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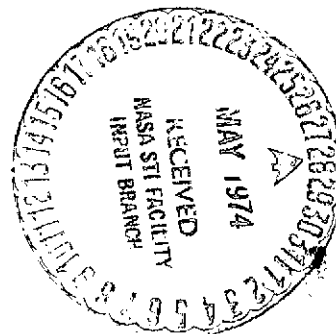
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CONDUCTIVITY OF BOULES OF SINGLE CRYSTAL SODIUM BETA-ALUMINA

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ABSTRACT

The ionic and electrochemical polarization characteristics of two boules of single crystal sodium beta-alumina ($Na_2O.8Al_2O_3$), 2 cm in diameter, were investigated over the range of 25° to 300° C using 2- and 4-probe ac and dc techniques with reversible and ion-blocking electrodes. Textural (or internal) polarization at 27° C was present only in boule 1 which cleaved easily. Interfacial polarization, using solid sodium electrodes, was present at 27° C in the 2-probe conductivities for both boules. Cleaning with liquid sodium at .300° C reduced its magnitude, but some interfacial polarization was still present in the 2-probe conductivities for boule 2 below about 140° C. Above 140° C, with liquid sodium electrodes, the 2-probe conductivities, essentially polarization-free, were given by KT = 3300 exp(-3650/RT). The conductivity of boule 2 at 180° C remained essentially constant with increasing current density up to about 140 ma/cm^2.

CONDUCTIVITY OF BOULES OF SINGLE

CRYSTAL SODIUM BETA-ALUMINA

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SUMMARY

The ionic and electrochemical polarization characteristics of two boules of single crystal sodium beta-alumina ($Na_2O \cdot 8Al_2O_3$), 2 cm in diameter, were investigated using 2- and 4-probe ac and dc techniques over the range of 25° to 300° C. Reversible electrodes of sodium and ion-blocking electrodes of platinum were used.

Textural (or internal) polarization was present only in boule 1 and was about 30 times the value expected for the polarization-free single crystal at 27° C. This polarization may reflect the physical quality of the crystal as suggested by its relative ease of cleavage.

Interfacial polarization, using solid sodium electrodes, was present in the 2-probe conductivities prior to cleaning of the surfaces of the sample by contacting with liquid sodium at 300° C. Although greatly reduced in magnitude after cleaning, interfacial polarization was still observed for the 2-probe conductivity of boule 2 below 100° C in the solid sodium region. At 25° C, at 10^4 Hz, this polarization was about twice the value of the resistivity for the polarization-free single crystal. For the liquid sodium region above about 140° C, however, the conductivity of boule 2 was independent of frequency and the temperature dependence

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could be fitted by a straight line Arrhenius equation. An extrapolation of this straight line region to 40° C was in good agreement with the 4-probe conductivity measurement at 40° C. This polarization-free conductivity for sodium beta-alumina can be expressed by $KT = 3300 \exp(-3650/RT)$ giving an activation energy of about 3.65 kcal/mole and a conductivity at 25° C of about 2.4×10^{-2} ohm^{-1}cm^{-1}. These values are in reasonable agreement with literature values.

The conductivity of boule 2 at 180° C with liquid sodium electrodes remained essentially constant with increasing current density up to about 140 ma/cm^2 suggesting that the sample was essentially ohmic in character at these conditions.

The results suggest that similar (or improved) boules of this type of sodium beta-alumina might be developed as a suitable sodium ion solid electrolyte operating at current densities of practical interest.

