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On the deterioration of ß″-alumina ceramics under electrolytic conditions

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The degradation of β''-alumina under electrolytic conditions was investigated at room temperature. With the use of an electrical–mechanical analogue, it was demonstrated that a large current concentration exists at the peripheries of blocked or unwetted areas. Thus, actual current densities at the sites of failure can be several times larger than the average current density. Implications regarding wetting of β''-alumina by sodium are discussed. The concept of current focusing at the tips of sodium-filled cracks is demonstrated in a room temperature test.

1. Introduction

With the invention of the sodium–sulphur battery a little over a decade ago [1, 2], increasing attention has been given by scientists and technologists to the fabrication of rapid ion-conducting electrolyte tubes from the standpoint of improved microstructure and high conductivity [3–7]. To date several cells, particularly the sodium–sulphur, have been built in various industrial, research and university laboratories. The most commonly used solid electrolytes in the sodium–sulphur batteries are either the β''-alumina (the so-called three-block structure) or the β-alumina (two-block structure). More recently, another solid electrolyte called Nasicon [8] has also been investigated as a solid electrolyte in the Na–S battery. It has been observed, however, that when these batteries are charged above some critical current density, often the batteries fail. The failure in many cases can be traced to the failure of the solid electrolyte tube.

The cracking of β''-alumina ceramic under electrolytic conditions was studied by Richman and Tennenhouse [9] and also by Armstrong *et al.* [10]. Both of the studies invoked the concept of current focusing as an integral part of their models. The Richman–Tennenhouse model is a stress corrosion model where crack growth is assumed to occur by the stress-assisted dissolution of the ceramic (β''-alumina) at the tip. Richman and Tennenhouse assumed the width of the crack to be an adjustable parameter and deduced that the critical current densities above which degradation occurs are of the order of 1 to 2 A cm^{-2}. These calculations were consistent with their experiments on bar shaped specimens of β''-alumina which were electrolysed at 300° C for 10 min at various current densities using $NaNO_3$–$NaNO_2$ eutectic as the anode and mercury as the cathode. The value of i_{cr} (critical current density), however, is strongly dependent on the crack width which is an adjustable parameter in the Richman–Tennenhouse model. These authors assumed the crack width to be ~ 40 to 50 Å. However, calculation of crack width at the values of critical stresses using the method of Sneddon and Das [11] or Stallybrass [12] shows that the crack width is of the order of 300 to 400 Å for a 25 μm crack length as assumed by these authors. Critical current density calculations using this actual value of crack width yield a value of i_{cr} which is two orders of magnitude larger than the deduced value.

The model presented by Armstrong *et al.* [10], on the other hand, invoked the concept that the crack was opened simply by the pressure of sodium formed at the tip and flowing towards the open end. Qualitatively, they argued that the crack must arrest as soon as it propagates a small distance since the pressure will drop instantaneously below the critical (Griffith) value. The concept presented by Armstrong *et al.* appears quite logical although

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the mathematical development is, in parts, incorrect and incomplete. Shetty *et al.* [13] have extended these concepts from a fracture–mechanical standpoint with somewhat more mathematical rigor. Unlike the other two approaches, a crack opening displacement was not assumed but was, in fact, determined using the method of Sneddon and Das [11]. This approach leads to the determination of i_{cr} without the necessity of an adjustable parameter. However, the calculated value of i_{cr} is considerably greater than the observed values. (As mentioned earlier, cells often fail when charged over a current density of the order of 1 to $2\,A\,cm^{-2}$.) Using a value of γ_{eff} (fracture surface energy) $= 10\,J\,m^{-2}$ * and an inherent flaw of $100\,\mu m$ [14] with viscosity of sodium at 300° C as 3.4×10^{-3} P, the calculated value of i_{cr} is $95\,A\,cm^{-2}$. At a first glance this discrepancy appears irreconcilable. The object of this paper is to demonstrate that such a high value of i_{cr} can, in fact, be completely rationalized even though cells often fail at current densities of the order of $1\,A\,cm^{-2}$ or below. Also, some of our tests on sodium β''-alumina sodium cells at 400° C have shown that current densities up to 4 to 5 A cm^{-2} can be achieved without immediate failure. Demot [15] and co-workers have also operated Na–Na cells at high current densities without immediate failure. The model presented by the present author and co-workers suggests that degradation, once started, can proceed in extremely rapid manner – crack-growth rates being of the order of a few $mm\,sec^{-1}$. This, in fact, has been observed in our experiments which will be discussed in Section 3. Also, the concept of current focusing has not been experimentally investigated even though it is central to the three models. During the course of the present investigation, the concept of current focusing has been experimentally verified.

