Self-stabilizing mount for impedance measurements of solid electrolytes-with special applications to beta-alumina ceramics

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Because of deficiencies in the common methods, a new self-stabilizing mount has been developed for the impedance measurement of solid electrolytes. The prominant feature of the new mount is that clamping of the electrodes to the sample faces is not executed by springs or spring shackle screws or by other elastic forces, but instead just by weight. Its design allows quick sample change even at elevated temperatures, and it is, at the same time, suited for accurate laboratory investigations of samples of varying configurations and for routine quality control work. The versatility of the new self-stabilizing mount is demonstrated by the application of beta-alumina ceramic tubes. The temperature dependence of the axial and radial resistivities of different tubes of a special sintering lot is investigated and compared to a Na/Na-cell test result.

1. Introduction

Impedance measurement is one of the main tools for the characterization of solid electrolytes that are to be used in an electrochemical cell. The following work has been stimulated by the need for an accurate and quick impedance measuring apparatus for the quality control of beta-alumina tubes for Na/S-cell application. The required apparatus should allow precise and controllable clamping of the electrodes and quick sample change even at elevated temperatures. It should at the same time be suited for accurate laboratory investigations of samples of varying configurations and for routine quality control often performed by semi-skilled persons.

The usual device is a temperature-controlled oven which contains the actual sample compartment. The sample holder itself generally consists of spring-loaded electrodes. As the spring force is more or less temperature dependent, clamping may be an uncontrollable, or at best a low precision way of contacting the electrodes to the sample under investigation. Another common method is the clamping of the sample into a U-shaped sample holder by the insertion of as many pads of different thicknesses between the sample faces plus electrodes and the sample holder as are necessary for a tight fit. This procedure is intricate and is no more reliable than the spring method.

Because of the deficiencies of these common methods, a new self-stabilizing mount has been developed. It has now been tested for more than a year and a half. It has caused no problems in routine work and has been adaptable to changing requirements of electrode design, sample geometry, temperature range and electrical instrumentation that have arisen from research work on beta-alumina.

2. Description of the self-stabilizing mount

The prominent feature of the new mount is that clamping of the electrodes to the sample faces is not executed by springs or spring shackle screws or by other elastic forces, but instead just by weight. The physical principle behind this idea is the same as that of toys like the 'rocking fellow' that are now popular all over the world.

The sample is measured vertically. It stands on

the lower electrode, which is fixed to a stable plat-form. The upper electrode is placed on the upper sample face. Mechanical fixing and stabilization of the sample and pressing of the electrodes to the sample faces are all ensured by weights that are hung downwards from the upper electrode with their centre of gravity being below the centre of the lower electrode. Thus, the clamping pressure of the elec-trodes against the sample faces is known exactly and is independent of the sample temperature.

In Fig. 1, such a sample holder is presented. It is one of eight identical measurement units of a pivoted multiple impedance measuring apparatus. The sample (A) shown is an off-cut of a beta-alumina ceramic tube (dimensions; 80 mm length, 25 mm outer diameter, 1.3 mm wall thickness). It is mounted for the measurement of the so-called axial resistivity at $350°$ C, which is part of the routine programme for the quality control of solid electrolyte ceramics that are being developed for the Brown Boveri beta battery. The mount will be further discussed in connection with this standard configuration.

The weights (F) that serve to press the elec-trodes to the sample faces hang on two bars that are connected to the upper electrode holder like a yoke. They have a mass of 50 g each. The upper and lower electrode-holders (D) and the corre-sponding electrodes (B+C) are each mechanically linked by screws but are electrically insulated by alumina rings (E). Each 'non'-blocking electrode consists of an electrolytically gilded steel felt (B) soaked with $NaNO_3$ salt and fixed to a platinum foil by a screwed-on ring. The platinum foil is connected to the electrical leads via a flexible flag (C). For routine purposes, two-probe measure-ments are performed using an HP 4800 A vector impedance meter at 5 kHz, 50 kHz, and 500 kHz. Resistance values are accepted if they do not differ for more than 5% for the three frequencies, other-wise the steel felt has to be reimpregnated and the sample in question has to be remeasured.