INTRODUCTION

Sodium beta-alumina is used as a solid electrolyte for high energy density battery systems. For example, a sodium-sulfur cell, using sodium beta-alumina as a solid electrolyte at 300° C operates at a current density of about 200-250 ma/cm^2 (ref. 1). Most of the conductivity and diffusivity measurements for sodium beta-alumina have been made on polycrystalline materials (refs. 2 and 3). The anisotropic character of sodium beta-alumina is well known (ref. 4). For example, the sodium ion diffuses more rapidly in the direction perpendicular to the C axis. As a consequence, a single crystal, if properly oriented, might be more

valuable as a sodium ion solid electrolyte because of the expected increase in conductivity. Previous measurements on sodium beta-alumina single crystals have been restricted to relatively small samples since large, synthetic boules have not been available. Conductivities have been reported for crystals occurring naturally in Monofrax-H fire brick (ref. 4), and for relatively small, single crystals obtained from the Carborundum Company (ref. 5). It was stated that the latter crystals were optically free of a second phase and contained a 16 percent excess of sodium over that expected for $Na_2O \cdot 11Al_2O_3$ (i.e., $Na_2O \cdot 9.5Al_2O_3$).

Recently, cylindrical boules of single crystal sodium beta-alumina (nominal composition of $Na_2O.8Al_2O_3$) of about 2 cm diameter were prepared and made available to NASA-Lewis Research Center by the Crystal Products Department of Union Carbide Corporation. The present study is the first made on such large, single crystal material. In general, the investigation followed our previously reported procedures for examining potentially useful candidates as solid electrolytes (refs. 6, 7, and 8). Ac conductivity measurements were made using ion-blocking electrodes (Pt) and a more detailed ac and dc conductivity evaluation was made using sodium electrodes.

EXPERIMENTAL

Two colorless boules of sodium beta-alumina, each obtained from separate single crystal growths, were investigated. Boule 2 was relatively clear but boule 1 had some opaqueness, apparently at some of the cleavage (or conduction) planes. The duplicate analyses of boule 2 were as follows: Na, 5.31 and 5.11 percent; Al, 49.15 and 49.15 percent; in agreement with

the composition $Na_2O.8Al_2O_3$. Five (5) ppm of lithium was found.

Attempts were made to cut disks from these boules in air with a diamond string saw using an organic coolant. Whereas boule 2 was cut without cleavage producing samples 2A (an irregular shaped sample) and 2B, boule 1 cleaved readily into many fragments. After removing the coolant with benzene and acetone, samples 2A, 2B, and the largest fragment of boule 1 (sample 1) were heated for 4 hours at 125° C in a vacuum oven. The dimensions of the three samples were as follows: (1) Sample 1, 0.8 cm length and 0.07 cm^2 area; (2) Sample 2A, 1.3 length and 0.08 cm^2 area; and (3) Sample 2B, 1.3 cm length and 2.0 cm diameter. The samples were then maintained under an argon atmosphere (O_2 of 1 to 5 ppm and H_2O of less than 1 ppm). The faces of sample 2B (perpendicular to the conduction plane) were smoothed gently with fine carborundum paper.

Using ion-blocking electrodes, ac conductivity measurements were made on sample 2A. Contacts of platinum were sputtered on the faces of the sample. Platinum lead wires were connected to these contacts by a conducting silver epoxy cement. The sample was suspended in a low temperature cryostat by means of a three-lead coaxial probe. The temperature was allowed to vary slowly from room temperature to -170° C. For higher temperatures, varying between room temperature and as high as 225° C, a commercial resistance-wound tube furnace was used. Capacitance and conductance measurements were made on sample 2A using a commercial automatic balancing bridge which provided frequencies of 10^3, 10^4, 10^5, and 10^6 Hz. The bridge employed a guard circuit to minimize stray capacitance

effects. Background conductivities were found to be less than 2 percent
of the signal in the worst case. The error in the conductivity of sample
2A from the measured conductance is estimated to be about 50 percent
largely due to the systematic error in determining the geometric factor
(ratio of effective length to contact area) of the irregularly shaped
sample.