In the following, use is made of the fact that an exact analogue exists between electrical and mechanical systems under certain conditions exhibiting symmetry [16]. It is easy to see that what represents a force in a mechanical system, represents current in an electrical system, i.e. $F \equiv I$†. For unit area, $\sigma \equiv i$ where σ is the stress and i is the current density. Also, what constitutes a displacement, δ, (elastic) in a mechanical system constitutes voltage, ϕ, in an electrical system, i.e. $\delta \equiv \phi$. Similarly, the analogy between the Young's elastic modulus, E, and the electrical resistivity ρ, can be given as $E \equiv 1/\rho$. The use of this analogy provides a powerful tool to attack several problems in electrical systems since the elastic systems have been studied in great detail by several engineers and mathematicians over the past century. Recently, the above equivalence was verified [17] on a cracked aluminium foil where cracks of various lengths were introduced in an aluminium foil and the voltage was determined for a fixed current (passing perpendicular to the crack). The equivalence was found to be exact. Thus, many‡ of the equations developed in plane stress fracture mechanics can be extended to electrical systems. The present paper demonstrates the use of the electrical–mechanical analogue and its implications with regards to degradation of rapid ion conductors with particular reference to β''-alumina. While the actual batteries are operated at 300° C, the data presented in this paper were obtained in room temperature tests where the sodium formed in electrolysis tests is solid. The room temperature tests are considerably easier and permit more information to be gained. Moreover, several salient features of ceramic degradation can be elucidated by room temperature tests. Results of Na–Na test cells at 300° C will be reported at a later date.

2. Theory

Consider a centre-cracked thin plate shown in Fig. 1a which is externally acted upon by a stress σ. Young's elastic modulus of the material is E. The stress intensity factor is given as [18]

$$K_I = \sigma \left[W \tan \left(\frac{\pi C}{W} \right) \right]^{1/2} \qquad (1)$$

where W is the width. It can be easily shown that the deflection is given by [17]

$$\delta(C) = \delta(0) + \frac{4\sigma W}{\pi E} \ln \sec \left(\frac{\pi C}{W} \right) \qquad (2)$$

where $\delta(0)$ is the deflection for zero crack length and $\delta(C)$ is the deflection of the plate with crack

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* In the paper Shetty *et al.* [13] a value of $20\,J\,m^{-2}$ was used. This value was for hot-pressed material which exhibits preferred orientation. Sintered specimens have yielded a value γ_{eff} of $10\,J\,m^{-2}$.

† The symbol $\equiv$ is meant to signify analogous to and not equal to.

‡ Only so far as mode I loading is considered. Also, only the plane stress analogy appears appropriate since there is no analogue of Poisson's ratio in electrical systems. The analogies used here are only valid for symmetric problems since in general $\sigma \not\equiv i$ or $E \not\equiv 1/\rho$, as σ is a second rank tensor and i is a vector.

