

Graphite electrodes for conductivity measurements on beta Alumina

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Graphite was painted as an electrode material onto polycrystalline specimens of the solid electrolyte beta alumina for two-electrode measurements of electrolyte conductivity. Graphite turned out to be useful between room temperature and at least 600 °C giving frequency independent resistances in the range above, say, 20 kHz.

1. Introduction

The solid electrolyte β -Al₂O₃, a sodium poly-aluminate, exhibits high sodium ion conductivity [1]. The material is used in the form of a dense polycrystalline ceramic as electrolytic separator in the sodium-sulphur battery [2]. This type of battery has become of high technical interest as a potential power source for car and rail traction and as a large-scale battery for load levelling and peak power storage purposes.

The conductivity of β -Al₂O₃ at a given temperature depends on its composition, grain size, impurity level, etc. For screening purposes, a rapid and accurate method of conductivity determination in the range from room temperature up to about 600 °C is desirable. It is convenient to use bars or pellet-shaped specimens and to apply two electrodes to the end faces. The impedance of this arrangement can then be measured by comparison with a known combination of a resistor and a capacitor in parallel or series connection. It has become common practice (with all types of solid electrolytes) to identify the frequency-independent resistance at high frequencies with the electrolyte resistance. Recently, Armstrong *et al.* [3] have treated this method of measurement in a general manner.

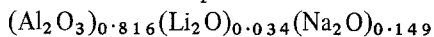
Several types of electrodes have been tried for resistivity measurements on β -Al₂O₃. The authors of [3] investigated, for example, fused NaNO₃, aqueous NaNO₃, Au, and NaHg and indicated for each the useful frequency range. Pt, Ag or

pure fused Na have been examined by other investigators [4, 5, 12]. While only noble metal electrodes cover the whole temperature range of interest, they unfortunately give frequency-dependent resistivity values below 10 kHz. Therefore, Kennedy and Sammells [4] extrapolated the resistivity to infinite frequency assuming a $\omega^{-1/2}$ dependence. As measurements by Demott and Hancock [5] have shown, a constant frequency exponent can, however, not be obtained in all cases. In this note the usefulness of graphite electrodes on polycrystalline β -Al₂O₃ specimens is discussed.

2. Experimental

2.1. Solid electrolyte

We chose the composition



described by the Ford Laboratories as having been developed for optimum conductivity and fabrication characteristics before the problem of electrolyte degradation became evident [6]. The method of preparation used by us was the same as in [6] with the exception that sintering was carried out at 1530 °C for 20 min. During sintering the pellets were embedded in commercial β -Al₂O₃ powder (Alcoa) and contained in a closed α -Al₂O₃ capsule. The surrounding gas atmosphere was dry oxygen. The final pellet diameter was 10.6 – 10.8 mm, corresponding to a linear shrinkage of 17 – 18.5%. The apparent density was 3.14 – 3.18 g cm⁻³.

Pellets having a thickness of about 3.5 mm were translucent. The polished section showed uniformity and no detectable pores.

2.2. Electrodes

The faces of the pellets were painted twice with colloidal graphite (Acheson DAG dispersion 568 Y, 1:1 diluted with isopropanol). Each coat of paint was dried at 70 °C for 10 min. The final coverage was about 0.4 mg cm⁻². The graphite layers were contacted with platinum foils under a spring pressure of about 15 kg. The arrangement was kept in a stream of purified argon during the measurements.

For comparison platinum electrodes and nitrate melt electrodes were used, and the contacting platinum foil was also used alone. Pt electrodes: two subsequent coats of paint of 8% platinum resinate (Heraeus) were applied, each was baked in dry air at 800 °C for 30 min. Nitrate electrodes: patches of glass fibre tissue were soaked with an eutectic NaNO₃-KNO₃ mixture and pressed against the pellet. All comparative measurements were carried out in a stream of dry air.

2.3. Resistivity measurements

We used two impedance bridges (Siemens Rel 3R217a1a and General Radio 1656) with external generators and tunable detectors. The temperature was varied in the range of 20–600 °C and was kept constant within ±0.5 °C. The impedance was measured as a series combination of resistance R_s and capacitance C_s in the frequency range between 300 Hz and 100 kHz. The amplitude of the alternating current was kept below RT/F (≈ 25 mV). The resistance of the current leads was determined independently and subtracted from R_s . The geometry factor f for conversion from resistance to resistivity varied between 0.37 and 0.43 cm⁻¹ for the four specimens used. Each was measured with at least two types of electrodes. In order to compare R_s values for different specimens and different electrodes, the ratio R_s/f was plotted versus frequency.

3. Results

Typical results are illustrated in Figs. 1 and 2.

