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DETERMINATION OF THE LIFE PROPERTIES OF BETA ALUMINA TUBES*

REINHARD KNÖDLER and WERNER BAUKAL
Battelle-Institut e.V., Frankfurt am Main (F.R.G.)
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Summary

A method has been developed for the determination of the life properties of beta alumina tubes for the sodium–sulphur battery. The tubes are placed into Na/β-Al_2O_3/Na cells and the faradic efficiency is measured at a current density beyond a critical value. Screening of different batches of tubes showed that high density and a fine-grained microstructure of the ceramic material are necessary to ensure good life properties.

Introduction

In the sodium–sulphur battery, the electrolyte consists of tubes of the sodium-ion conducting ceramic β-Al_2O_3. The performance of the battery depends critically on the quality and the lifetime of these tubes. Lifetime generally is defined as the charge flowing through the wall of the tubes in Na/S cells until degradation occurs. Testing procedures are necessary in order to determine the properties of the tubes outside the Na/S cells. The experimental procedure generally used is to operate the tubes in Na/β-Al_2O_3/Na cells [1 - 8].

The following difficulties are encountered with this type of measurement: degradation of the ceramic can only be judged by inspecting a cross-section after completion of the experiment, since degradation is not necessarily associated with a measurable change in the electric resistance of the cell; for rapid screening purposes, the test period is rather long. Even at relatively high current densities (*e.g.* 0.9 A/cm^2) testing times of up to one year have to be expected if high grade tubes are used.

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The purpose of our work, therefore, was to develop a method which allows, first, the degradation to be identified during current flow and, second, the testing time to be reduced.

Experimental

Tubes 50 mm in height, 11 mm in diameter (inside) and 0.8 mm in wall thickness of different composition and preparation were used†. The tubes described in the present paper are all of the same composition: 9.3 wt.% Na_2O, 3 wt.% MgO, bal. Al_2O_3.

The lifetime experiments were carried out at a temperature of 300 °C. The experimental arrangement is shown in Fig. 1. The current density ranged from 0.3 to 2 A/cm^2. A current was forced to flow across the wall of the tube. The current direction was reversed every 2 min. The faradic efficiency was measured by cycling the sodium between probe A and probe B. The faradic efficiency η (ratio of the ionic conductivity to the overall conductivity) was calculated from the time needed for this procedure, the volume of Na between the fixed positions of probes A and B, and finally from the charge applied. The apparent resistance of the cell was recorded and the specific resistance was calculated by using the mean value of the surface area during operation. The resistance changed its value by less than ±10%. After

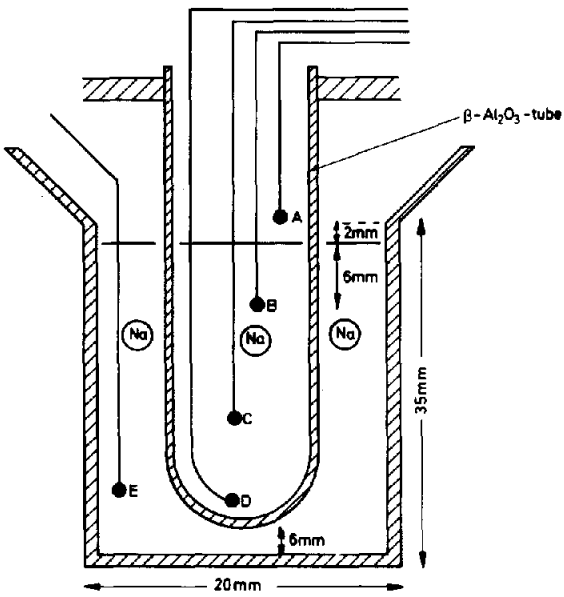

Fig. 1. Experimental arrangement for testing β-Al_2O_3 tubes. Probes A and B: faradic efficiency measurements; probes C and E: current collector; probe D: voltage probe.

†Kindly supplied by Brown, Boveri & Cie, AG. Heidelberg.

the experiments, cross-sections of the tubes were made and examined microscopically.

Results

At current densities of up to 1 A/cm^2, we observed in all cases, that if η remained at 100%, the micrographs never showed signs of degradation. On the other hand, if η fell below 100% cracks were inevitably observed. Figure 2 shows the crack-free cross-section of a good quality tube. The corresponding cell was operated for more than 600 Ah/cm^2 at 0.66 A/cm^2 and, continuously, at 100% faradic efficiency. If after 300 Ah/cm^2 of operation at 2 A/cm^2 the faradic efficiency had reached the low value of about 50%, large cracks became visible. This is shown in Fig. 5.