Preliminary dc conductivity measurements were made along the conduc-
tion plane, on samples 1 and 2B at 27° C using solid sodium electrodes.
For sample 1, 2- and 4-probe conductances were determined with time
(after current initiation) at a constant current density of 0.2 ma/cm^2.
These conductances were calculated from the voltages developed across
the probes as measured with an oscilloscope or an electrometer. The
conductivities were then calculated using the geometric factor. For
sample 2B, 2-probe conductances were determined at a constant voltage of
1.53. The conductances were calculated from the voltages developed
across the sample and across a series standard resistor. Conductivities
were then calculated using the geometric factor.

For more complete studies, sample 2B was placed between two stain-
less steel blocks which contained the sodium electrodes and positioned
so that proper contact was maintained between the sample and the sodium
during preheating for cleaning and during subsequent conductivity measure-
ments. The apparatus is shown in figure 1. Spring tension against the
steel blocks pressing on the smoothed sample was adequate to maintain a
leak-proof seal for the liquid sodium. The surfaces of both faces of the

sample were cleaned with sodium by preheating to 300° C for about one hour.
After cleaning, 2-probe ac conductances were measured at three frequencies
(10^2, 10^3, and 10^4 Hz) over the temperature range of 35° to 300° C. For
these measurements, an ac impedance comparator bridge with standard resis-
tors and capacitors was used.

Using the same apparatus, 2-probe dc conductances were obtained for
sample 2B (at 0.1 volt) over the same temperature range. A constant cur-
rent density of about 30 microamps/cm^2 was maintained by means of a vari-
able standard resistor in series with the sample. In addition, at 180° C,
2-probe dc conductances were measured at larger current densities ranging
between 1 and 140 milliamps/cm^2. To minimize localized heating at these
higher currents, the conductances were determined within 10 seconds of
initiation of current flow.

A 4-probe dc conductivity was obtained for sample 2B at 40° C. For
this measurement, a constant current density of about 5 milliamps/cm^2 was
maintained. The conductivity was determined after about 1 minute.

RESULTS

The data are summarized in table I and figures 2, 3, 4, 5, 6, and 7.
Conductivities for sample 2A, using ion-blocking electrodes of platinum,
were obtained from ac conductance measurements and are shown in figure 2.
For 10^3 and 10^4 Hz, the conductivity data could be fitted by one straight
line over a relatively long temperature range before deviation occurred.
This deviation was due to polarization of the sodium ions at the platinum
electrodes (ref. 9). For example, deviation from the straight line

started at about -70° and -50° C for the two frequencies. At 10^5 and 10^6 Hz, however, the conductivities could be fitted essentially to one straight line over the temperature ranges investigated, i.e., -140° to 125° C for 10^6 Hz. At 25° C, the conductivity at 10^6 Hz was about 3×10^{-2} $ohm^{-1}cm^{-1}$ (table I).

Preliminary 2- and 4-probe dc conductivities, obtained for samples 1 and 2B at 27° C (using solid sodium electrodes), are shown in figure 3 where the conductivity is plotted against time after current initiation. For sample 1, the conductivity had decreased after one second to about 2/3 of its initial conductivity at 10^{-4} seconds. After one second, the decrease in conductivity became more rapid. The 4-probe conductivity, however, remained essentially constant at about 6.5×10^{-4} $ohm^{-1}cm^{-1}$. For sample 2B, the 2-probe conductivity was larger than for sample 1 at 10^{-4} seconds, decreasing then with time.

After cleaning both faces of sample 2B with liquid sodium at 300° C, 2-probe ac conductivities were obtained over the temperature range of 35° to 300° C. A 4-probe dc measurement, using solid sodium electrodes, was also made at 40° C (table I). The results for the 2- probe ac measurements at 10^4 Hz are shown in figure 4 and are compared with the 4-probe dc conductivity at 40° C.

Below about 140° C, the 2-probe ac conductivities of sample 2B decreased with decreasing frequency. This frequency dependency became smaller with increasing temperature. Above about 140° C, the 2-probe conductivities now were essentially independent of frequency. The results

for two representative temperatures (37° and 174° C) are shown in table I and in figure 5 where the ac resistivities are plotted against (frequency)$^{-1/2}$.

