

THE SODIUM/SULPHUR BATTERY

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Summary

It is now seventeen years since Kummer and Weber first disclosed details of the sodium/sulphur cell. The characteristics described by them showed that this system was capable of high specific energy and power, and groups in several countries immediately began research programmes aimed at producing a viable battery. This early work revealed a number of severe problems regarding cell life and performance, and only in the last few years have solutions to these been found. In the intervening years the literature on this cell has grown enormously, although much basic scientific work still remains to be done before the operation of the cell is fully understood. Nevertheless, reliable long-lived cells with acceptable performance are now available and the next phase in the development of this battery, directed towards the solution of such problems as thermal management, safety and cell reliability in a battery environment, has now begun.

Introduction

In 1966 Kummer and Weber [1] published the results of their work on a new electrochemical system — the sodium/sulphur cell. The use of these two highly reactive materials, sodium and sulphur, was made possible by separating them with a solid electrolyte, a refractory material known as beta alumina whose crystal structure was well established [2] but whose sodium ion conductivity had passed unnoticed.

The theoretical specific energy of this couple is 760 W h/kg [3] and it was claimed that the specific energy of a cell could be as high as 300 W h/kg. The results reported by Kummer and Weber [1] showed that the cell could be recharged at high rates (up to 680 mA/cm²) and that it had a low internal resistance (less than 1 Ω cm²). It was claimed that the use of liquid electrodes would result in a long life because of the absence of morphological changes which affect many solid electrodes. The potential applications of this cell were soon recognised by other companies, and research programmes were begun in the U.S.A., the U.K., France and Japan.

In the U.K., work started almost simultaneously but independently at British Rail and the Electricity Council. The aim of the work at British Rail was to reproduce the results reported by Kummer and Weber and to identify any problem areas.

The first problem was the life of the beta alumina electrolyte: after a very short time, often only a few days, this developed electronic conductivity and upon examination was found to have been penetrated by numerous black filaments which were later identified as sodium dendrites [4]. The resistivity of the material was also rather high ($20 \Omega \text{ cm}$ at 350°C was typical), resulting in a high cell resistance.

In those cells in which the ceramic electrolyte did not develop electronic conductivity, a second problem was encountered: the cell capacity declined with cycling until it reached a steady value of about 40% of the theoretical value. This usually happened over approximately 100 cycles and was due partly to progressively less conversion of the sodium sulphides into elemental sulphur on each charge half cycle, and partly to some of the sulphur becoming unavailable for electrochemical reaction by combination with the stainless steel case to form iron, nickel and chromium sulphides.

Two further problems which were not actually met in the initial stages of cell testing were thermal management and safety — predictably these were encountered as cell capacities increased and batteries were built in the later phases of the programme.

Despite these problems the results from some cells were encouraging enough to justify continuing. The other organizations who had begun research programmes also continued developing the cell, and in the last fifteen years considerable progress has been made in all these laboratories in attaining the characteristics required for a practical sodium/sulphur battery.

Beta alumina

Although the solid electrolyte is referred to as beta alumina, there are two distinct crystal structures: beta alumina and beta'' alumina [5, 6]. Both have a plane of sodium ions sandwiched between spinel blocks, but in beta alumina this plane is separated by two spinel blocks and in beta'' alumina by three spinel blocks. The main difference in properties is in the electrical resistivity, which is considerably lower for beta'' alumina (typically $5 \Omega \text{ cm}$ at 350°C) than for beta. For many years some workers maintained that the higher resistivity two block form was more resistant to degradation in cells than the three block material, but although it is certainly the case that the latter is more moisture sensitive, there is no convincing evidence to support this claim and the three block form has been widely adopted as the preferred electrolyte in sodium/sulphur cells.

There is still no agreement on the mechanism of electrolyte degradation, but the most favoured theories [7, 8] predict that mechanical properties will be important and most developers try to fabricate beta alumina with a fine

grain structure and a high strength. No experiments have been reported which prove conclusively that fine grain material has a longer life than coarse grain material, but the former is preferred as it reduces the risk of damage to the electrolyte during handling and cell assembly.