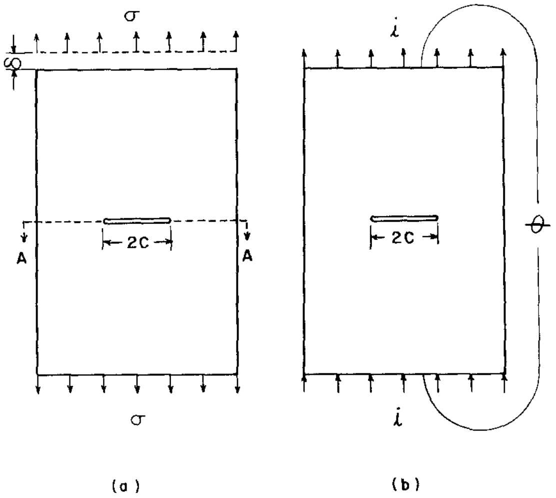

Figure 1(a) A centre-cracked thin plate under the action of stress σ applied at its boundaries that are parallel to the crack. δ is the deflection. (b) A similar thin centre-cracked plate through which a current of density i is passing in a direction perpendicular to the crack. ϕ is the voltage.

length $2C$. The electrical–mechanical analogue implies that if we were to pass a current of density, i, perpendicular to the crack (see Fig. 1b), then the voltage will be given by

$$\phi(C) = \phi(0) + \phi^0 \ln \sec \left(\frac{\pi C}{W}\right) \qquad (3)$$

where ϕ^0 is a constant.

The above equivalence has been verified in [17]. We know that in the mechanical system the stress σ_{yy} is nearly zero immediately above and below the crack while the stress at the tip is very high. The electrical analogue implies that the current density immediately above and below the crack will be zero while, at the tip, it will be very high. If the crack tip radius is r then the value of the current density at the tip will be given by

$$i_{\text{tip}} \equiv i\left(2\sqrt{\frac{C}{r}} + 1\right). \qquad (4)$$

Thus the current density can be easily magnified by one or two orders of magnitude at the tip of a crack. From the standpoint of an electrical analogue, it is not necessary to have a crack perpendicular to the flow of current. An inclusion of infinite resistivity of similar shape would give an identical current intensification at the tips of the inclusion. Moreover, with reference to a solid

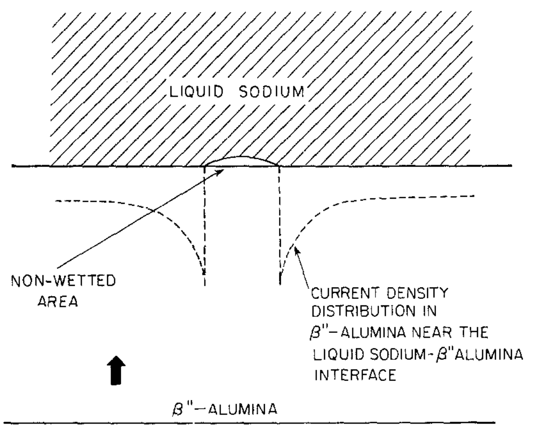

Figure 2 A schematic illustration showing a non-wetted area on the electrolyte surface in contact with sodium. The dotted lines show the current density distribution. The arrow indicates the direction of ion flow.

electrolyte such as β''-alumina used in sodium–sulphur batteries, if a small area on the surface of the electrolyte in contact with the sodium is not wetted, then this area represents a thin layer of essentially infinite resistivity. Moreover, owing to the fact that the electrical resistivity of sodium is orders of magnitude less than β''-alumina, the electrical potential near the interface between liquid sodium and β''-alumina in liquid sodium is essentially constant. Thus the mechanical analogy is similar to the one shown in Fig. 1a since across the line A–A (not in the crack) in Fig. 1a the deflection δ is uniform. Fig. 2 is a schematic illustration of the solid electrolyte in contact with liquid sodium with part of the surface not wetted. Also shown is the current density distribution. Depending upon the size of the non-wetted area and the thickness of the β''-alumina membrane, the current density intensification can be evaluated using the standard stress concentration (or stress intensity) factors from linear elastic fracture mechanics.