Two-probe dc conductivities were also measured for sample 2B between 35° and 300° C. The results for two representative temperatures (37° and 174° C) are shown in table I and in figure 6 where the resistivities are plotted against (time)$^{1/2}$. The corresponding ac resistivities at 10^2 Hz are also shown in figure 6 for comparison. Similarly to the ac measurements, the dc conductivities decreased somewhat with time at temperatures below 140° C. Above 140° C, however, the dc conductivities were essentially independent of time and were also in good agreement with the ac values.

The dc 2-probe conductivities of sample 2B were measured at 180° C, using liquid sodium electrodes, at current densities up to about 140 milliamps/cm^2. As shown in figure 7, the conductivity remained essentially constant at about 0.127 ohm^{-1}cm^{-1} over this current density range.

DISCUSSION OF RESULTS

The preliminary dc conductivity measurements, (fig. 3) with solid sodium electrodes, showed that interfacial polarization (at the electrode-electrolyte interface) was present in the 2-probe resistivities for both samples (1 and 2B) at 27° C prior to cleaning with liquid sodium. This interfacial resistances are obtained from the relation:

$$R_{Interface} = R_{2-probe} - R_{4-probe} \tag{1}$$

where R is resistance. For example, even at 10^{-4} seconds, a comparison of the 2- and 4-probe values (extrapolated to 10^{-4} seconds) for sample 1 gave an interfacial resistivity of about 710 ohm cm. This corresponds to about 1/3 of the total 2-probe resistivity. While smaller in magnitude than for sample 1, interfacial polarization was also present in sample 2B at 27° C. This is shown by a comparison of the preliminary 2-probe conductivity for sample 2B at 10^{-4} seconds (27° C) with its conductivity free of interfacial polarization. The latter value at 27° C was obtained from an extrapolation of the 4-probe and higher temperature data (dashed line) in figure 4. Since the preliminary dc resistivity for sample 2B at 10^{-4} seconds was about 140 ohm cm, its interfacial polarization was about 100 ohm cm.

Apparently, considerable textural polarization (i.e., blocking of the sodium ions within the single crystal) was also present in sample 1 as shown by a comparison of its 4-probe conductivity at 27° C with polarization-free conductivities for sample 2B. For this comparison, it is assumed that samples 1 and 2B are similar in composition. The value for the polarization-free resistivity at 27° C was obtained from the dashed line in figure 4. Since the 4-probe resistivity for sample 1 at 27° C was about 1540 ohm cm, its textural resistivity was about 1500 ohm-cm or about 40 times its polarization-free resistivity. Although other factors may contribute, the textural resistivity may reflect the physical quality of the crystal as suggested by the relative ease of cleavage. For example, sample 1 cleaved readily during cutting while sample 2 remained uncleaved.

Since sample 2B was superior to that of sample 1, as suggested by ease of cleavability and conductivity, subsequent studies were made only on boule 2. First, ac conductivity measurements were made on sample 2A using ion-blocking electrodes of platinum.

The polarization of ions, using ion-blocking electrodes, occurs with a characteristic relaxation time (τ). The onset of resonance (or attenuation of the conduction) is a function of both frequency and temperature given by the relation:

$$\omega\tau = (\epsilon_s - \epsilon_\infty) \omega/K \tag{2}$$

where ω is the angular frequency $(\sec^{-1})$; K is the conductivity $(\text{ohm}^{-1}\text{cm}^{-1})$; ϵ_s is the low frequency limit of the real part of the dielectric constant and ϵ_∞ is the high frequency limit. Resonance occurs when $\omega\tau$ is equal to unity (refs. 6, 7, 9, and 10). For sample 2A, resonance (or the onset of sodium ion polarization) occurred for 10^3 and 10^4 Hz at about -70° and -50° C. For 10^5 and 10^6 Hz, resonance was not observed at the highest temperatures investigated. The conductivity of sample 2A at 10^6 Hz, therefore, was assumed to be polarization-free and could be fitted by a straight line over the temperature range -150° to 125° C given by:

$$KT = 4000 \exp (-3790/RT) \qquad \text{ohm}^{-1}\text{cm}^{-1}\ {}^\circ K \tag{3}$$

where R is the universal gas constant.