The starting powder for fabricating beta alumina can be a mixture of the reactants [9] or the material itself prepared by calcining the reactants [10] which are alumina, a sodium compound, plus small amounts of lithium and/or magnesium compounds. These dopants are necessary to stabilize the three block material which would otherwise decompose to the two block material at the temperature needed to form a fully dense ceramic [11] (> 1600 °C). If the starting powder is a mixture of the reactants, it is usually made by spray drying a slurry of alpha alumina in a solution of sodium hydroxide plus the appropriate dopants. If the calcination route is used for preparing the powder, this is then dry milled. The resulting powder is formed into the shape required, almost invariably a closed end tube with a wall thickness in the range 1 - 4 mm, by either isostatic pressing or electrophoretic deposition from an organic medium [12, 13]. Isostatic pressing is a well-established production route, and when a dry-bag semi-automatic press is combined with a slurry spray dryer for powder preparation very high rates of production can be achieved.

Sintering the green tubes is complicated by two factors — the need to control the atmosphere around the tubes to prevent loss of volatile sodium oxide, and the tendency of the material to form a duplex structure consisting of large grains in a matrix of fine grains. In batch sintering processes the atmosphere can be controlled by encapsulating the tubes in a refractory container [14]. Initially, platinum was used [15] but magnesia is cheaper and equally acceptable [16]. Platinum-lined alpha alumina tubes (R. S. Gordon, personal communication) provide a compromise between long life and high cost. There is no need to have a gas-tight seal on these containers and indeed this would be impractical: loose fitting caps are quite satisfactory on the magnesia saggars, especially if the tubes are fired upright, as is usually the case. If pass through sintering is used, similar methods of encapsulation can be used (R. S. Gordon, personal communication, and ref. 17), but the sagger material needs to be more resistant to thermal shock. In one method of pass through sintering — zone sintering — it is possible to dispense with the sagger if an appropriate atmosphere can be maintained in the furnace tube [18].

Tubes up to 600 mm long have been produced [19] and it will be appreciated that the production of a straight thin walled tube of this length presents some problems. Up to certain aspect ratios (10:1 length to diameter), firing the tubes vertically, open end down, on an unfired disc of beta alumina to prevent distortion at the open end, is quite satisfactory [16]. For higher aspect ratios, rotation of the tube during sintering can give very straight tubes [18, 20] (this is only feasible if the zone sintering process is used). Hanging the tubes from their open end has also been tried with some success [21].

Clearly, there is as yet no consensus on the best fabrication route for beta alumina. It is likely that material with the required characteristics can be made by any of the processes described above, and the route adopted in future will be determined by economic considerations.

The problem of degradation of beta alumina in cells is now much less acute: mean times to failure (MTTF) in excess of 1000 cycles have been reported by several laboratories [22], and no fundamental life limiting mechanism has been identified. This has been achieved despite the lack of agreement on mechanisms of failure, and largely by empirical methods. It appears that there are certain levels of dopants lithia and magnesia which result in a stable material; if these levels are exceeded a dramatic reduction in life occurs. Although the most widely accepted theory of ceramic failure invokes fracture of the ceramic by the Poiseuille pressure resulting from generation of sodium in narrow fissures [8], there is no strong evidence to relate life to mechanical strength, and it has been found that ceramics with very similar mechanical properties and microstructure, but different chemical composition, can have an MTTF orders of magnitude different [22]. A composition that has been adopted by a number of laboratories is 0.7% lithia, 8.9% soda, remainder alpha alumina. This produces a ceramic with a low resistivity and a long life.

The sodium electrode

The problems with the sodium electrode are associated with the sodium/beta alumina interface. Polarization at this interface manifests itself in a number of ways [23, 24]: non-linear current-voltage curves; asymmetry of resistance between charge and discharge; transient high resistances after open circuit periods and, perhaps most serious, an increase in cell resistance with cycling. These phenomena are still not completely understood, but some of the important factors have been identified: wetting of the ceramic by sodium, impurities in the sodium, impurities in the beta alumina and dopant level in the beta alumina [25, 26].

