RAPID TESTING OF BETA ALUMINA CERAMICS

J. L. SUDWORTH

Beta Research & Development Ltd., 50 Goodsmoor Road, Sinfin, Derby DE2 9GN (U.K.)

Beta alumina is used as a solid electrolyte in sodium–sulphur cells.

In the cell the material is used as a thin-walled tube and it serves both as a separator for the reactants, sodium and sulphur, and as a solid electrolyte. Clearly, any test used to determine the quality of the material should provide information on its properties as a ceramic and as an electrolyte.

When a change is made in the process for fabricating the solid electrolyte, *e.g.*, a change of raw materials, the only satisfactory way at present to determine if the change has affected electrolyte life is to test the material in a sodium/sulphur cell. Using current densities expected in load levelling applications, it can take a year to amass a thousand cycles. Clearly, there is a need for a test which will give rapid results and which will determine the point at which the electrolyte will no longer function in a sodium–sulphur cell.

By increasing the discharge current density to 0.5 A cm^{-2} and the average charge current density to 0.25 A cm^{-2}, the number of cycles per day can be increased from three to sixteen. This does, of course, raise the question of whether such high current densities will shorten the life of the beta alumina, and it was to try and answer that question and to establish the validity of this rapid test that the present work was undertaken.

The cell used for this work is shown in Fig. 1. The sulphur electrode is designed to allow rapid charging. This is achieved by incorporating polysulphide wicks in the electrode. During the test, the cell is suspended in an air bath held at 350 °C.

The circuit for charge and discharge is shown in Fig. 2. The cycle is controlled by three clocks and a voltage "trip". The sequence of events during a complete cycle is as follows. The cell switches to discharge and the discharge clock starts running, discharge continues until the voltage falls below the "trip" level, which is set to give an open circuit voltage of 1.78 V, or until the time allowed for discharge (25 min) has elapsed. After 25 min, the circuit is broken and the cell held on open circuit for 5 min by the second clock. At the end of this time, the cell is switched to charge, *i.e.*, it is connected directly to the 2.7 V supply. Charging continues for a time period controlled by the third clock (1 h), then the cell is switched to discharge and the next cycle begins.
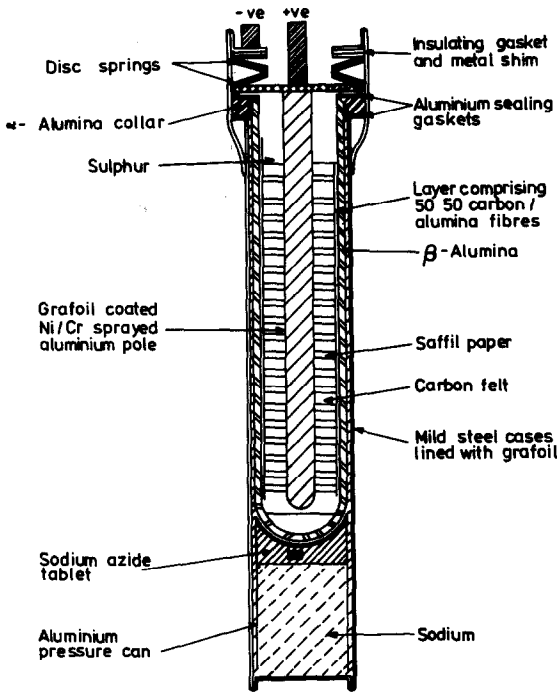
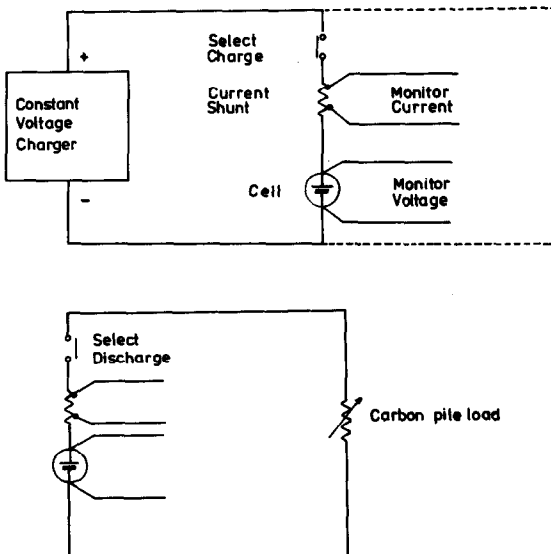Fig. 1. Sodium–sulphur cell for rapid cycling.