3. Experimental procedure and results

3.1. Specimen preparation

Lithia-stabilized β''-alumina specimens of composition 8.8 wt% Na_2O–0.75 wt% Li_2O and 90.45 wt% Al_2O_3 were prepared by the procedure described in [5]. Dried $LiNO_3$ and de-agglomerated α-Al_2O_3* were ball milled and calcined at 1250° C for 2 h to yield $Li_2O:5Al_2O_3$. Subsequently, dried Na_2CO_3 and α-Al_2O_3 powders were ball milled and calcined at 1250° C to yield β-alumina and $NaAlO_2$. These two calcined powders were

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* Meller Company.

mixed to yield the desired composition. Rectangular bars were first die pressed followed by isostatic pressing at 30 000 psi[†]. The specimens were sintered for 5 min at 1600° C in sealed platinum capsules to minimize loss of soda by evaporation. Finally the specimens were annealed at 1400° C for 2 h.

3.2. Blocking experiments

A specimen of β''-alumina was machined in the form of a thin rectangular plate. One edge of the specimen was partially coated with silver paint. The other end was dipped into a solution of $NaNO_3$ in water. A small d.c. current was passed through the sample. Sodium filaments were seen to form from the cathode. Sodium penetration at room temperature has also been observed by DeJonghe *et al.* [19]. As part of the area was not silver painted, the filament penetration did not originate from this area. However, the penetration was seen to occur first at the edges separating the coated and the uncoated areas. The filament penetration was quite rapid (of the order of 1 mm sec^{-1}).

To explore further the effect of blocking, the following experiments were done. Specimens of β''-alumina of size 4.5 cm × 1 cm × 0.5 cm were chosen for the study. One of the two 4.5 × 1 cm^2 faces were painted with silver paint. The specimens were electrolysed at 50 mA current for 1 min at room temperature. The specimens were subsequently broken in bending. The strength (average of three specimens) was found to be 132 MN m^{-2} as compared to a value of 170 MN m^{-2} for the as-sintered (non-electrolysed) specimens. The lower value of the strength for the electrolysed specimens was due to the sodium filament penetration.

In order to simulate the situation where a small area on the electrolyte surface is not wetted by sodium in an actual cell, the following experiments were done. One face each of three specimens was coated with silver paint except a small circular area of 0.15 cm radius in the centre. (See Fig. 3). The specimens were subsequently electrolysed as before. The circular non-painted area simulates the non-wetted area. A high current concentration should exist near the periphery of it. If so, one should expect considerably lower strength. The electrolysed specimens were tested for strength.

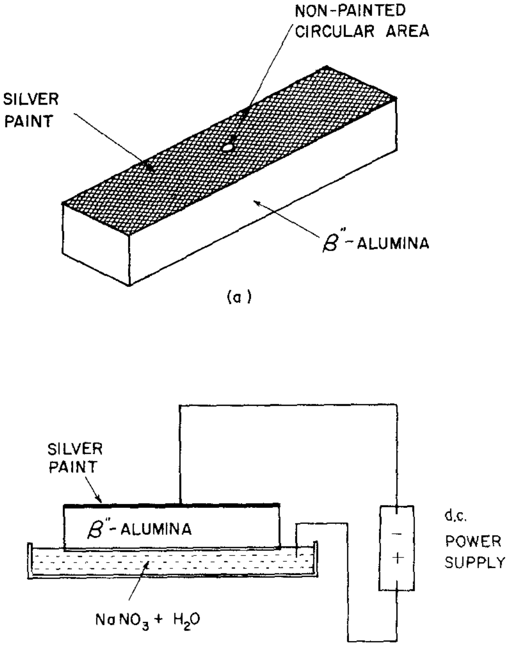

Figure 3 A schematic illustration showing specimens used in blocking experiments. A small circular area was not silver-painted. A high current concentration exists at the peripheries of the blocked off area. The figure also shows schematic illustration of testing.

The strength was found to be 55 MN m^{-2} which is less than half of the value for degraded specimens where the entire surface was coated with silver paint. This is only possible if there is a considerable current intensification. The considerably lower value of strength cannot be explained on the basis of simply reduced area[‡] since the reduction in area is only 1.5%. Thus in an actual cell, the attainment of complete wetting is extremely necessary since high current concentrations can exist near the periphery of non-wetted areas. Similar experiments were conducted with circular areas blocked off with various radii. Fig. 4 shows strength plotted as a function of the radius of the blocked off area. As can be seen, the strength decreases with increasing radius of the blocked off region.