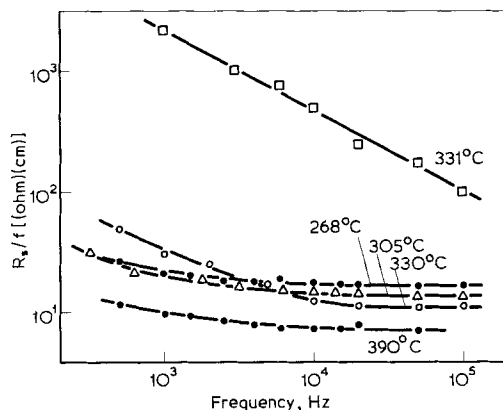


Fig. 1. Series resistance of β -Al₂O₃ at temperatures of about 300 °C, measured with several types of electrodes and corrected for specimen geometry. \circ Pt paint; \bullet graphite; \triangle nitrate melt; \square Pt foil.

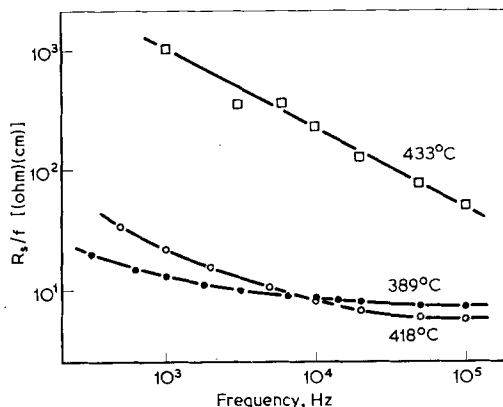


Fig. 2. Series resistance of β -Al₂O₃ at temperatures of about 400 °C, measured with several types of electrodes and corrected for specimen geometry. \circ Pt paint; \bullet graphite; \square Pt foil.

A number of additional measurements which are not included in these figures for reasons of clarity revealed the same frequency dependence. Nitrate melt electrodes and graphite electrodes yield frequency-independent values of R_s/f above about 20 kHz, platinum paint electrodes do likewise above about 50 kHz. Platinum foil electrodes do not give meaningful results.

The frequency-independent value of R_s/f was identified with the electrolyte resistivity ρ . Its temperature dependence is shown in Fig. 3. This Fig. also includes results obtained by Weber and Venero [7]. The agreement in the activation energy is excellent. We had expected our curve to be closer to curve *Ba* which corresponds to pure β'' -Al₂O₃ since our material contained the β'' -phase in excess

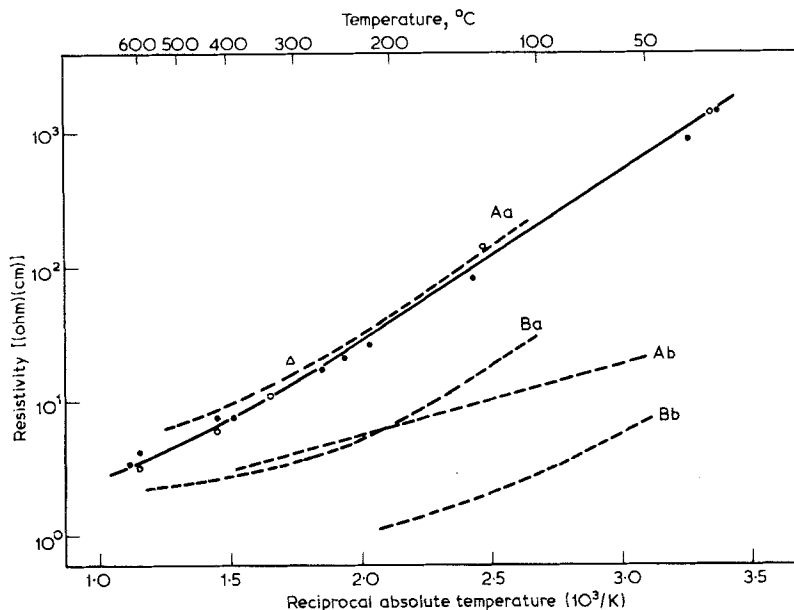


Fig. 3. Resistivity of several β - Al_2O_3 compositions. Full line (this work): \circ Pt paint; \bullet graphite; \triangle nitrate melt; Dashed lines: (A) β - Al_2O_3 ; (B) MgO-stabilized β'' - Al_2O_3 ; (a) polycrystalline; (b) single crystals [7].

of the β -phase. The difference might be due to the different stabilizing oxide (Li_2O instead of MgO).

The measured point obtained with nitrate melt electrodes shows a deviation to higher resistances. This may possibly be attributed to the fact that the resistance of the melt electrodes had been neglected when the lead resistance was subtracted. It might also be due to the uptake of K^+ from the melt because according to [8], potassium accumulates irreversibly in β - Al_2O_3 .