There is reason to believe that textural imperfections in a sample, leading to internal ionic polarization, would result in shorter relaxation times than those expected for more perfect samples (refs. 7 and 9). This

would lead to a shift of the resonance region at any given frequency to a lower temperature. It should be noted that the resonance peak temperatures observed for sample 2A at 10^3 and 10^4 Hz are among the highest we have ever observed at these lower frequencies. Furthermore, no resonances were observed for 10^5 and 10^6 Hz even at 125° C. This implies a high degree of perfection in boule 2.

Cleaning the surfaces of the samples by preheating in contact with liquid sodium at 300° C is found to reduce interfacial polarization. However, even after cleaning, some interfacial polarization was still present in sample 2B up to about 140° C. This is shown by a comparison of the 2- and 4-probe conductivities, by the decrease in the ac conductivity with decreasing frequency, and by the decrease in dc conductivity with increasing time. For example, at 25° C, the interfacial resistivity at 10^4 Hz was about twice the resistivity of the polarization-free single crystal. Interfacial polarization was negligible, however, above 140° C, illustrated by the essential constancy of the conductivity with varying ac frequencies or with dc time. Furthermore, extrapolation of the 2-probe conductivities from above 140° C, where the sodium is liquid, down to 40° C was in good agreement with the 4-probe conductivity measurement at 40° C. This represents the polarization-free conductivity for single crystal sample 2B and can be expressed by:

$$KT = 3300 \exp (-3650/RT) \qquad \text{ohm}^{-1}\text{cm}^{-1} \text{ }^\circ K \qquad (4)$$

This activation energy of 3.65 kilocalories/mole and conductivity at 25° C of 2.4×10^{-2} ohm^{-1}cm^{-1} for sample 2B are in reasonable agreement with the

data obtained for sample 2A using ion-blocking electrodes where an activation energy of 3.79 kcal/mole and a conductivity of 3×10^{-2} $ohm^{-1}cm^{-1}$ was obtained. Furthermore, the values for sample 2B were in good agreement with the literature values. For example, an activation energy of 3.8 kcal/mole was reported for crystals obtained from Monofrax-H (ref. 4) and 3.79 kcal/mole for crystals obtained from the Carborundum Company (ref. 5). And, the respective conductivities were about 3.0×10^{-2} and 1.4×10^{-2} $ohm^{-1}cm^{-1}$ (table I).

The conductivity of sample 2B remains essentially constant with increasing current density at 180° C, using liquid sodium electrodes up to about 140 milliamps/cm^2. This suggests, therefore, that when liquid sodium electrodes were used, the conductivity of boule 2 (after precleaning with liquid sodium at 300° C) was essentially ohmic even up to these relatively large current densities.

CONCLUDING REMARKS

Some textural (or internal) polarization was present in single crystal sodium beta-alumina boule 1. In addition, boule 1 cleaved readily. Boule 2, however, was of better quality. It remained uncleaved when handled in an inert atmosphere. Whereas some interfacial polarization was observed when solid sodium electrodes were used, boule 2 (after precleaning) was essentially polarization-free when liquid sodium electrodes were used even at current densities of 140 ma/cm^2. Finally, the conductivities of boule 2 were in reasonable agreement with those reported previously for

crystals obtained from Monofrax-H fire brick and from Carborundum Company.

The results suggest that similar (or improved) large, synthetic boules of this type of sodium-beta-alumina might be developed as a suitable sodium ion solid electrolyte operating at current densities of practical interest. The material is potentially important for lower temperature applications. However, the polarization noted in this work with sodium as it solidifies suggests that only liquid electrodes can be used effectively. Below 100° C, sodium amalgams may be applicable for this purpose (refs. 11 and 12). The main limitation of the material in practical application as exemplified by boule 1 appears to be its relative ease of cleavage. Modifications in composition and/or improvements in the single crystal growth techniques may be beneficial for preparing boules which cleave less readily.