When a series of up to eight tubes has been checked, the top of the oven is lifted by the handle, one upper electrode holder after the other is raised, and the samples are removed. New tubes,
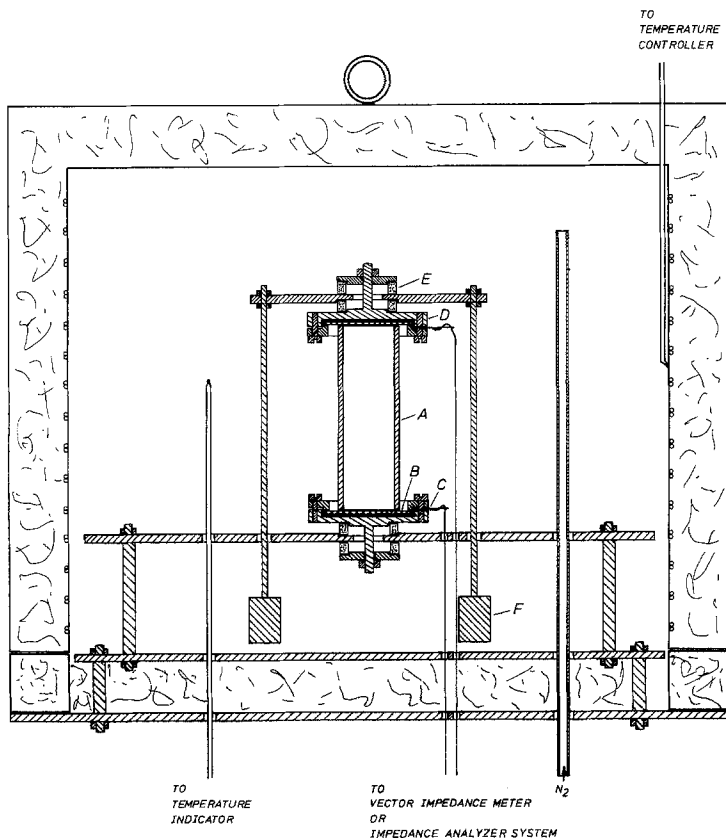

Fig. 1. Multiple impedance measuring apparatus with one of eight impedance measuring units. The self-stabilizing mount shown here serves for the measurement of the axial resistivity of a solid electrolyte ceramic tube.

freshly painted with a $NaNO_3$ salt–ethanol slurry, can be inserted in the same manner: by lifting of the upper electrode holder, placing a new tube upon the corresponding lower electrode, and lowering the upper electrode onto the upper sample face. One only has to pay attention to obtaining an upright and centred configuration. A skilled operator may change all eight tubes in less than a minute. Thus the temperature inside the reclosed oven will not have dropped below $250°$ C, which allows a quick reheating to the measuring temperature and an overall fast measuring cycle. (The routine measuring cycle can additionally be accelerated by preheating the sample tubes elsewhere, shortly before they are inserted into the impedance measuring apparatus.)

The sample holder is also suitable for non-routine work. Minor variations of sample dimensions may be coped with by proper selection of the length of the bars and the diameter of the electrodes. Sample lengths that are out of the range of the bars – either too short or too long – are no special problem; the bars are just exchanged for bars of the proper length. For special purposes, the weights can be changed as well. And the electrodes, too, can be adjusted to a selected purpose. Figure 2 shows an example of a specially designed blocking electrode system. Each electrode is simply replacing the platinum foil plus steel felt in the electrode holders of Fig. 1. The altered system is used for the measurement of radial impedances of segments of beta alumina ceramic tubes.