Experiments have also been conducted where a strip of width $2C$ (Fig. 5) has been blocked off on the silver painted side. The maximum width chosen was 9 mm which is less than the separation between the inner loading points on the four-point jig used to determine strength. The specimens were electrolysed for 1 min each. Subsequently,

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[†] 10^3 psi = 6.89 N mm^{-2}.

[‡] And thereby somewhat higher current density.

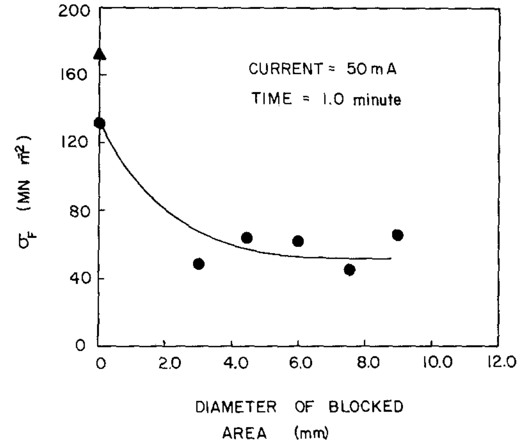

Figure 4 Strength versus diameter of the blocked off area showing strength degradation.

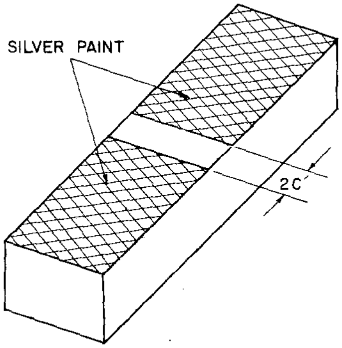

Figure 5 A schematic illustration showing specimens used in blocking experiments where a strip of length $2C$ was not silver-painted.

the specimens were broken in bending. As discussed earlier the current density at the tip of the blocked off region is given by

$$i_{\text{tip}} = i\left(2\sqrt{\frac{C}{r}}+1\right). \tag{4}$$

Experimental observations in our laboratories as well as by DeJonghe *et al.* [19] have shown that the sodium penetration at a given current density occurs at a constant velocity. Moreover, the higher the current density, the faster is the penetration. If it is assumed that the penetration rate (crack propagation) is linearly proportional to the current density, then the crack length after a certain time t of electrolysis will be given by

$$l = l_0 + \left(\frac{\mathrm{d}l}{\mathrm{d}t}\right)\cdot t, \tag{5}$$

where l_0 is the inherent flaw size. Now

$$\frac{\mathrm{d}l}{\mathrm{d}t} = Ai_{\text{local}}, \tag{6}$$

where A = constant. Now

$$i_{\text{local}} = i\left(2\sqrt{\frac{C}{r}}+1\right)$$

therefore,

$$l = l_0 + Ait + \frac{2iAt}{\sqrt{r}}\sqrt{C}. \tag{7}$$

If electrolysis is conducted for a fixed time at a given current density but with varying blocked off areas, then

$$l = l_0 + Ait + B\sqrt{C}, \tag{8}$$

where $B = 2iAt/\sqrt{r}$. From the Griffith relation, we know

$$\sigma_F = \sqrt{\left(\frac{2\gamma E}{\pi l}\right)}. \tag{9}$$

Eliminating l between Equations 8 and 9,

$$\frac{1}{\sigma_F^2} = \frac{\pi}{2\gamma E}(l_0 + Ait) + \frac{\pi B}{2\gamma E}\sqrt{C} \tag{10}$$

or

$$\frac{1}{\sigma_F^2} = \frac{1}{\sigma_{F_0}^2} + \frac{\pi B}{2\gamma E}\sqrt{C},$$

where σ_{F_0} is the strength of electrolysed specimens without any non-wetted area. Fig. 6 shows a plot of $1/\sigma_F^2$ versus $\sqrt{C}$. The plot is linear as predicted by Equation 10.