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12. Will, F. G., et al., Ibid., 120, 227c (1973).

TABLE I.—CONDUCTIVITIES OF SODIUM BETA-ALUMINA SINGLE CRYSTALS

Sample	Temperature, °C	Electrode	2-Probe ac Conductivity at 10^6 Hz $(ohm^{-1}cm^{-1})$	2-Probe ac Conductivity at 10^4 Hz $(ohm^{-1}cm^{-1})$	2-Probe ac Conductivity at 10^2 Hz $(ohm^{-1}cm^{-1})$	2-Probe dc Conductivity after 30 sec. $(ohm^{-1}cm^{-1})$	4-Probe dc Conductivity $(ohm^{-1}cm^{-1})$
2B	25	Solid Na	-	8.1×10^{-3}	5.4×10^{-3}	-	2.4×10^{-2}[a]
2A	25	Pt	3×10^{-2}	-	-	-	-
2B	37	Solid Na	-	1.12×10^{-2}	8.2×10^{-3}	7.2×10^{-3}	-
2B	40	Solid Na	-	-	-	-	2.8×10^{-2}
2B	174	Liquid Na	-	1.16×10^{-1}	1.15×10^{-1}	1.18×10^{-1}	-
Crystal obtained from Monofrax-H (ref.4)	25	In	3×10^{-2}[b]	-	-	-	-
Crystal obtained from Carborundum Co. (ref.5)	25	$Na_{0.4}WO_3$	-	1.4×10^{-2}	-	-	-

[a] Extrapolated to 25° C
[b] Average of 6 crystals at 5×10^5 Hz

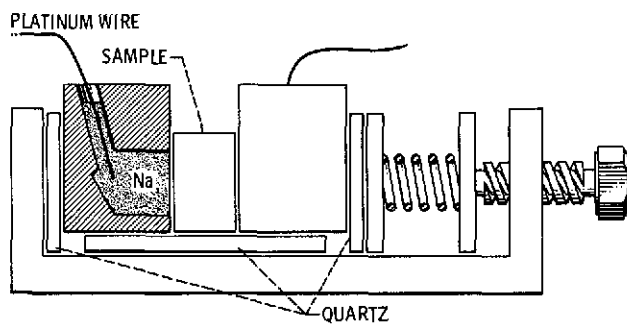Page intentionally left blank

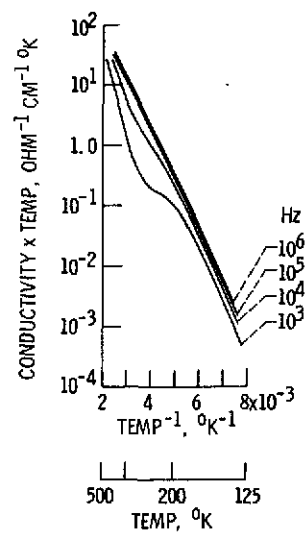Figure 1. - Stainless steel apparatus for 2-probe conductivities of sample 2B.

Figure 2. - ac Conductivity of
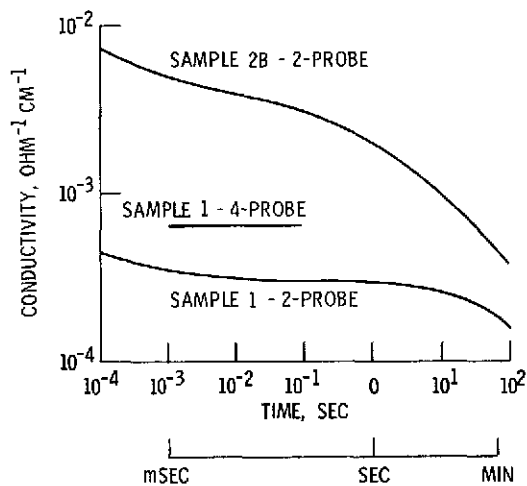sodium beta-alumina 2B.
using platinum electrodes.

