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A.c. impedance studies on sodium β-alumina tubes for use in sodium-sulphur cells

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A.c. impedance studies on sodium β-alumina tubes as used in the sodium/sulphur cell have been made at ambient temperature. It was not found possible to obtain satisfactory impedance spectra from complete tubes. However, polished annulets cut from the tubes and prepared with sputtered gold blocking electrodes were found to give reliable impedance spectra.

1. Introduction

The practical application of polycrystalline sodium β-alumina in the sodium/sulphur cell is well known and has led to many techniques being employed in the study of its basic physical properties. One such technique is that of a.c. impedance measurements from which the electrical properties of the sample may be obtained.

The theory behind a.c. impedance measurements on polycrystalline sodium β-alumina has been covered elsewhere [1]. Fig. 1 shows the theoretical a.c. impedance spectrum, plotted in the complex plane, for the cell:

blocking electrode/polycrystalline
sodium β-alumina/blocking electrode

The spectrum consists of two semi-circles arising from the bulk (C_g and R_b) and intergranular (C_{gb} and R_{gb}) regions of the sample and a vertical line derived from the double layer region of the electrode/electrolyte interface (C_{dl}). If a sodium ion conducting liquid electrolyte is incorporated between the blocking electrode and the solid β-alumina, the equivalent circuit for the cells is that shown in Fig. 2. The circuit shows two double layer capacitances arising from the blocking electrode/liquid electrolyte interface (C_{dl}) and the

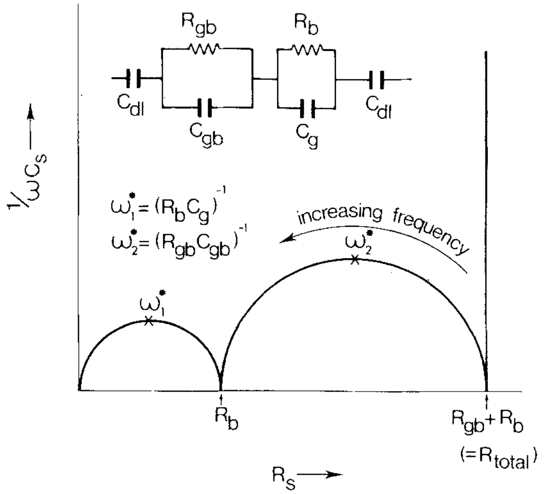

Fig. 1. The theoretical equivalent circuit and a.c. impedance spectrum for polycrystalline sodium β-alumina with blocking electrodes.

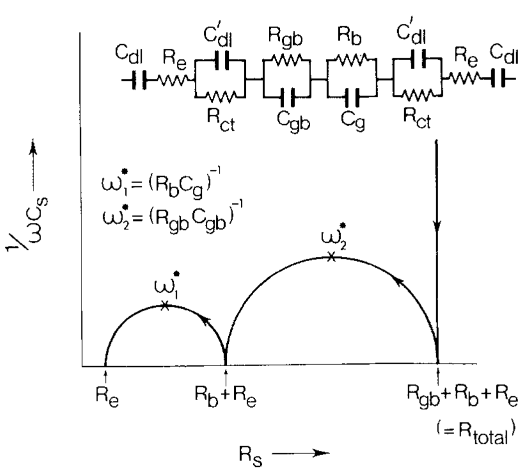

Fig. 2. The theoretical equivalent circuit and a.c. impedance spectrum for polycrystalline sodium β-alumina with a sodium ion conducting liquid electrolyte and blocking electrodes, when R_{ct} is very small.

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liquid electrolyte/sodium β-alumina interface (C'_{dl}). A series resistance (R_E) arising from the liquid electrolyte (which should be kept as small as possible) is also present. Provided the charge transfer resistance (R_{ct}) for the liquid electrolyte/sodium β-alumina interface is very small, this equivalent circuit will give rise to the complex plane a.c. impedance spectrum shown in Fig. 2. Should R_{ct} be significant, a third semi-circle arising from the parallel combination of C'_{dl} and R_{ct} will be observed in the a.c. impedance spectrum.

To date, the majority of a.c. impedance studies on sodium β-alumina have been carried out on samples prefabricated to a particular form convenient for experimental use, generally a disc. However, in the sodium/sulphur battery the sodium β-alumina is likely to be in the form of tubes. Therefore, in this present work we have explored a number of different methods for measuring the a.c. impedance of sodium β-alumina tubes. We have restricted the temperature range for our investigation to ambient temperature since at higher temperatures the part of the impedance spectrum derived from the intergranular region of the samples cannot be easily separated from that of bulk effects.