Incomplete wetting of the ceramic by sodium metal has been observed by many people [27 - 29]. Sodium only wets beta alumina above a certain temperature which depends upon the ceramic composition and the presence of moisture. Once wetting has been initiated, de-wetting does not occur when the temperature is reduced. The ability of sodium to wet the beta alumina is also affected by the presence of sodium oxide. Wetting of beta alumina by sodium can be achieved by coating the ceramic with a thin film of lead. This can conveniently be applied by dipping the ceramic in a saturated solution of lead acetate, drying and subsequently decomposing the lead acetate in an inert atmosphere [26, 30]. If this treatment is combined with addition to the sodium metal of oxygen getters such as titanium or aluminium [26, 31], the interfacial phenomena described above can be completely eliminated.

The increase in resistance of untreated ceramic with cycling implies a de-wetting process. The cause of this has not been definitely established, but calcium, which occurs as an impurity in alpha alumina, is a mobile ion in beta alumina and is known to cause an increase in cell resistance when added as an impurity to the sulphur electrode [32]. It is possible that during cycling the calcium ions in the beta alumina migrate to the sodium interface and interfere with wetting. The mobility of the calcium, if this is the cause of the problem, seems to be affected by the level of dopants in the ceramic. It has been shown [26] that the level of both lithia and soda in the beta alumina affect the propensity of the cell to increase in resistance. At certain levels of soda and lithia the rate of resistance rise is minimal, but this increases sharply as the dopant levels are increased. Thus, although these complex phenomena are not fully understood, it appears that they can be controlled either by adjusting the composition of the beta alumina or by treating the ceramic and sodium metal to improve wetting.

The sulphur electrode

The problem with the sulphur electrode was identified as loss of capacity. Even if corrosion is eliminated by using a carbon current collector, loss of capacity can still occur [33]. In a cell with a sulphur electrode consisting simply of carbon felt impregnated with sulphur there is no difficulty in discharging the cell, but on recharge the sodium polysulphides are only converted completely to elemental sulphur if a critical current density is not exceeded [34]. The value of this depends upon the type of carbon felt used and on the temperature of operation, but is usually not more than 100 mA/cm² (based on the electrolyte area) and can be considerably less.

The end of recharge is marked by a sudden increase in cell resistance. Normally this only occurs when the polysulphide composition is in the two-phase region, indicating that it is associated with the production of insulating elemental sulphur. It seems unlikely that the sulphur film is passivating the carbon felt, since the current density at the carbon surface is considerably less than that known to cause passivation at smooth carbon electrodes [35].

Examination of cells which have polarized prematurely on charge has shown that there is a sulphur-rich layer adjacent to the beta alumina [34] indicating that it has become coated with sulphur, preventing the flow of sodium ions through the electrolyte.

If deposition of sulphur in the vicinity of the solid electrolyte can be reduced, then this should lead to an improved charge performance. Graduated resistance electrodes, in which the carbon felt adjacent to the electrolyte has a higher resistance than the bulk of the carbon felt, have been evaluated [36, 37] and some improvement in performance is claimed. An alternative approach is to accept that sulphur will be generated near the solid electrolyte and build into the electrode structure a means of keeping the surface of the electrolyte at least partially clear of sulphur. This can be achieved by capillary

action. Layers of alumina felt, which is preferentially wetted by sodium polysulphides, incorporated in the sulphur electrode will wick ionically conducting melt from the interior of the electrode to the electrolyte surface [38, 39]. If the surface of the electrode adjacent to the electrolyte is then coated with a mixture of carbon and alumina felt [40], the build-up of sulphur on the electrolyte surface is deferred until the cell is almost fully charged. With this electrode structure 95% charge acceptance can be achieved in under five hours and 80% in 40 minutes [39]. An advantage of this type of electrode is that its resistance remains low (less than one third of the total cell resistance).