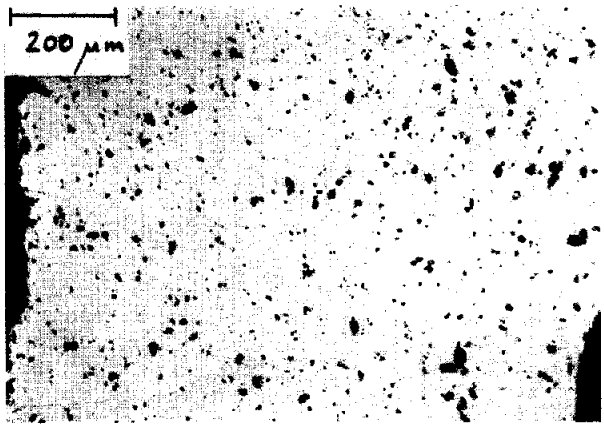

Fig. 2. Cross-section of a good-quality ceramic after about 600 Ah/cm^2 of operation at a current density of 0.66 A/cm^2.

Further experiments showed that most tubes did not degrade if they were operated at, say, below 1 A/cm^2. Only if the current density exceeded this value, did the faradic efficiency decrease. For the accelerated test a three-step current density/charge programme was applied to the cell: 0.66 A/cm^2 during about 80 h, 1.3 A/cm^2 during another 80 h and subsequently 2 A/cm^2 until degradation.

The behaviour of tubes with poor and good life properties is compared in Fig. 3 and Fig. 4, respectively: in the first step, where the current density lies well below 1 A/cm^2, both qualities show identical behaviour and the faradic efficiency remains constant at a value of 100%. In the second step (1.3 A/cm^2), the two grades can be distinguished: the faradic efficiency of the poor-quality tube decreases rapidly, whereas the good-quality ceramic shows only a small deviation from 100% faradic efficiency; moreover, the value remains constant. Even in the third step (2 A/cm^2) η does not drop below 80% for a period of more than 100 h.

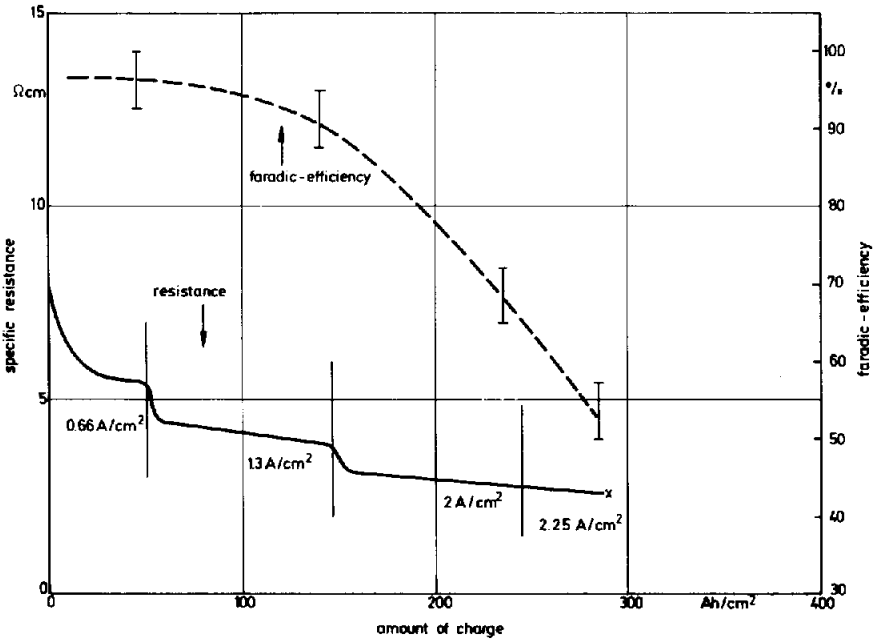

Fig. 3. Accelerated lifetime test using a β-Al_2O_3 tube of poor quality.