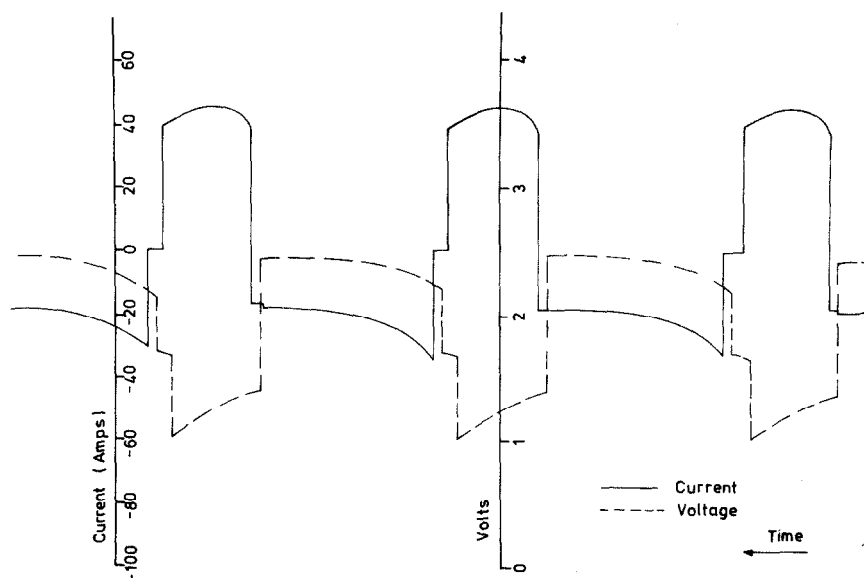Fig. 2. Schematic circuit diagram for charge and discharge.

Fig. 3. Current and voltage *vs.* time during charge and discharge.

TABLE 1

Dimensions and physical properties of beta alumina tubes

	Beta R & D tubes	Ceramatec tubes
Strength (MN m^{-2})	199 ($\sigma = 15$)	193 ($\sigma = 18$)
Density (g cm^{-3})	3.23	3.22
Wall thickness (mm)	1.65	2.60
Internal diameter (mm)	29.70	28.00
External diameter (mm)	33.00	33.20
External length (mm)	157.2	157.2
Dome thickness (mm)	2.0	3.90
Internal length (mm)	155.20	153.30
Radial resistivity at 350 °C (ohm cm)	5.76	4.08

The charge/discharge curves obtained are shown in Fig. 3.

The physical properties of the tubes are given in Table 1.

The lower resistivity of the Ceramatec material can be explained by the higher ratio of the beta double prime phase, as shown in Table 2.

The cells were activated by heating to 350 °C in about three hours. They were then held overnight at this temperature before being discharged. Thereafter the cells were charged and discharged automatically 16 times every 24 h. The temperature, which was monitored by attaching a thermo-couple to the outside of the cell, rose by 40 °C during the discharge (Fig. 4). Very little heat was generated on charge, and the cell temperature fell back to normal.

TABLE 2

Chemical composition of beta alumina tubes

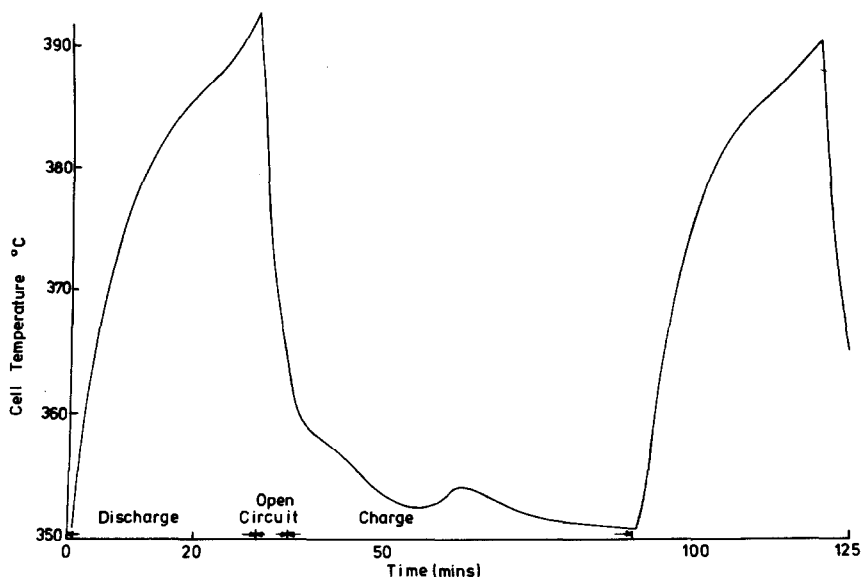|	Beta R & D tubes	Ceramatec tubes
Na_2O (% w/w)	9.02	8.71
Li_2O (% w/w)	0.67	0.72
β''-Alumina	89	97
CaO (ppm)	91	38