2. Experimental

A.c. impedance measurements were carried out on two types of polycrystalline sodium β-alumina samples. Type 1 was a lithium doped sample with 80–90% β''-alumina, whilst type 2, doped with both lithium and magnesium, had a composition corresponding to approximately 50% β''-alumina. Both samples were supplied in the form of tubes (non-permeable to helium) 16 cm long (closed at one end), with an outside diameter of approximately 3·2 cm and wall thickness of 0·15 cm. The ceramic tubes were utilized in two ways, measurements being made on annulets cut from the open end of the tubes with a diamond saw, and on the complete tubes themselves.

The annulets, approximately 6 mm in length, were polished with successive grades of diamond lapping compound (Hyprez spray, supplied by Engis Ltd) down to 1 μm. Studies on unpolished annulet samples were also carried out. The samples were oven dried at 200° C for 4 hours and stored under vacuum over silica gel. Two types of blocking electrodes were applied to the prepared samples, 'Aquadag' (a colloidal suspension of graphite in water, dried in an oven at 200° C for 2 hours after application to the sample), and sputtered gold (0·04 μm thick).

Three experimental arrangements were employed in the attempt to obtain a.c. impedance data from complete ceramic tubes at room temperature:

(a) Mercury blocking electrodes, with and without a thin film of an organic electrolyte, in which the outside of the tube was immersed to a depth of approximately 2·4 cm into a beaker of triply distilled mercury (the tube having previously been wetted with the organic electrolyte, if employed). Mercury was then poured into the tube to a depth equal to that of the outside. Platinum wires were used for electrical contacts.

(b) Platinum blocking electrodes with an organic electrolyte (supported on glass fibre filter paper 1 mm thick), the electrodes being attached to perspex 'tweezers' allowing the arrangement to be damped to the inside and outside walls of the tube.

(c) Platinum wire blocking electrodes with an organic electrolyte, where the platinum wires (0·535 mm diameter) were wrapped around the outside of the tube 1 cm apart, after having been dipped in the organic electrolyte.

In all cases the organic electrolyte was propylene carbonate (dried over molecular sieves) saturated at room temperature with dry sodium iodide.

A.c. impedance measurements were carried out using a Solartron 1174 Frequency Response Analyser over a frequency range of 10^6 Hz to approximately 10^2 Hz (depending upon the experimental conditions). A description of this measuring technique has been given elsewhere [2].

A study of the effect of water vapour at SVP (295 K) on the a.c. impedance data of an annulet sample (type 2) with gold sputtered blocking electrodes was carried out. The sample, contained in a perspex cell holder, was suspended over 200 ml of water in a sealed desiccator stored in a constant temperature room.

A.c. impedance measurements were also carried out on an annulet (type 1) over a temperature range 298–153 K. Cooling of the sample was achieved by passing a stream of cold nitrogen gas over the sample. A thermocouple attached to the cell was used to monitor the temperature.

3. Results and discussion

3.1. *A.c. impedance measurements on annulet samples at room temperature*

Shown in Fig. 3a is the complex a.c. impedance spectrum of an 'as cut' annulet sodium β-alumina sample (type 1) with sputtered gold blocking electrodes. A similar spectrum was obtained when 'Aquadag' was employed as blocking electrodes. It is evident that the spectrum obtained deviates from the theoretical spectrum (Fig. 1) and may be resolved into two components, part of a semi-circle overlapped by a straight line region at 45° to the Z'-axis. The deviation from the ideal 90° (to the Z'-axis) of the straight line region is indicative of surface roughness of the electrode/electrolyte interface, a topic covered more thoroughly elsewhere [3]. The semi-circle component corresponds to the a.c. impedance of the intergranular region of the polycrystalline sample.

