte failure. In the absence of such features, critical current densities far in excess of those previously quoted have recently been measured [28]. One of the possibilities for improving wetting is the addition of a benign element to the liquid sodium [28].

Under certain conditions of high current density, sodium dendrites may develop in the electrolyte during recharge, but consideration of this phenomenon is held over for discussion in the section dealing with failure modes.

The role of surface finish is significant as regards interaction with electrode materials. Rough surfaces are not only more prone to develop sodium dendrites and to be less easily wetted by sodium, but they also exhibit a higher resistivity than does a smooth surface [29].

It has been found that samples of $\beta''$-alumina ceramic with high soda compositions exhibit an asymmetric resistance to d.c. current flow. The voltage measured across the electrolyte is noticeably larger during discharge than during charge [30]. This behaviour is attributed to a thin passivating film of Na$_2$O between the $\beta''$-alumina surface and the liquid sodium. The mechanism by which the layer is generated is not known, but it is clear that its presence is detrimental to both efficiency and cell life. Resistance increases in sodium–sulphur cells during extended periods of cycling have been reported from several laboratories. This seems to be an interface phenomenon at the $\beta$-alumina surface, and experiments in which the sodium electrode is renewed have shown that the original cell resistance can be recovered [31]. There is also evidence that calcium impurities may lead to resistance rise effects [32].

Interactions between the electrolyte and the cathodic material are important in that the uniformity of current density at the interface must not be disturbed. An analysis of failed $\beta''$-alumina tubes [33] has revealed a strong correlation between the shape of the electrode in contact with the electrolyte and the crack patterns observed. This is thought to be due to high local current densities resulting from non-uniform current distribution as a result of shaped electrodes and operation in the two-phase (sulphur plus $Na_2S_5$) region.


## Failure modes

The experience of all laboratories engaged in sodium/sulphur battery development is that one of the principal causes of cell failure is electrolyte breakdown. The useful life of an electrolyte tube (in terms of charge/discharge cycles or A h/cm$^2$ of electricity passed) is very variable, with the longest-lived tubes already being satisfactory for commercial use. Several laboratories have found that their best cells have lives of 1000 - 2000 cycles at realistic charge/discharge rates. This shows the performance which is practically achievable; unfortunately, the majority of cells deteriorate or fail well before this.

TABLE 4

Failure modes for $\beta$-alumina tubes

| Mode of failure | Cause | Observation |
|---|---|---|
| Electrical breakdown | Excessive current density on charge | Short circuit by sodium dendrite penetration from negative to positive electrode |
| | Application of excessively high voltage | Gross physical damage leading to melting of the electrolyte on the sulphur side |
| Mechanical shock | Intrinsic defect in tube | Cracking or fracture of tube at weak spot |
| | Externally applied shock | |
| Thermal cycling of cell | Expansion mismatch between tube and seal | Cracking near seal |
| | Expansion of solid electrodes on heating and melting rapidly | Tube cracks at temperatures below ~150 °C |

There are several prime causes of cell deterioration which lie outside the scope of this paper, *e.g.*, corrosion of container materials, seals failure. Here we are concerned only with $\beta$-alumina which may fail in one of several ways as shown in Table 4. These failure modes are closely interactive, but it is convenient to discuss them individually.

*Electrical failure*

It is a common experience that, after a quite variable period of charge/discharge cycling, a cell will fail to hold its charge. An internal short-circuit has developed spontaneously, and this worsens rapidly if further cycling is attempted. This phenomenon has been studied extensively [34 - 38], particularly by the convenient technique of life-testing in the sodium–sodium mode, using an applied voltage to pump $Na^+$ ions through the electrolyte at a controlled current density [39]. The use of liquid sodium reservoirs on either side of the electrolyte has several advantages; the experiments are easier to conduct than Na/S tests, the electrolyte is more readily recovered for post-test examination, and by passing current in one direction only it is possible to distinguish between effects at the entry and exit surfaces of the electrolyte.