Furthermore, the multi-sample apparatus of Fig. 1 is obviously not restricted to eight single units, it can, of course, simply be reconstructed to comprise a larger number of mounts. On the other hand, such an enlarged multiple impedance measuring apparatus tends to become rather big and impractical for high frequency measurements. In the actual appartus used, the lead inductance of each amount is $0.7 \mu H$, and two-probe impedance measurements above 1 MHz become problematic for low resistance samples; an equivalent restriction applies for samples with resistances in the $k\Omega$-range due to a parallel capacitance of 19 pF. But the new mount can, of course, also be incorporated into a specially designed single-sample chamber with shorter electric connections.

3. A special application of the new mount. Comparison of axial and radial resistivities of beta-alumina ceramic tubes

Simplicity of sample preparation and a resistivity range which fits without any problem to standard electronic measuring equipment, are the main reasons that most investigations of the resistivity of polycrystalline solid electrolyte tubes have up to now been concerned with the axial resistivity of these tubes (i.e., the resistivity parallel to the tube axis). Principally speaking, the axial resistivity of a solid electrolyte ceramic tube is of no use for Na/S-cell application, since the current inside of the cell only flows perpendicularly to the wall of the tube i.e., in the radial direction.

Therefore, some knowledge of the correlation between axial resistivities (that are preferentially
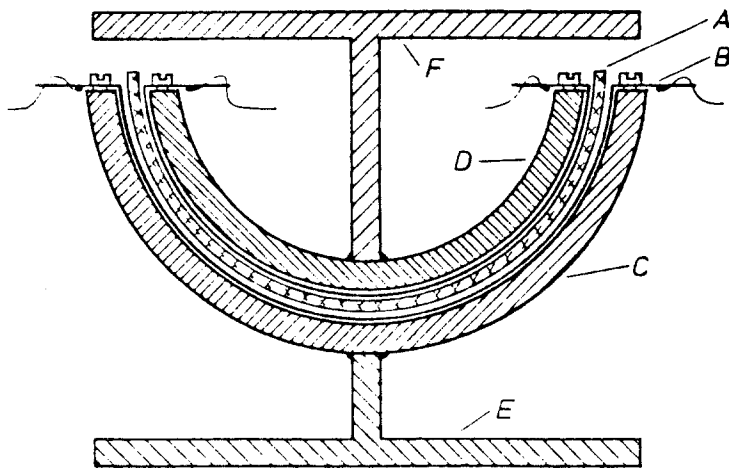

Fig. 2. Alternative electrode system that may replace the electrode system in Fig. 1. It is used for four-probe (B) radial resistivity measurements of curved ceramic tube segments (A). The cylindrically shaped lower (C) and upper (D) electrodes with the screwed on platinum foils are fixed to the electrode holders of Fig. 1 via the supporting plates (E) and (F), respectively.

measured) and radial resistivities (that are in fact
needed) is required. Consequently a comparison
was initiated for the Brown Boveri standard elec-
trolyte, comprising of the measurement of the
axial and radial resistivities of ceramic samples cut
from standard solid electrolyte tubes, and the
measurement of the d.c. resistivity of a whole tube
in a Na/Na-cell. The aim of this work was not only
to correlate the axial and radial resistivities at a
given temperature, say at 300 or 350° C, but also
to find out, whether the correlation is also tem-
perature dependent. It should be established,
whether both resistivities are controlled by the
same activation energy, at least in so far as an
Arrhenius behaviour applies. The result for one
sintering charge of beta-alumina tubes with the
BBC standard composition 8.70%Na_2O, 2.25%
MgO, balance Al_2O_3, which was used for finding
an appropriate method, will now be presented.

A Na/Na-cell serves as a standard. Above 100° C,
it is in principle the most direct way to measure
the correct resistivity, and it yields additional in-
formation about the sodium/solid electrolyte
interface. But such a cell is time-consuming to
prepare and needs some effort during operation,
and an alternative method for the measurement
of the resistivity must be available.