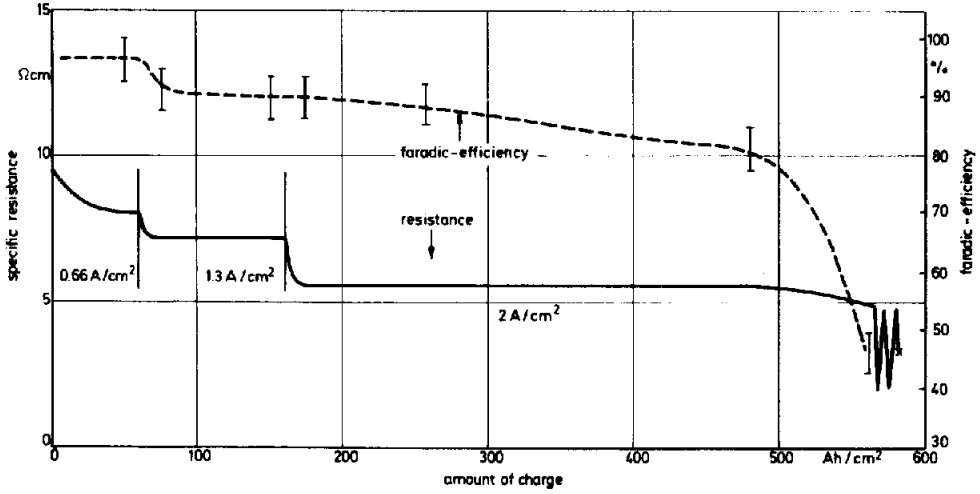

Fig. 4. Accelerated lifetime test using a β-Al_2O_3 tube of good quality.

The operation of tubes from the same batch at Brown Boveri in complete Na/S cells (personal communication) furnished results similar to the Na/Na-cell experiments described here so that a correlation exists between the long-term experiments of Brown Boveri and our own findings.

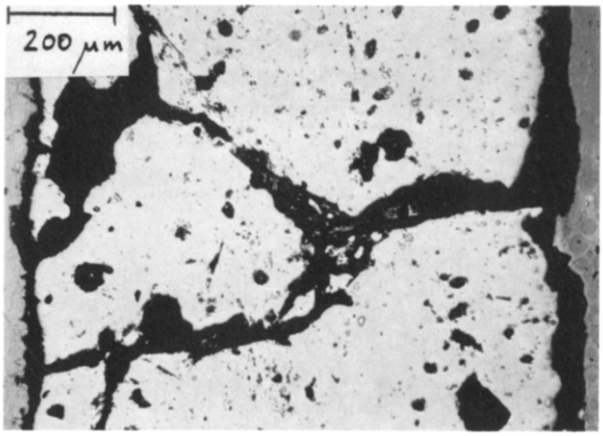

Fig. 5. Cross-section of a degraded ceramic (faradic efficiency: 50%).

Discussion

The decrease in resistance observed after switching from 0.66 to 1.3 and to 2 A/cm^2 is not due to degradation. If the current density is switched from 2 to 0.66 A/cm^2, the resistance assumes the value previously observed at 0.66 A/cm^2. The resistance steps can rather be attributed to a local increase in temperature due to the high current flowing. The faradic efficiency in the case of a good quality ceramic decreases only by a few percent on changing from 0.66 to 1.3 A/cm^2 (Fig. 4).

This small deviation does not necessarily mean that the ceramic had developed cracks; it could well reflect the development of a slight partial electronic conductivity [8]. This effect, however, need not happen in an actual Na/S cell, since the current densities applied for the present rapid life determination method were far higher than the values expected in the complete cell. The decrease in the faradic efficiency is far more rapid in the case of the poor quality ceramic (Fig. 3).

Several batches of β-Al_2O_3 tubes were tested according to the method described above and those with good life properties were identified: they had a high bulk density ($\geq$ 3.20 g/cm^3) and a homogeneous and fine-grained microstructure (grain size $<$ 10 μm). Ceramics with a lower density ($\leq$ 3.18 g/cm^3) and with a duplex structure (grain size 10 to 50 μm) showed the behaviour illustrated in Fig. 3. Since the composition of all tubes tested was the same, an effect of the microstructure on lifetime could, thus, be demonstrated.

Conclusion

It is possible to identify different grades of β-Al_2O_3 electrolytes by measuring the faradic efficiency of corresponding Na/β-Al_2O_3/Na cells. The current density applied to the cell has to exceed a critical value, about 1 to

1.5 A/cm^2 in order to reveal the long-term behaviour of the ceramics in a reasonable period of time. This method enables rapid screening of different tubes. The determination of the lifetime behaviour of the ceramic in actual Na/S cells can, thereafter, concentrate on these selected grades.

Acknowledgements

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