These experiments have shown that, under favourable circumstances, electrolyte can pass in excess of 1000 A h $cm^{-2}$, unidirectionally, at a current density of 1.25 A $cm^{-2}$ without failure [34]. Other workers have reported lives of 7000 A h $cm^{-2}$ at a current density of about 1 A $cm^{-2}$ for magnesia stabilized $\beta$-alumina tubes [40]. Failure ultimately occurs by penetration of liquid sodium through the electrolyte; on cooling this is seen as a sodium filament or "dendrite" that grows through the electrolyte starting from the exit side. Experiments have revealed that:

(1) this phenomenon is associated with the sodium formation reaction $Na^+ + \epsilon \rightarrow Na$, and is therefore a function of cell charging and independent of cell discharge;

(2) the higher the current density on charge the shorter the electrolyte life;

(3) long electrolyte life is favoured by fine-grained ceramic;

(4) highly doped material of high conductivity does not generally show good resistance to sodium penetration; in particular, it has been stated that $\beta''$ $Al_2O_3$ containing $> 0.9$ wt.% $Li_2O$ is particularly susceptible to dendrite breakdown [34].

The flaws involved in the breakdown of $\beta$-alumina may be decorated electrolytically or chemically to render them more easily observable [41].

Dendrites are initiated at microcracks or imperfections at the exit surface and these propagate progressively into the body of the ceramic. Two explanations were originally advanced for this phenomenon; one invoked crack growth in a sub-critical manner by stress-induced dissolution of the ceramic in the liquid sodium [38]; the other proposed that sodium was discharged preferentially into the microfissure, raising the stress intensity to the critical value for crack propagation [35]. Both mechanisms depend upon the micro-cracks acting as current concentrators, thereby causing a Poiseuille pressure in the cracks due to flow of sodium.

The absence of stress corrosion cracking in $\beta$-alumina [23] implies that the mechanism involving sub-critical crack growth [38] is not directly applicable.

The concept of pressure developing due to sodium flowing inside a crack has been extended by an evaluation of the crack shape and crack-opening displacement under the action of the Poiseuille pressure instead of assuming the crack width [42]. This treatment led to the development of an expression for the critical current density, $i_{cr}$, above which sodium penetration can occur. The expression is $i_{cr} = A/\eta l$, where $A$ is a constant containing elastic and fracture properties of the solid electrolyte, $\eta$ is the viscosity of sodium, and $l$ is the crack length. The equation suggests [43] that sodium penetration may occur at very low current densities when the temperature is below the melting point of sodium since the viscosity of solid sodium would be very high. This prediction has been tested [43] and found to be correct in that at the rather low current density of 30 mA/cm$^2$ sodium penetration was observed in a specimen of $\beta''$-alumina below the melting point of sodium but not above.

It is evident from the delayed fracture studies [23], and from the observation that the strong electrolyte tubes still fall short of reliability targets [44], that factors other than those which determine purely mechanical strength are influential in producing electrolyte breakdown. In the light of this conclusion the electrochemical aspects of the electrolyte's environment take on a greater significance.

A recently published model [44] of the degradation of $\beta$-alumina seeks to develop the central themes of the earlier theories a stage further by incorporating a number of previously unconsidered factors. These are:

(i) the back e.m.f. developed by sodium metal under compression [45];

(ii) changes in the charge transfer resistance at the sodium/electrolyte interface which result in previously sub-critical cracks attaining criticality;

(iii) a semi-quantitative model of the effects of current focussing. Despite the assumption of a simplified crack shape, the calculations made on the basis of this model agree with experimental observations. The calculations suggest that the time required for full penetration of the electrolyte tube is of the order of minutes from the instant a crack achieves criticality. Hence, electrolyte life is seen, not as a continual process of degradation, but rather as an induction period during which time changes are occurring at the sodium/electrolyte interface which lead ultimately to criticality and rapid electrolyte failure. The two main factors which can contribute to tube failure are seen as being increases in the interfacial charge transfer resistance, and high local current densities arising from non-uniform operation of the sulphur and/or sodium electrodes.

It is interesting to note that another model published recently [28], although derived in a quite different manner, reaches some similar conclusions to those in the study referred to above. Thus, the model [28] based on an electrical–mechanical analogue of the electrolyte also emphasizes the importance of large, local current concentrations and suggests that degradation, once initiated, can proceed extremely rapidly with crack growth rates of a few mm s$^{-1}$. Once the difficulties of the interfacial region are overcome it is thought that critical current densities of several A cm$^{-2}$ should be achievable

[28]. This view is supported by the results of an experiment designed to pass high bulk current densities through a constricted electrolyte while maintaining low current densities at the electrode contacts [46]. It was found that direct bulk breakdown did not occur below at least 10 A/cm$^2$.