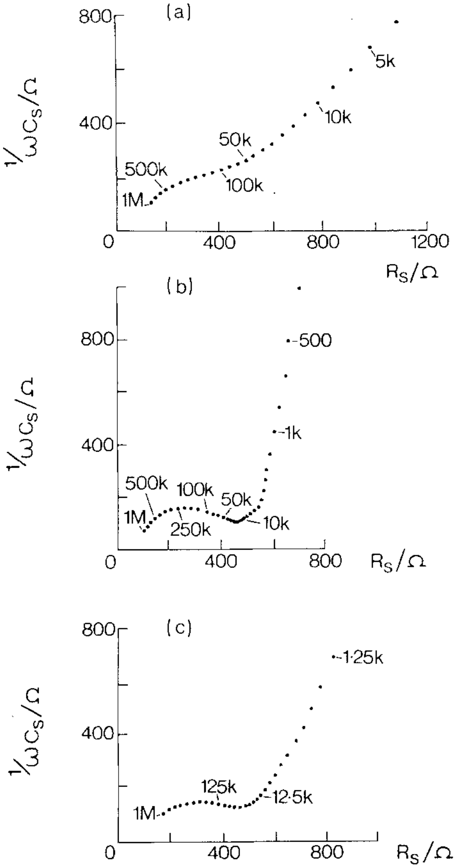

Fig. 3. The a.c. impedance spectra of annulet sodium β-alumina samples at 295 K. (a) Unpolished with sputtered gold blocking electrodes, (b) polished with sputtered gold blocking electrodes, (c) polished with 'Aquadag' blocking electrodes (frequency in Hz).

When the effect of surface roughness is reduced by polishing, the resulting spectra (Figs. 3b and c) are more clearly resolved. Fig. 3b was obtained utilizing sputtered gold electrodes, whilst Fig. 3c shows the result of employing 'Aquadag' as the blocking electrodes. Of the two spectra, Fig. 3b is the more ideal and it was noted during the experiment that the 'Aquadag' electrodes did not completely adhere to the polished surfaces of the sample. In Fig. 3b however, there is still deviation of the straight line region from the ideal 90°, the best angle obtainable being 78°. It may also be observed that there exists a shorter straight line section in the overlapping region of the semi-circle and the capacitance line. Experiments show that the length of this line decreases with increasing wall thickness of the ceramic tubes. Previous studies on sodium β-alumina in the form of flat discs (13 mm in diameter) [3], gave spectra with a capacitance line approximately 85° from the Z'-axis, with a rounded overlapping region. The authors believe therefore that the presence of the short straight line section in the overlapping region and the increased deviation from 90° of the capacitance line is due to the physical geometry of the annulet samples. These samples have a wall thickness of 1·5 mm resulting in a very high edge/surface area ratio, leading to edge effects of non-parallel conduction paths.

The 'semi-circle' region of the spectrum has its centre point below the Z'-axis, i.e. it appears to be flattened. This observation is believed to result from a distribution of relaxation times [4].

3.2. *A.c. impedance measurements on whole tubes*

The major difficulty in trying to obtain well-resolved complex a.c. impedance spectra from whole, unprepared ceramic tubes is the presence of surface roughness. In an attempt to overcome this, a liquid organic, sodium ion conducting electrolyte, propylene carbonate saturated with sodium iodide, was employed in a variety of cells, as shown below.

Hg | propylene carbonate + NaI | Na β-alumina | propylene carbonate + NaI | Hg (1)

Pt | propylene carbonate + NaI on glass fibre support | Na β-alumina | propylene carbonate + NaI on glass fibre support | Pt (2)

Pt wire | propylene carbonate + NaI | Na β-alumina | propylene carbonate + NaI | Pt wire (3)

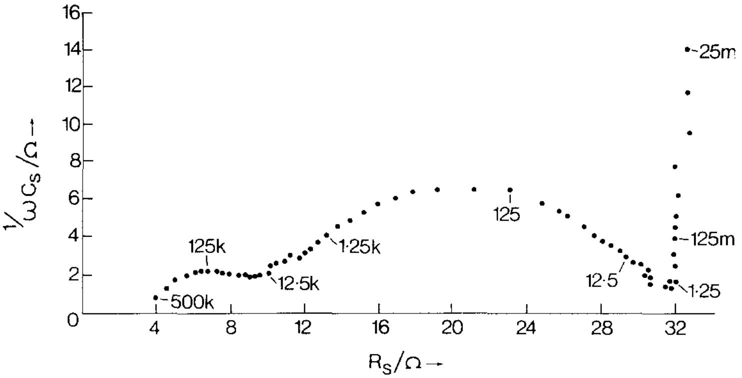

Fig. 4. The a.c. impedance spectrum for cell 1 at 295 K (frequency in Hz).