For the Na/Na-cell test, a complete tube is
used. Its dimensions are 21 cm in length, 25 mm
outer diameter, and a wall thickness of 1.3 mm.
An α-Al_2O_3 header is attached to the open end of
the tube to prevent surface currents that could
short-circuit the test cell. The α-Al_2O_3 header
also serves as a support, from which the tube is
hung in the sodium. The experimental arrange-
ment is shown in Fig. 3. The current direction
is chosen such that the sodium level inside the
tube is moving up and down between the fixed
positions of probes A and B, which are 20 mm
apart. This method has two advantages: firstly,
the coulombic efficiency of the solid electrolyte
tube can be controlled, and, secondly, interfacial
problems that are often connected with a long-
lasting unidirectional current flow are avoided.
The voltage drop across the ceramic tube is
measured by probes B and E. The temperature of
the cell is recorded with the aid of a Ni–NiCr
thermocouple attached to the cell wall; it is
limited to 400° C to avoid problems at the flange
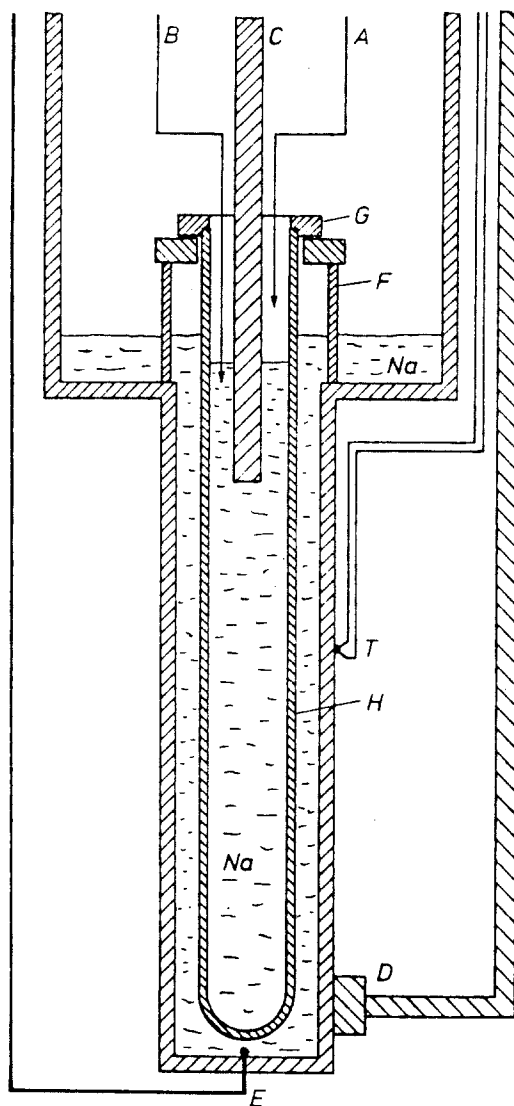of the cell.

Fig. 3. Experimental arrangement for testing beta-alumina
tubes in Na/Na-cells. Probes A and B; coulombic effic-
iency monitors (vertical distance 20 mm): probes C
and D; current collectors: probes B and E; voltage probes:
F; support and G; α-Al_2O_3-header to the beta-alumina
ceramic tube H: T; Ni–NiCr thermocouple.

The alternative resistivity determinations are
based on frequency-dependent a.c. measurements.
For these measurements, the above described
multiple impedance measuring apparatus is used
with appropriately selected electrode systems for
the evaluation of radial and axial resistivities. The
temperature of the oven can either be varied
manually or automatically in the course of a
computer-controlled measuring cycle. The imped-
ance measurements are either performed using a

lock-in technique with four contacts to each sample or a two-probe method based on a Solartron 1174 frequency response analyser and a MINC-11 computer; in the latter case, lead impedances and parallel capacitances have previously been measured separately and are digitally corrected for during each measurement. The frequency dependent values of the impedance moduli and of the phase shifts are processed to yield impedance and admittance plots. From these, the total resistance of a sample at a given temperature is evaluated by standard half-circle and straight-line methods [1, 2].