The electrical breakdown of $\beta$-alumina during the transport of sodium ions has recently been investigated by means of the acoustic emission technique [47]. In $\beta$-alumina compositions which are susceptible to dendrite penetration, many acoustic events were recorded prior to electrical breakdown. By contrast, compositions which have long life in Na/S cells showed no acoustic events until the current density exceeded 0.5 A cm$^{-2}$. This provides convincing proof that progressive micro-cracking precedes breakdown. Strength measurements reveal a marked decline in fracture stress during this period prior to electrical breakdown. [36]. It follows from these various findings that caution should be exercised in charging Na/S cells to ensure that the current density is below the level at which dendrites start to form. This will vary from one ceramic to another but will lie in the range 0.1 - 0.5 A cm$^{-2}$ for electrolytes and surface finishes presently produced on a large scale.

The electrical breakdown dealt with so far is due to the penetration of sodium metal filaments through the electrolyte. Filamentary growth is initiated only at the negative, sodium metal electrode during the recharge of sodium/sulphur cells and is associated with conditions in which a threshold value of current density is exceeded. A completely separate phenomenon occurs when high voltages are applied to membranes of $\beta$-alumina ceramic under blocking conditions [48]. At a given temperature there is a well-defined voltage limit (of some tens of volts) above which the electronic insulating properties of the ceramic break down and gross physical damage occurs. The significance of this observation is that although the charging voltage limit might be set at 2 - 3 V for a single sodium/sulphur cell, the connecting together of many cells into a battery configuration will generally require a higher total over-voltage and this is likely to be several tens of volts. If, as is likely, one cell in such a chain should become fully charged before the others, then all of the applied charging voltage would be dropped across that one high-resistance element, leading to voltage breakdown.

It has been shown [48] that above a certain threshold voltage, which is a function of temperature, the electronically insulating properties of the material are lost intermittently and gross damage takes place at the positive electrode face. Samples with two non-blocking electrodes did not suffer breakdown. Figure 5 shows the variation of breakdown voltage with temperature for fine-grained and coarse-grained ceramic specimens with both electrodes blocking. For the fine-grained specimen at 300 °C the breakdown voltage is around 60 V. A model has been suggested for this type of degradation in which, on application of a d.c. bias, the region of electrolyte close to the positive blocking electrode will become depleted of sodium ions (Fig. 6), and consequently its resistivity will increase. The majority of the applied voltage will then be dropped across the resistive layer and dielectric breakdown accompanied by melting and possibly charring will ensue. It was noticed that the voltage threshold above which breakdown occurred was independent of the lifetime of the electrolyte in a sodium/sulphur cell.
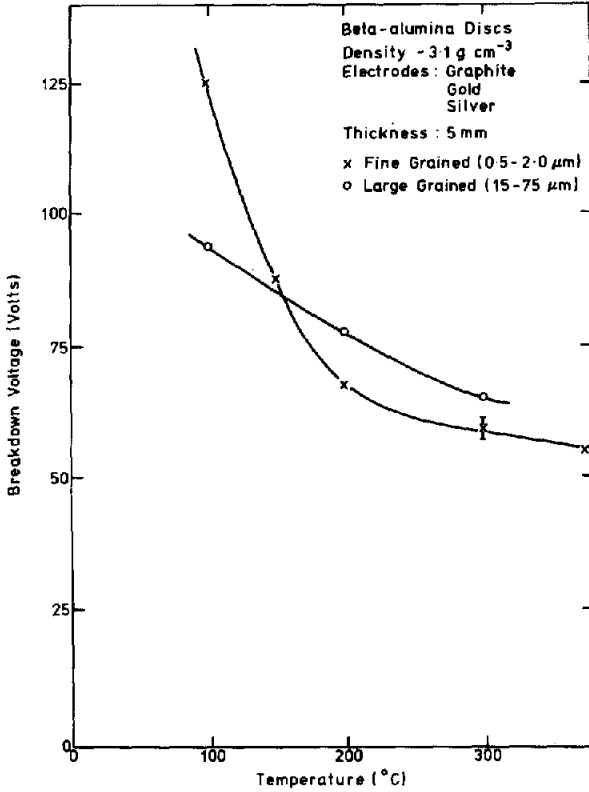
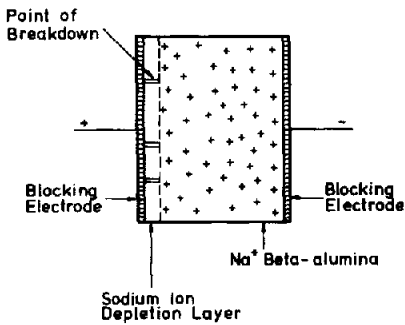Fig. 5. Variation of breakdown voltage with temperature for 2 grades of $\beta$-alumina.