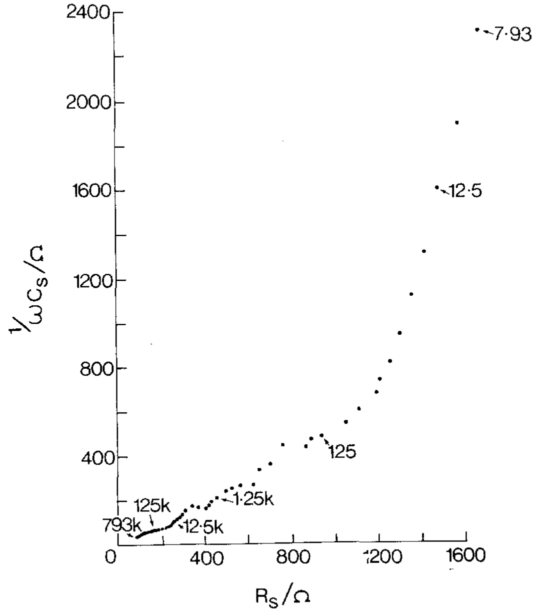

Fig. 5. The a.c. impedance spectrum for cell 2 at 295 K (frequency in Hz).

It should be noted that an attempt to use mercury electrodes without the organic electrolyte was unsuccessful due to the failure of the mercury to wet the surface of the sodium β-alumina, resulting in the presence of a thin air-film.

Complex a.c. impedance spectra for cells 1–3 are shown in Figs. 4–6, respectively. In cell 1, the contact area between the mercury and the tube was much larger than in the other cells, thus leading to smaller resistance data. It may be observed in Figs. 4 and 5 (also in the data for cell 3 although not shown in Fig. 6) that the spectra are terminated at the low frequency and with a capacitance line having an angle > 75° to the Z'-axis, indicating that the surface roughness effect has been largely overcome. However, data from all three cells show great deviation from the room temperature annulet spectra (e.g. Fig. 3b), which are believed to be correct for sodium β-alumina, by the incorporation of extra structure at the higher frequency end of the spectra. Possible reasons for

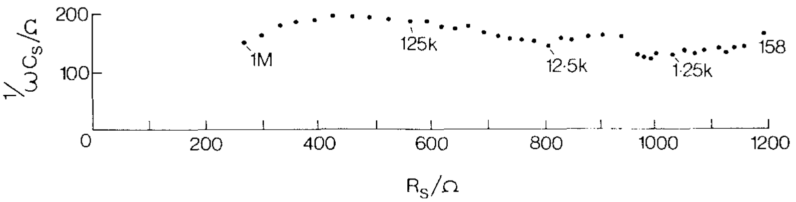

Fig. 6. The a.c. impedance spectrum for cell 3 at 295 K (frequency in Hz).

these deviations are: (a) due to the surface roughness of the ceramic, capillary action, resulting in a spreading of the liquid electrolyte, causes uneven current flows through the sample and (b) the charge transfer resistance, R_{ct} at the liquid electrolyte/sodium β-alumina interface may be measurable.

3.3. *The effect of water vapour at SVP (295 K) on the a.c. impedance spectra of annulet samples*

The effect of water on the conductivity of sodium β-alumina has been studied by Will [5] using an experimental arrangement similar to cell 2. The aim of this work is to report the effect of water vapour at SVP (295 K) on the a.c. impedance spectrum derived from an annulet sample of sodium β-alumina (type 2) employing sputtered gold as the blocking electrodes. Fig. 7a shows the short-term changes in the a.c. impedance spectrum due to the presence of water vapour, whilst Fig. 7b shows the long-term changes. It is apparent from Fig. 7a that fairly rapid changes occur in the low frequency, electrode/electrolyte interface region, of the impedance spectrum. Initial curving of the capacitance line leads to the formation of a series of overlapping semi-circles which over a long period of time combine to form a single semi-circle. In all cases, the existence of a low frequency straight line region (capacitance line) is evident. An interpretation of the observations may be as follows. Rapid penetration of the electrode/electrolyte interface by water molecules occurs, possibly lifting the electrode causing a surface roughness effect. Gradually, small pockets of 'water' film are created at the interface setting up their own finite impedances, causing overlapping semi-circles to be observed in the spectra. Over a long period of time a complete film of 'water' will exist, creating a single semi-circle. Although this thin film of liquid may be regarded as water, it will most probably be sodium hydroxide, formed by the reaction of water with sodium oxide in the β-alumina. As more sodium hydroxide is formed, the thickness of the film will increase, leading to the formation of a larger semi-circle in the spectrum. Surprisingly however, virtually no changes arising from the intergranular resistance and capacitance occur in the high frequency semi-circle, over the period of time studied.