Fig. 4. Variation in cell temperature during charge and discharge cycles.

The initial intention was to test the cells for 1000 cycles. Both the Beta Research & Development tubes and the Ceramatec tubes achieved this without any failures. The test of the Beat Research & Development tubes was continued until four of the cells had failed. This occurred at 2000 (1), 2800 (1), 2900 (2) cycles. The remaining cell was removed from test before failure at 3100 cycles.

The first Ceramatec cell failed at 1600 cycles and a second cell failed at 2200 cycles. The remaining three cells survived 2600 cycles and were then removed from test as signs of sodium leakage were visible.

Figure 5 shows the failure distribution plotted for Beta Research & Development and Ceramatec tubes.

The change in the average effective discharge resistance with time is shown in Fig. 6. It can be seen that the resistance of the Beta Research & Development tubes increased by about 10% per thousand cycles, whilst the resistance of the Ceramatec tubes remained constant up to 1500 cycles before starting to increase.
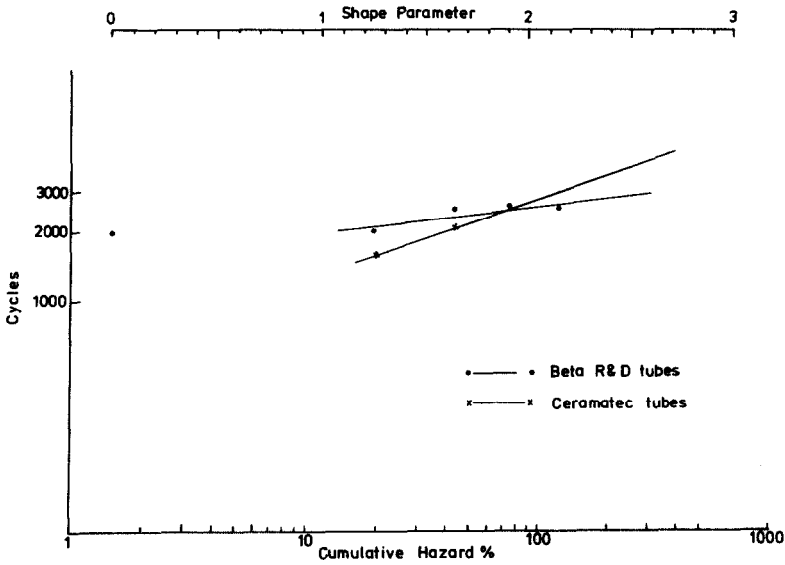
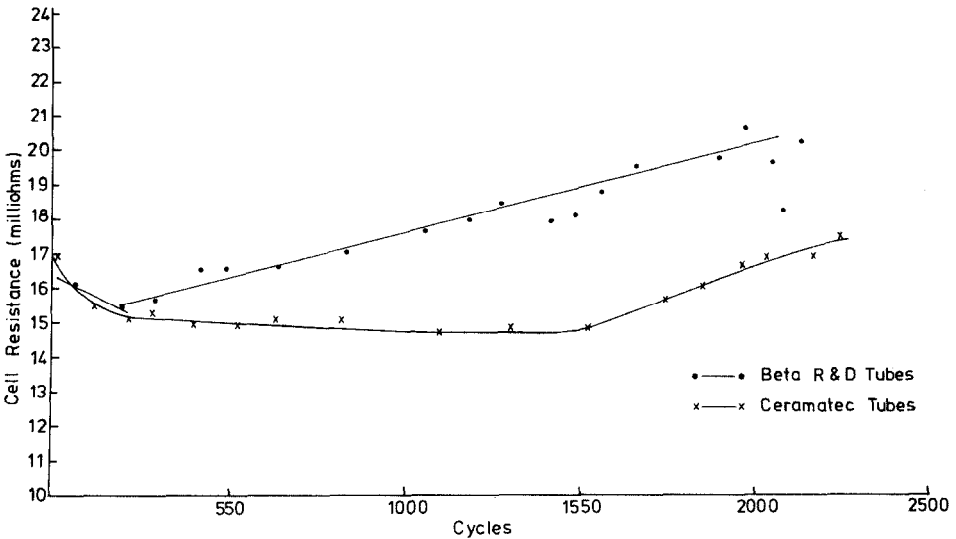Fig. 5. Weibull hazard plot of cell life Beta R & D tubes, Ceramatec tubes.