Fig. 6. Schematic of voltage breakdown mechanism.

Voltage breakdown has also been reported at room temperature [46]. In this case polycrystalline ceramic with a blocking negative electrode and a non-blocking positive electrode broke down at between 40 and 80 V. With this electrode configuration, and in view of the temperature difference, the mechanism of breakdown in this case may be different from that shown in Fig. 6.

The transmission electron microscope has been used to observe both intergranular and transgranular sodium following electrolyte degradation [46]. Blocking defects revealed in $\beta''$-alumina electrolytes which had not failed but which may have degraded in conductivity [49], are not easy to distinguish from faults induced by the electron beam.

## Mechanical breakdown

Macro-cracking of the electrolyte (mechanical breakdown) can result from in-built stresses in the tube, from stresses imposed during cell assembly, or from externally applied shock. The crack first formed allows some mixing of the liquid sodium and sulphur to take place. The resultant rapid temperature rise leads to thermal shock, which compounds the problem by extending the cracking until, ultimately, the electrolyte tube may disintegrate. Macro-cracking tends to occur preferentially at weak spots, *e.g.*, near the closed end of the tube, or near the glass seal at the open end, or at gross defects. Because there is often a progressive fall in strength of the tubes in use, as a result of micro-cracks and dendrites, it is important that mechanical shock tests should be carried out on cells which have been well cycled, as well as on new cells. The problem of external shock is, of course, more relevant to batteries intended for transport applications than for stationary applications, and one must allow for accident conditions as well as normal operations.

## Thermal breakdown

Thermal breakdown of $\beta$-alumina can result from three separate effects:

(i) A mismatch in the thermal expansion coefficients of the $\beta$-alumina tube and the glass which is used conventionally to bond it to the insulating $\alpha$-$Al_2O_3$ collar, can lead to cracking of the electrolyte. $\beta$ and $\beta''$-$Al_2O_3$ are both anisotropic materials, but the recent careful measurement of their expansion coefficients by high temperature X-ray diffractometry (Table 3) [25] shows that the values for both $a$ and $c$ directions of each phase lie close together, approximately in the range $7 - 8 \times 10^{-6}$ °C$^{-1}$. $\alpha$-$Al_2O_3$ has an expansion coefficient of $8.4 \times 10^{-6}$ °C$^{-1}$ and it is therefore necessary to choose a glass whose expansion coefficient is well matched to those of $\alpha$- and $\beta$-$Al_2O_3$. Other factors are also important in the choice of glass, *e.g.*, a low densification rate, resistance to attack by molten sodium,

and freedom from $K^+$ and other cations which are detrimental to $\beta$-Al$_2$O$_3$. Inevitably, the choice must involve some compromise, and if the glass reacts with the $\beta$-Al$_2$O$_3$ in the seal region, or if the matching is poor, then too rapid heating or cooling of the cell will lead to electrolyte cracking in the seal region.

(ii) A second mechanism of thermal breakdown results from primary electrical or mechanical failure, as described above. An internal short circuit of the cell, or mixing of sodium and sulphur through an initial crack, leads to a rapid localised rise in temperature. The associated thermal shock frequently results in extensive cracking or fragmentation of the electrolyte tube.

(iii) The third thermal effect which can cause electrolyte failure stems from the phase change of the sodium and sulphur/polysulphide electrodes on heating and cooling. Provision must be made in the cell design to accommodate the volume expansion which occurs on melting of the electrodes without introducing stresses on the electrolyte tube. Experience has shown the need for relatively slow heating/cooling through the temperature range where melting/solidification takes place. However, Hattori *et al.* [50] claim that their cell design is able to withstand repeated thermal cycles at heating and cooling rates of $> 50$ °C/h. This is adequate for commercial use, although it should be observed that these cells were based upon small diameter (15 mm) tubes.

In summary, failure of $\beta$-alumina may result from electrical breakdown by internal short circuiting or through the application of an excessive voltage, from external mechanical shock or from thermo-mechanical effects of heating and cooling. These are interactive in a complex manner and, under adverse conditions, can lead to degenerative breakdown with large temperature excursions. One of the objectives of cell design is to limit the quantities of reactants which can mix when the electrolyte fractures, so that the thermal reaction is controlled and contained. The general principles for the design of safe cells have been described [51].