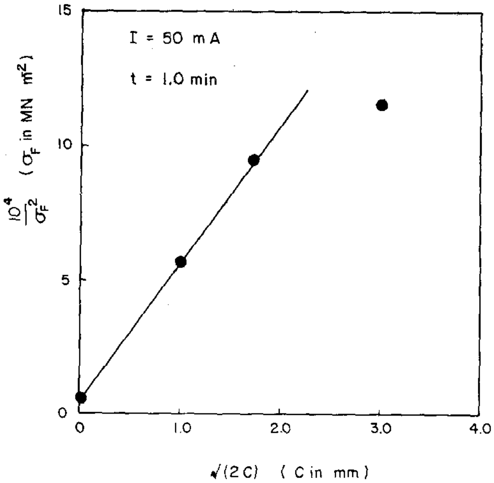

Figure 6 A plot of $1/\sigma_F^2$ versus $\sqrt{C}$. A linear relationship can be seen up to $2C = 3$ mm. Beyond $2C = 3$ mm, for the time of electrolysis (1 min), the length of the cracks formed was a considerable fraction of the thickness of the specimen. This may be the reason for a deviation from straight line for $2C = 9$ mm.

The solid electrolyte tubes used in batteries are typically 1 to 3 mm thick. The current concentration effect due to blocking may be somewhat smaller than for the thick specimens used here. To explore the effect of blocking on thin specimens, similar experiments have also been conducted on specimens of dimensions 4.5 cm x 1 cm x 0.2 cm with qualitatively somewhat similar results. The above experiments clearly show that if there is any kind of blocking on the surface of the solid electrolyte in contact with liquid sodium, the current concentration at the rims of the blocked off areas can be quite high. If the value of $2\sqrt{(C/r)}$ is 100, then the current density at the rim can be as high as 100 times the average current density. If the value of r is assumed to be on the order of 400 Å (which is typical of the crack tip radius in brittle materials), then if a circular area of radius 100 μm is blocked off, i.e. ion transport across it being negligible, then a current concentration factor of 100 can be easily attained.

3.3. Current focusing experiment

A thin (1.5 mm) specimen of β''-alumina was machined in the form of a double cantilever beam (DCB) specimen in which a 2 cm length crack was machined using a diamond blade. The edge containing the machined crack was silver painted including the inside of the crack. By making this edge as the cathode, the specimen was electrolysed using $NaNO_3$ solution in water as the anode. The sodium streaks were seen to emanate from the tip of the machined crack as shown in Fig. 7 but not from the flat edges within the immediate vicinity of the crack. This experiment, therefore, confirms the current focusing concept invoked by Armstrong *et al.* [10] and Richman and Tennenhouse [9]. Moreover, as seen in Fig. 7, the crack is tip fed.

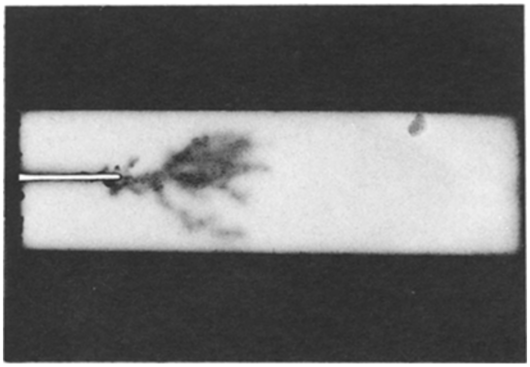

Figure 7 A DCB specimen that was electrolysed at room temperature. The left-hand edge as well as the machined crack was silver-painted. Thus, the crack simulates a metal-filled crack. When the specimen was electrolysed with the silver-painted side as the cathode, sodium streaks formed from the tip of the machined crack confirming the ion focusing concept.