The current collector

The development of a high performance sulphur electrode with associated high current densities exacerbated the corrosion problem in the sulphur electrode, and this added impetus to the search for corrosion resistant materials for use as the current collector.

Only three metals, molybdenum, chromium and some of its alloys, and aluminium, show good corrosion resistance in the sodium/sulphur cell. Molybdenum is expensive and difficult to fabricate, but it does have a very low corrosion rate. Unfortunately, when it is used as a current collector the cell develops a pronounced increase in charge resistance when the sulphur electrode composition reaches the two-phase region [41]. For these reasons it is not favoured as a current collector material.

Chromium has a very low corrosion rate, but because of its mechanical properties it cannot be used as a structural material in the cell. Chromium-plated steel has been investigated [42 - 44] but it is very difficult to get a defect-free coating, and localized attack at these defects eventually leads to the whole coating spalling off the substrate. Chromized mild steel, in which a duplex layer of iron-rich and chromium-rich metal is chemically bonded to the steel substrate, has shown more promise [45]. If the operating temperature of the cell is limited to 300 °C chromized steel is quite durable, but at higher temperatures corrosion is significant, and if the cell temperature exceeds 325 °C corrosion is increased significantly [46].

Aluminium is very stable in sulphur/polysulphide melts owing to the formation of a passive layer of aluminium sulphide. Unfortunately, this layer is insulating and aluminium alone cannot be used as a current collector material. It has very attractive properties as a substrate, however: low density, low electrical resistivity, and easily fabricated and bonded to other metals. Aluminium coated with a high chromium content alloy such as Nichrome [39] makes an excellent current collector — the Nichrome is resistant to corrosion and even when applied by flame spraying, which gives quite a porous coating, there is no evidence of spalling from the aluminium substrate.

Although Nichrome, when used in conjunction with uniform carbon felt electrodes, is quite corrosion resistant, in cells with layers of alumina felt in-

corporated in the carbon felt sulphur electrode, the current concentration effects produced can lead to visible signs of corrosion. This can be prevented completely if flexible graphite foil is bonded to the Nichrome layer by isostatic pressure [39]. Cells containing sulphur electrodes having this type of current collector have shown no evidence of corrosion after one thousand cycles, and more importantly have shown little evidence of capacity loss over the same period.

Cell design

The cell described by Kummer and Weber in 1966 [1] consisted of a beta alumina tube about 100 mm long with a diameter of 10 mm and a wall thickness of 0.8 mm. This was attached to a glass reservoir containing sodium metal, and sulphur-impregnated graphite felt, 3 mm thick, was wrapped around it and held in place by a metal backing electrode (the current collector).

The tubular geometry of this first cell has been retained by most developers. The use of discs or flat plates of solid electrolyte has been investigated [35, 47], but the problem of sealing proved too intractable and this type of cell has never progressed beyond the laboratory stage. Outside the U.K. the central sodium configuration described by Kummer and Weber is still preferred, but in the U.K. the central sulphur cell, in which the sulphur electrode is contained within a beta alumina tube, has been adopted [48].

The original reason for changing to the central sulphur design was to circumvent the problem of corrosion of the current collector; the choice of materials for this component in the central sulphur cell, where it is a thin rod, is much wider than for the central sodium cell where it forms the actual cell case. Since that decision was taken in 1973, considerable progress has been made in solving the problem of corrosion of the cell case, and this combined with the potentially higher specific energies attainable with the central sodium design has inhibited developers outside the U.K. from adopting the central sulphur design. In practice, the specific energies of the two types of cell are very similar and the performance of the central sulphur cell developed by British Rail [49, 50] is probably representative of the status of sodium sulphur cells generally. This was an 88 A h cell weighing 1.06 kg which had a 33 mm O.D. by 300 mm long electrolyte tube with a wall thickness of 1.8 mm. The central current collector was a 10 mm diameter aluminium rod, flame sprayed with a coating of Nichrome and protected by an isopressed layer of graphite foil. The sulphur electrode was prefabricated from spun pitch carbon felt and alumina fibre as described above. The outside surface of the electrolyte tube was treated with lead acetate and aluminium flake was added to the sodium. This effectively eliminated interfacial polarization. The sodium-containing annulus formed by the electrolyte tube and the cell case was 1.5 mm thick and was filled with carbon spheres to displace as much sodium as possible, thus reducing the amount immediately available