Fig. 6. Average cell resistance *vs.* cycles Beta R & D tubes, Ceramatec tubes.

One objective of this work was to establish whether the high current densities used in this test shortened the life of the beta alumina, *i.e.*, whether this is an accelerated test in the normally accepted sense of that term where the life under conditions more stringent than normal can be correlated with a longer life under normal conditions. An example of this would be the determination of the life of lead–acid batteries at elevated temperatures and

the use of the value obtained to predict the life at ambient temperature. A second objective was to establish whether rapid testing is a valid way of determining electrolyte life, *i.e.*, if the high current density does result in a shorter life, can this be correlated with life at normal current densities or, conversely, could high current density extend the cycle life?

It is not possible to state unequivocally that the rapid test has not shortened the electrolyte life, since there are very few data available on tests extending beyond 2000 cycles at normal current densities. A comparison of high rate and low rate tests can be obtained from the FACC load levelling battery [1] in which Ceramatec tubes were also used. The voltage of the cells in the battery was closely controlled, and the electrolyte tubes used, although longer than the Ceramatec tubes used in these tests, were otherwise identical. The characteristic life of 830 cycles is less than that of the cells in these tests. Thus, even when the difference in size of the population is taken into consideration, it seems unlikely that the use of high current densities leads to a reduction in ceramic life.

Whether rapid testing is a valid method for determining ceramic life is a more difficult question to answer. It is possible that there are mechanisms for electrolyte degradation which are time dependent, but none of the theories put forward by Armstrong *et al.* [2], and Richman and Tennenhouse [3], to explain electrolyte degradation, would predict this. Although time-related failures due to intrinsic ceramic properties are unlikely, extrinsic factors cannot be ruled out. Current concentration effects, caused by incomplete wetting of the electrolyte by sodium, or caused by the deposition on the surface of the electrolyte of corrosion products from the current collector, are possible causes of premature electrolyte failure. Both the above causes of current concentration could be time dependent rather than cycle dependent. Thus it is well established that corrosion products from the current collector can be transported through the sulphur electrode and deposit on the beta alumina.

Islands of insulating material would be deposited over a period of time and the boundaries of these islands could become locations where current concentration effects could occur.

Rapid testing, therefore, could be regarded as a valid method of determining intrinsic electrolyte life. In cells cycling at normal rates over longer periods of time, however, the electrolyte life would be modified by extrinsic factors arising from the other cell components. The effect of these extrinsic factors is illustrated by the failure mode of the Beta Research & Development tubes. In two of the cells containing these tubes, the electrolyte had fractured. In both cases, severe corrosion of the pole was noticeable in the vicinity of the fractures. It is possible that the corrosion was the aftermath of cell failure by beta alumina fracture, but the signs of an early stage of corrosion in the two failed cells in which the beta alumina had not fractured tend to support the view that the corrosion of the pole preceded the fracture of the beta alumina.

Rapid testing provides a quick assessment of the effect of ceramic fabrication parameters on electrolyte life. The absolute value of life obtained

must be treated with caution. In tests conducted over longer time scales the ceramic life could be reduced by factors extrinsic to the ceramic. The test is, however, a useful method of comparing the life of different beta alumina formulations, and a bench mark for such comparisons has now been established.

References

1 R. W. Minck, *Proc. 5th DoE/EPRI Sodium–Sulfur Battery Workshop, Washington, DC,* EPRI, 1983.
2 R. D. Armstrong, T. Dickinson and J. Turner, *Electrochim. Acta, 1* (1974) 187.
3 R. H. Richman and G. J. Tennenhouse, *J. Am. Ceram. Soc., 58* (1975) 863.