Figure 3. - Preliminary dc conductivities of
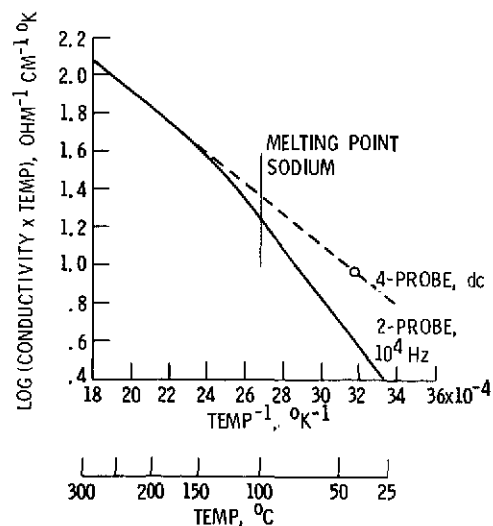sodium beta-alumina at 27° C using solid
sodium electrodes.

Figure 4. - Conductivity of sodium beta-alumina
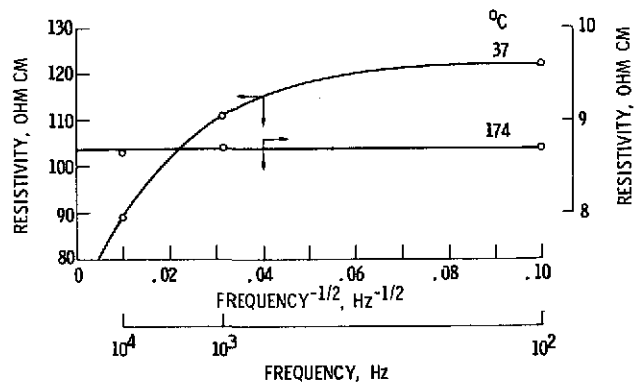sample 2B using sodium electrodes.

Figure 5. - ac Resistivity of sodium beta-alumina sample 2B using sodium electrodes.
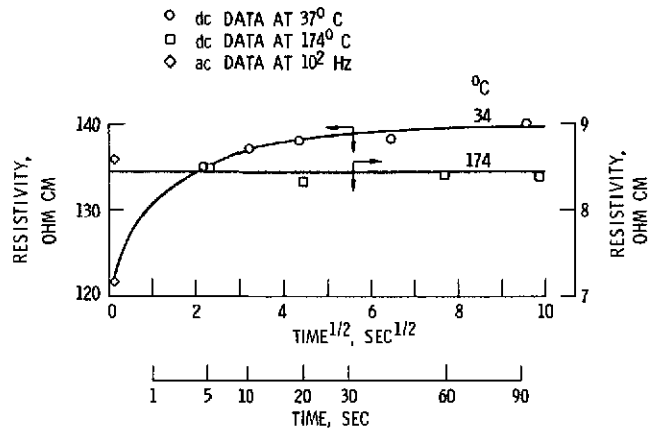

Figure 6. - dc Resistivity of sodium beta-alumina sample 2B using sodium electrodes.
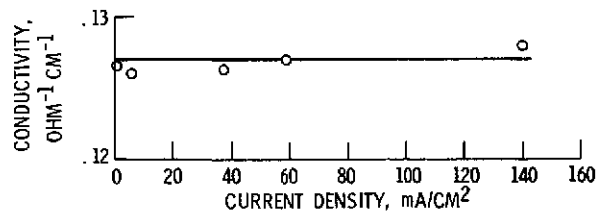

Figure 7. - dc Conductivity of sodium beta-alumina sample 2B at 180° C using liquid sodium electrodes.

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