for reaction in the event of fracture of the electrolyte tube. The remaining sodium was contained in a nitrogen pressurized reservoir, either at the end of the cell or in a second annulus around the cell case [51] — this latter design had a higher volumetric specific energy but a lower gravimetric specific energy. Access to the inner annulus by the sodium was restricted by interposing a barrier with a 1 mm diameter hole. The inside of the cell case was lined with flexible graphite to prevent rupture of the cell case in the event of cell failure [52].

The specific energy of these cells at the two hour discharge rate was 140 W h/kg for the end reservoir design and 125 W h/kg for the annular reservoir design, and their internal resistance was 7.5 m Ω . These cells could be cycled at the two hour discharge rate and the three hour charge rate with no loss of capacity or increase in cell resistance [50].

Battery design

Performance characteristics similar to those described above have been attained by several developers, but this is only the first step in producing a sodium/sulphur battery. Although the first sodium/sulphur powered road vehicle — a light van — was demonstrated in 1971 [53], little information has been published on the design and performance of this and subsequent batteries. Nevertheless, it is possible to draw some general conclusions from the published data.

The capacity of a sodium/sulphur cell is effectively determined by the dimensions of the electrolyte tube and is usually in the range 40 - 300 A h. This means that in most batteries the cells must be connected in parallel as well as in series. Groups of cells can be connected in parallel and a number of these then connected in series, or, at the other extreme, groups of series-connected cells may be connected in parallel. Between these extremes, groups of series-connected cells may be connected in series and parallel with other groups of cells. In the first configuration it is essential that cells should fail high resistance and this is usually accomplished by fusing each cell. In the second configuration it is necessary for failed cells to continue to pass current if the rest of the cells in the series chain are to contribute to the battery capacity, and thus the cell resistance after failure should remain low. The series-connected chains can be isolated from each other during open circuit periods and, if desired, during charge, thus reducing the chances of cells becoming overdischarged when the number of cells in each chain is no longer equal. Prevention of overdischarge in batteries in which groups of series cells are connected in series and parallel is more difficult, and for this type of battery very high cell reliability is required.

The mean time to failure is a measure of cell reliability, and for groups of cells tested individually this can be as high as 10 000 cycles [22] (the MTTF is a measure of cell reliability and should not be confused with cell life). This is approaching the value required for a commercially viable battery.

Few results have been reported for the reliability of cells in batteries, but these indicate that reliability is dependent upon battery configuration with reliability increasing with the number of cells connected in parallel [50].

Whatever cell configuration is adopted, it is necessary to maintain the temperature of the cells in the region 300 - 400 °C. This requires a thermal management system which will dissipate the heat produced on discharge and yet keep the heat loss to a minimum at other times. The method usually adopted is to provide a well-insulated container which has provision for blowing cold air over the cells either directly or indirectly. With relatively short cells, direct cooling is possible without generating a large temperature gradient. For longer cells indirect cooling, in which some insulation is interposed between the airstream and the cells, may be necessary. Both systems have been used successfully in batteries installed in road vehicles [50, 54]. For low rate applications the heat generated can be absorbed by the battery and a degree of thermal cycling allowed, although it is desirable to retain the ability to cool the battery in the interests of safety.