## Present position and future research

From the foregoing review it is apparent that the problems of developing $\beta$-alumina electrolytes for use in sodium/sulphur batteries may be divided into three categories:

(1) Scientific problems of understanding how the electrical, mechanical, and chemical properties of $\beta$-alumina depend upon its composition, phase equilibria, and microstructure. This area of investigation, which is directed towards defining an improved electrolyte, involves solid state chemistry and ceramic science.

(2) Technological problems of how to fabricate and manufacture electrolyte tubes to the desired specification, as set out in Table 1. This involves fairly conventional ceramic technology, but with a degree of sophistication and control which has not formerly been encountered in the manufacture of tubes.

(3) Design problems of how to incorporate the electrolyte tube in the sodium/sulphur cell so that it will be protected from electrical, mechanical, or thermal stresses which lead to fracture and, if incipient fracture does occur, to minimise its propagation. This is a complex, inter-disciplinary problem involving the materials scientist, the battery designer, the stress analyst and the production engineer.

Considerable progress has been made with the first category of problems and we now have some understanding of how to manufacture $\beta$-alumina ceramic which combines reasonably low resistivity with satisfactory strength, chemical inertness, and durability in use. Scope still exists for further work to define the optimum composition in terms of dopants and for selecting the preferred sintering procedure.

The second category of technical problems is much more difficult as the specification which the tubes must meet is severe, and involves many different branches of science, technology, and production engineering. Moreover, a manufacturing procedure which is satisfactory for one size of tube at one production level may not readily be capable of scaling up to larger tubes or greater outputs. Steady progress has been made with the production technology of $\beta$-alumina tubes, and it is now routine to manufacture high quality tubes of diameter 33 mm and lengths of up to 650 mm. Furthermore, the acceptance rate has improved steadily: of 800 tubes (33 mm dia., 160 mm long) produced by the British Rail laboratory in the first six months of 1977, 680 were usable in cells [52].

Despite these successes, much remains to be done in the field of ceramic production technology. As yet, there seems to be no consensus view on the best methods for powder preparation, tube forming (isostatic pressing or electrophoretic deposition), or fabrication (zone or programmed sintering). Presumably, with further work, a consensus will emerge. Again, little has been reported on the incidence and nature of microscopic defects in $Al_2O_3$ tubes, their origin, and how to identify and eliminate them. Improved techniques for non-destructive testing and quality control are needed. However, perhaps the subject most worthy of further attention is the surface of the electrolyte tube, where the importance of wetting and of interfacial charge transfer resistance have only recently been emphasized.

Turning finally to cell design, we may identify the following problems relating to the electrolyte:

(1) The basic decisions as to whether to adopt a central sodium or central sulphur cell design, and whether the cells should be vertically or horizontally disposed; the first of these decisions influences electrolyte diameter and the second is important with regard to mounting and support of the electrolyte tube.

(2) The selection of a glass which is suitable as regards thermal expansion coefficient and chemical inertness for joining the $\beta$-$Al_2O_3$ to the $\alpha$-$Al_2O_3$ collar.

(3) The design of a cell seal which is hermetic and yet flexible enough to accommodate small movements of the tube without exposing it to high stress. One such design has been described by Hattori and colleagues [50].

(4) Provision to accommodate the volume expansion associated with melting of the electrodes on heat-up, again without exposing the electrolyte to large stresses. The orientation of the cell is important in this context also.

(5) Provision in the electrode design to ensure that parts of the ceramic are not exposed to high current densities during charge, which would favour dendrite formation.

(6) Safety design features to ensure that incipient cracking of the electrolyte does not lead to disintegration of the tube.

These topics are outside the scope of this review, but are mentioned to emphasise that electrolyte development and manufacture is not an end in itself, but must be seen in the context of the overall cell and battery design and the performance specification laid down. Unlike some technologies, where components can be developed in isolation, the sodium/sulphur battery is a highly integrated and interactive system. At its heart lies the solid electrolyte, but the successful development of this component, as we have seen, involves understanding a wide range of scientific and technological disciplines, all of which interact in a complex and subtle fashion. Herein lies the intellectual fascination and challenge of the problem of $\beta$-alumina electrolyte development, with the reward for success being an entirely new battery to meet the expected energy storage needs of the 21st Century.

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