For the measurement of the axial resistivity, tube sections, 80 mm in length, are cut from five different tubes; the end faces of each section are ground, they are painted with silver-paste and each tube is fired in air at 400° C for half an hour and at 800° C for a further two hours, they are allowed to cool under flowing, dry nitrogen. Each tube section is placed in a mount that resembles the mount in Fig. 1. Only the electrode system is slightly changed. The stainless-steel felt with the salt impregnation is omitted, and contact to the silver-coated tube faces is directly established via the platinum foils. The sodium nitrate electrodes that are displayed in Fig. 1 have the disadvantage that they solidify at 308° C and are therefore inapplicable at lower temperatures; other possible 'non'-blocking electrodes are also only useful for limited temperature ranges. The fired-on silver paste works from above 350° C down to below room temperature, though it is not a pure blocking electrode and yields additional structure to the low frequency portion of impedance and admittance plots. The resistivity values at 350° C have been checked against measurements using $NaNO_3$ 'non'-blocking electrodes, showing good agreement of both results.

From other developers of beta-alumina ceramics, it is known that measurements of the radial resistivity pose special problems. For example, Rasmussen et al. [3] try to avoid the expenditure connected with Na/Na-cells by the use of molten $NaNO_2$–$NaNO_3$ eutectic cells. Duncan et al. [4] use a 10 kg load on shaped MgO supports to press their grafoil + $NaNO_3$ electrodes to the surface of a ceramic sample. It became apparent that high clamping pressures are in fact necessary when such 'non'-blocking electrodes are

used in connection with thin highly conducting samples, when we first applied $NaNO_3$–$NaNO_2$–soaked steel-felt electrodes to the electrode system of Fig. 2 in order to measure radial resistivities. We replaced the standard weights by weights with masses up to 1.5 kg without seeing the measured impedances reach meaningful values.

We therefore, prefer a different method: 30 mm long rings are cut from tubes that have been sectioned for the measurement of axial resistivity. Each ring is further subdivided into segments of different areas and the cut surfaces are ground. Then the samples are dried at 750° C for two hours and cooled to room temperature under dry nitrogen. The cold samples are transferred to a sputtering apparatus, where they are completely covered with a gold layer of approximately 1.2 μm thickness. After sputtering, the gold layer on the cut surface is thoroughly removed by polishing. The prepared samples are measured using the electrode system of Fig. 2. As already stated above, this electrode system replaces the platinum foil plus steel felt electrodes in the configuration of Fig. 1. In addition, heavier weights are used to press the electrodes onto the sample faces, in total 250 g. This alteration achieved better stability of the system, especially for smaller samples; the measured impedances did not change for loads in the range 100–900 g.

Before entering into the discussion of the relation of the radial resistivities to the axial resistivities, a strange size effect has to be reported.

Figure 4 shows the dependence of the apparent resistivities at 110, 300 and 350° C on the sizes of segments three different tubes. The size here is represented by the geometry factor $G = A/d$, where A is the sample area and d its thickness. For geometry factors less than 12 cm the apparent resistivity does not depend upon the size of the sample, but for larger samples, the apparent resistivity increases considerably, at 300 and 350° C. At lower temperatures, with increasing resistance of the samples, the size dependence vanishes.