The specific energy of a battery will be less than that of the cell, and this is illustrated by the characteristics of the 11 kW h battery constructed using the 88 A h central sulphur cells described above [50]. In this battery two thermally insulated modules, each containing a double row of 20 cells connected in series, were cooled by air from four fans and the whole assembly was contained in a thermally insulated box. At the six hour rate the specific energy of the modules was 90 W h/kg, and of the complete battery 72 W h/kg. No doubt the ratio of cell weight to inert compounds could be increased to give a battery specific energy in excess of 100 W h/kg, but these figures give an indication of the reduction in specific energy which occurs when cells are assembled into a battery.

A high specific energy is not the only criterion for a successful battery; it must also be safe in operation and able to withstand the environmental stress associated with the particular application. In this respect, vehicle batteries have to withstand the most rigorous conditions, including vibration and thermal cycling. The battery described above was installed in a road vehicle after cycling in the laboratory and it performed surprisingly well [50]. Although power levels corresponding to the one hour rate were often exceeded, the battery delivered its full capacity and the cooling system prevented the temperature from exceeding 360 °C.

Future developments

There is little doubt that long life high performance cells can now be produced which are suitable for vehicle and stationary batteries. The main questions still to be answered are the following: Will these cells perform satisfactorily in batteries, i.e. will the reliability achieved in single cell tests be maintained in a battery environment and will the battery be able to operate satisfactorily when cells do fail? Can a thermal management system

be devised which will keep the battery near its operating temperature under all conditions? Can the safety of the battery be guaranteed under the expected conditions of abuse? Lastly, can all this be achieved at an acceptable cost?

Regarding reliability, there is no reason to believe that cell reliability in load levelling batteries, which have many cells in parallel and where close control of the cell voltage is possible, will be any different to that observed in single cell tests. For vehicle batteries, where long series chains can result in cell voltages exceeding or falling below the limits normally set for individual cell tests and where thermal cycling over a significant temperature range is also likely, the question of reliability remains open. If the variation in initial resistance and capacity can be maintained at the level achieved in the laboratory, and can be guaranteed to remain stable over the life of the battery, then there is no reason why the reliability targets for vehicle batteries should not be met. Reliability is almost certainly enhanced by maximizing the number of cells in parallel and keeping the charging rate low [50]. This may result in a trend towards lower capacity cells. The level of reliability required in vehicle batteries will be very much reduced if cells can be induced to remain low resistance after failure for a time corresponding to service intervals. Little has been reported on this important factor.

The thermal management system must prevent heat loss when no current is being drawn and allow heat loss when current is drawn. These seemingly contradictory requirements can be met using evacuated multifoil insulation coupled with gas cooling, but at present this appears to be too costly and considerable effort is being devoted to the development of evacuated powder insulation to replace it [55]. Again, the problem is most severe for vehicle batteries; for load levelling applications existing technology should be adequate.

The question of safety is one that must be faced and all developers have recognised this by building safety features into their cell designs. The most obvious danger is uncontrolled mixing of sodium and sulphur in the event of fracture of the electrolyte tube. The chances of this causing rupture of the cell case can be reduced to a very low level if the appropriate design principles are adhered to [52, 56]. Unless the probability of a cell rupturing can be reduced to zero, precautions must be taken to prevent propagation of the failure throughout the battery. One effective way of achieving this is to surround each cell with a composite material made by sandwiching flexible graphite between resin-bonded mica sheets [57]. Such a composite is light in weight and also provides good electrical insulation and, if made in the form of a closed ended box or tube, will contain any liquids which escape from a cell.

Escape of liquid sodium from defective welds is always a possibility, but in a battery box with restricted access of oxygen it is not a significant hazard, being quickly converted to sodium oxide. Escape of liquid sulphur is unlikely, as it is absorbed in carbon felt, but the boiling point of sulphur is 444 °C and if the temperature of the battery exceeds 600 °C venting of the sulphur vapour or rupture of the cell is almost inevitable. For this reason it is

essential that the thermal management system should prevent the battery temperature from approaching this value.

To summarize, the early technical problems have been largely solved, even if the science is still not fully understood, and the sodium/sulphur battery is now entering a phase of technological and engineering development which will provide answers to the queries raised here and which will determine for which applications this battery is technically and economically suitable.

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