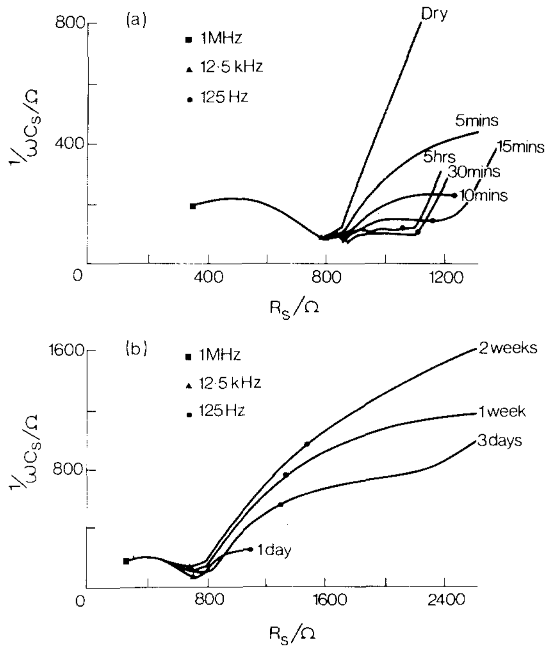

Fig. 7. The effect of water vapour at SVP (295 K) on the a.c. impedance spectrum of an annulet sodium β-alumina sample with gold blocking electrodes: (a) Short term, (b) long term.

3.4. *The effect of lowering the temperature of sodium β-alumina on its a.c. impedance spectrum*

The a.c. impedance spectra studied so far have all been the result of measurements at room temperature. These spectra have contained only half the detail shown in the theoretical spectrum of Fig. 1, the missing semi-circle being that which arises

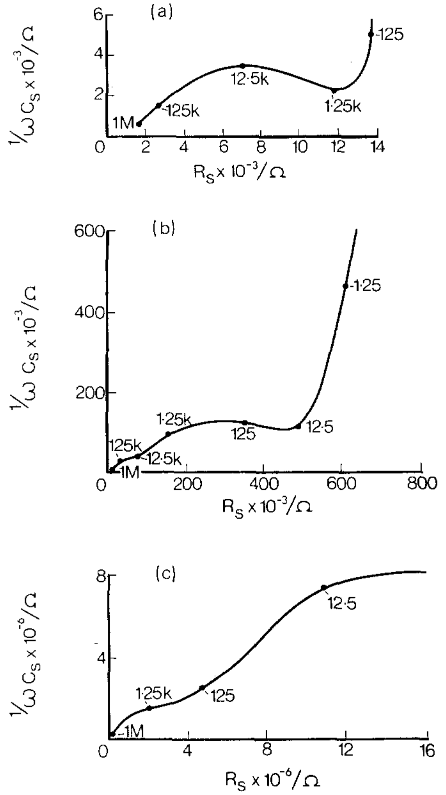

Fig. 8. The effect of temperature on the a.c. impedance spectrum of an annulet sodium β-alumina sample: (a) 231 K, (b) 185 K, (c) 153 K (frequency in Hz).

from the resistance and geometric capacitance of the (bulk) grains in the polycrystalline material. In order to observe the complete spectrum we must either: (a) increase the measuring frequency, or (b) increase the resistance of the material causing ω^*, the frequency at the peak of the semi-circle ($\omega^* = 1/RC$ where $\omega = 2\pi f$), to decrease. Of the two possibilities, the second is the most easily carried out, simply by lowering the temperature of the sample.

Fig. 8 shows the a.c. impedance spectra for an annulet sample of sodium β-alumina (type 1) with gold blocking electrodes, over a temperature range of 153–213 K. The room temperature spectrum for the sample is shown in Fig. 3b. At low temperature, the impedance spectrum may be resolved into two overlapping, flattened semi-circles, with a low frequency capacitance line overlapping with the second, intergranular, semi-circle.

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