Obviously, a sample that shows such an effect cannot be used for resistivity measurement or for the evaluation of an activation energy. The origin of the dependence of the resistivity of a given sample upon its geometry factor (or its area or its resistance) is not yet resolved. It was first thought that it might be due to insufficient thickness of
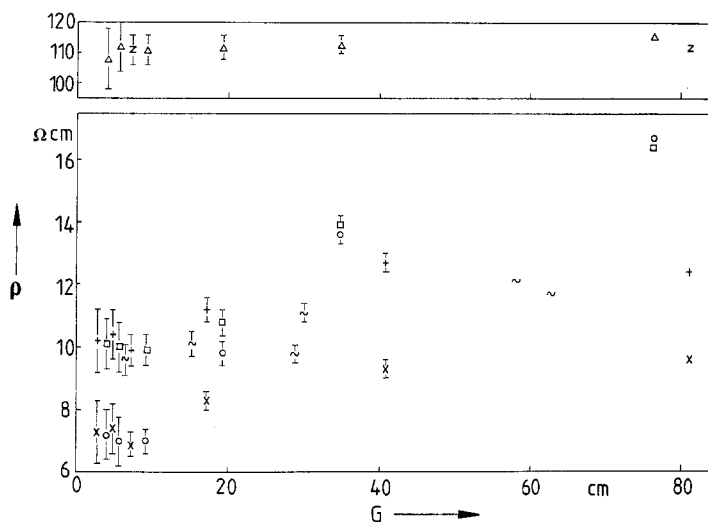
Fig. 4. Influence of the size of a sample upon its apparent radial resistivity ρ. $\rho = RG$, where R is the measured resistance and G the geometry factor. Samples 1 and 2 are taken from the present investigation, their thickness is 1.3 mm, whereas sample 3 was used for preliminary measurements. Its thickness is 1.7 mm. Sample 1: $\triangle$, 110° C; $\square$, 300° C; $\circ$, 350° C: sample 2: Z, 110° C; +, 300° C; X, 350° C: sample 3: ~, 300° C. The uncertainties of the resistivities are solely based on the uncertainties of the respective geometry factors.

the gold electrodes i.e., to the resistance of the electrode metal itself, because electrodes that are considerably thinner than 1 μm yield much higher resistivities. But thicker electrodes on samples with geometry factors larger than 40 cm that have been simulated by an additional layer of silver paint do not lead to a reduction of the apparent resistivities of these samples below those values that were previously obtained with electrodes of 1.2 μm thickness.

It must be concluded that the best choice for a thin sample for the investigation of the radial resistivity and the activation energy is a sample with a geometry factor between 5 and 12 cm, corresponding to an area of about 1 cm². For smaller samples, the uncertainty of the geometry factor increases too much.

The overall effect is certainly connected with the electrode/electrolyte interface. Comparable strange electrode effects have recently been discussed by Engstrom et al. [5] in connection with the investigation of β''-Al$_2$O$_3$ single crystals.

Now the results of the comparison of axial and radial resistivities may be discussed further. They are listed in Table 1. The values for the a.c. radial measurements are only based on samples with a geometry factor between 6 and 10 cm, which are best suited for this purpose, as has been shown above and as can be seen from the good agreement with the (radial) resistivity value obtained from the Na/Na-cell test. The ratio of the radial to axial resistivity is 1.10 for the BBC standard composition of this special sintering batch. If this ratio is

computed separately for each of the five tubes that have been cut up and investigated, the same mean value follows for all five tubes: 1.10 ± 0.05.

The activation energy E_a in Table 1 refers to the usual Arrhenius equation for ionic conduction:

$$\ln (\sigma T/\Omega^{-1}\,\mathrm{cm}^{-1}\,K) = C - E_a/RT,$$

where σ is the conductivity, T the thermodynamic temperature, and R the molar gas constant. It is based upon the temperature range from 290 to 380° C for the Na/Na-cell and upon the temperature range from 50° C to 350° C for the a.c. measurements with the multiple impedance measuring apparatus. The different methods all yield the same activation energy. This is not surprising, since the inequality of the axial and radial resistivity of ceramic tubes should only be caused by texture effects, which should have no influence on the conduction mechanism itself. But

Table 1. Resistivity of beta-alumina ceramic tubes with the BBC standard composition; comparison of the d.c. resistivity obtained from a Na/Na-cell with a.c. axial and a.c. radial resistivities obtained with the new self-stabilizing mount

Method	ρ (Ωcm)		E_a (kJ mol^{-1})
	300° C	350° C	
Na/Na-cell	10.1	6.9	26.9
a.c. radial	9.9 ± 0.3	6.8 ± 0.2	26.7 ± 0.3
a.c. axial	9.0 ± 0.4	6.2 ± 0.2	26.7 ± 0.5

it demonstrates the good applicability, versatility and reliability of the new self-stabilizing mount. This mount is of course not only useful for the investigation of beta-alumina ceramics, but may be applied to any other solid electrolyte, as well.

Acknowledgements

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