4. Discussion

The results indicate that graphite electrodes may be used for reliable conductivity measurements on polycrystalline β - Al_2O_3 in the frequency range between 20 and 100 kHz. They are easy to use and handle, and they offer the advantage of covering the entire temperature range from room temperature up to 600 °C and presumably even higher. Graphite calls for a gas-tight apparatus and an oxygen-free flushing gas. An arrangement of this type should be used with any electrode as β - Al_2O_3 is hygroscopic, even at elevated temperatures.

The frequency dependence of R_s/f in Figs. 1 and 2 seems to be characteristic of each type of electrode. It may be explained qualitatively by the processes taking place at the interface electrode/solid electrolyte. Mitoff and Charles [9] discussed several electrochemical mechanisms at this interface. Armstrong *et al.* [10] showed, especially for β - Al_2O_3 , that the equivalent circuit of a two-electrode arrangement need not correspond to the simple theory in all cases, but rather depends on a variety of properties such as surface roughness, wetting behaviour.

If the two-electrode arrangement is used for electrolyte conductivity measurements as in the present work, the electrodes fulfil a twofold purpose: they act as potential probes and as source and sink for the ions which are mobile in the electrolyte. The importance of the latter purpose varies according to the frequency applied.

4.1. Low frequency range

In the range up to, say, 1–10 kHz, an electrochemical transfer step forms the electric connection between electrode and electrolyte. It changes its direction with every anodic and cathodic half wave. If this step or other steps of the overall reaction are hindered (electrode polarisation), additional resistances and

capacitive components will arise in the impedance. As soon as the ohmic part becomes frequency-independent, one generally assumes that it corresponds to the undisturbed electrolyte resistance.

This assumption should be checked by additional measurements. A relatively simple check which from experience is sufficiently convincing is to examine the impedance in a wide frequency range. This has been done in the present work.

A more accurate method is to apply at some distance from the electrodes in question two additional voltage probes and to carry out four-contact d.c. or a.c. measurements. Using an arrangement of this type at the solid electrolyte stabilised ZrO_2 it has been proved that the frequency-independent value of R_p/f is indeed the electrolyte resistivity ρ [11]. This was confirmed for a variety of end electrodes, including Pt/ O_2 , Ag/ O_2 , Pt/ H_2 , Ag/ H_2 , and Ni/ H_2 . Moreover, a correlation was shown to exist between the frequency-dependent additional resistance and the electrode polarisation under d.c. conditions (i.e. electrodes of the same type actually working in a fuel cell).

At the interface $NaNO_3$ melt/ $\beta-Al_2O_3$, a simple transfer of Na^+ ions will take place. An exchange reaction of this type should only be hindered to a minute extent, and we would expect even lower additional resistances than those shown in Figs. 1 and 2. It may be argued that the frequency behaviour rather reflects the processes at the interface nitrate melt/platinum. An easy exchange of sodium ions between electrode and $\beta-Al_2O_3$ will also take place at liquid sodium metal electrodes [12]. Sodium tungsten bronze electrodes [13] are likely to behave in the same manner; their usefulness has, however, been disputed [4]. Recent measurements of the chemical diffusion coefficient of Na^+ in Na_xWO_3 by Steele [14] do indeed indicate a very low ionic mobility.

Concerning graphite electrodes, their relatively low polarisation might be attributed to a partial intercalation of sodium into the layered structure of graphite and, consequently, to an equally simple transfer between electrode and electrolyte. Graphite has also been used to measure the conductivity of doped calcium fluoride which is

a fluorine-ion-conducting solid electrolyte. The fact that a frequency-independent value is obtained in a range as low as 1 to 10 kHz [15] seems to indicate that a similar intercalation of fluorine into graphite has taken place.

4.2. High frequency range

At frequencies of 10 kHz and above the electrochemical reaction between electrode and electrolyte becomes increasingly negligible and the nature of the electrode used becomes insignificant. The mobile ions are no longer supplied by a phase transfer step, but rather remain in a space charge layer within the electrolyte. As this layer will be very thin the method of taking the frequency-independent value for the electrolyte resistance should still be correct.

This type of mechanism was probably involved in our measurements using platinum paint electrodes in the oxidizing environment. Platinum paint ensured good electric contact over the whole interface area so that a frequency-independent resistance was observed at about 50 kHz. When platinum was used in the form of a foil, however, the contact was poor and meaningful results were not obtained.

In order to decide which of the two mechanisms is involved at a given frequency and a given electrode material, further impedance measurements are envisaged.

Acknowledgement

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