4. Discussion

The preceding experiments have confirmed the value of the electrical–mechanical analogue in the study of solid electrolytes. The analogy appears to be quite exact under certain conditions; namely for mode I loading of plane stress problems. Thus, stress in a mechanical system is analogous to current density in an electrical system, deflection is analogous to voltage in an electrical system. Hence, just as the applied stress is intensified ahead of a crack in a thin plate, if a current density i is passed through a plate perpendicular to the crack, current density near the tip is intensified in a similar manner. Thus the void volume of the crack is a region of zero elastic modulus in a mechanical system and of zero conductivity (infinite resistivity) in an electrical system. In an electrical system, however, the presence of a crack is not necessary to attain current density intensification. An inclusion of very high resistivity can also result in large intensification at its boundaries inside a conductor. With reference to the sodium–sulphur battery which uses a sodium ion conductor such as β''-alumina, β-alumina or Nasicon, the existence of a small non-wetted area in contact with liquid sodium during charging can provide high current density concentrations in the ionic conductor near the boundaries of the non-wetted area (see Fig. 2). In the non-wetted region, the contact resistance is very high. Thus sodium ions cannot pass through this region into the sodium reservoir. Depending upon the size of the non-wetted area and the thickness of solid electrolyte, intensification factors of the order of 10 to 50 can be easily attained. It is thus reasonable to expect that the applied average current density of 1 to 2 A cm^{-2} can be easily magnified to a value in the range of 10 to 100 A cm^{-2}. Theoretical calculations given in [13] have shown critical current densities that are well in excess of 1 to 2 A cm^{-2} in agreement with the above analysis. Sodium–β''-sodium cells have been made and operated in our laboratories [20] at 400° C under a current density as high as 4.5 A cm^{-2} without failure for as long as 2 days, clearly showing that the critical current density is much higher than 1 to 2 A cm^{-2} reported by Richman and Tennenhouse [9]. The value of

$\sim 1\,\mathrm{A\,cm^{-2}}$ for the critical current density obtained by Richman and Tennenhouse [9] was obtained from Na-salt–β''-mercury cells. Our experience [21] with these cells has shown that mercury does not wet β''-alumina completely. This is evidenced by a rather large contact resistance. This results in current intensification as discussed earlier giving an apparently low value for the critical current density.

The above discussion demonstrates the importance of complete wetting with regard to the operation of a sodium–sulphur battery or any other device of similar nature involving a molten metallic electrode and a solid electrolyte. Several investigators have reported that β''-alumina is not easily wetted by sodium and several hours at high temperatures (~ 400° C) are required to improve wetting. The wetting of β''-alumina by sodium as a function of time has been investigated by monitoring the cell resistance as a function of time immediately after filling. The present work shows that a complete wetting is needed if long life of the battery is desired since even very small non-wetted areas (of the order of $1\,\mathrm{mm^2}$) can give very high local current concentrations thereby yielding apparent critical current densities that are too low, resulting in premature failure. Unfortunately, small non-wetted areas cannot be detected by cell resistance measurements much in the same way that small cracks do not influence compliance measurements but yet are extremely deleterious to strength. The above discussion therefore suggests that every attempt should be made to improve wetting. One of the possibilities is an addition of a benign element in liquid sodium to improve wetting. Furthermore, the thinner the tube, the less is the current concentration effect. However, the thickness cannot be reduced indefinitely as the intrinsic mechanical integrity could break down.

The non-wetting of the solid electrolyte presents another interesting problem. If one assumes that there are small circular areas of non-wetted regions distributed randomly on the surface of a tube such that they are of varying size governed by some statistical function, then the larger the area of the tube, the greater the probability of finding a large non-wetted area. Moreover, the larger the size of the tube, the higher is the probability of finding the largest flaw near the peripheries of the largest blocked off area. This, in effect, implies an even lower Weibull modulus, m, than the case of simple mechanical strength measured by conventional tests. This implies that, statistically, cells made with larger tubes will have lower critical current densities and effectively shorter life. This aspect must be investigated in detail if the cell design is to be realistic.

Finally, the current focusing experiments have shown that the crack is tip fed as has been assumed in all of the theoretical models.

Acknowledgement

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