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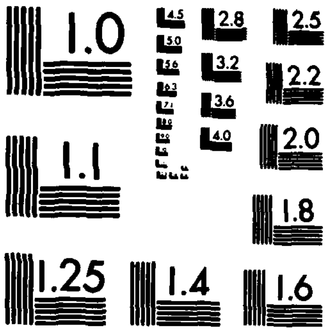

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Voltage fluctuations at electrodes to polycrystalline sodium and silver beta alumina superionic conductors have been observed in the frequency range 1-10,000 Hz. Noise voltages in excess of bulk sample Nyquist noise exist in the absence of dc current and the noise power increases with current for both two- and four-terminal specimens. The noise spectra are strongly frequency dependent and spectra varying between f^{-3} and $f^{-0.5}$ are observed. Conductivity fluctuations in four-terminal measurements indicate a f^{-2} noise spectra.

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TECHNICAL REPORT NO. 1

CONTACT NOISE IN SUPERIONIC CERAMICS

by

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of the

7th International Conference on Noise

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May, 1983

Contact Noise in Superionic Ceramics

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Voltage fluctuations at electrodes to polycrystalline sodium and silver beta alumina superionic conductors have been observed in the frequency range 1-10,000 Hz. Noise voltages in excess of bulk sample Nyquist noise exist in the absence of dc current and the noise power increases with current for both two- and four-terminal specimens. The noise spectra are strongly frequency dependent and spectra varying between f^{-3} and $f^{-0.5}$ are observed. Conductivity fluctuations in four-terminal measurements indicate a f^{-2} noise spectra.

1. INTRODUCTION

The objective of this study is to measure experimentally conductivity fluctuations in fast ionic conductors[1] and to interpret results in terms of transport mechanisms in the solid and at crystal-electrode interfaces. Electrode properties are expected to introduce experimental difficulties and it is well established that the electrochemical properties of electrical contacts to solid ionic conductors are conventionally avoided by employing high frequency ac techniques[2]. Conductivity fluctuations, on the other hand, are most easily examined under dc conditions and at low frequencies[3]. A series of experiments has been completed on the low frequency properties of contacts to sodium and silver beta alumina ceramics which give the noise characteristics of contacts alone and demonstrate that suitable electrodes for conductivity fluctuations can be devised.

2. SODIUM BETA ALUMINA

Sodium β" alumina[4] ceramic samples 1 cm x 0.5 cm x 0.2 cm shaped to provide either transverse or longitudinal potential electrodes use current contacts consisting of a sodium nitrate-sodium nitrite eutectic mixture or a sodium amalgam. Sodium β' polycrystalline "brick" specimens are less regularly shaped but can be examined in the transverse 4-probe electrode configuration. Samples are baked for several hours above 800 °C to eliminate adsorbed moisture. Noise measurements using the eutectic contacts are carried out in the temperature range 250 °C to 300 °C where the current contacts are molten. Both blocking and conducting potential-probe electrode materials have been examined.

The eutectic current contacts exhibit a non-linear current-voltage characteristic which suggests a large dc resistance at zero applied voltage compared to the sample resistance of 4 ohms. At temperatures above the melting point of the eutectic mixture, dc currents can be maintained for extended periods with no indication of polarization effects. The dc voltage at the potential probes is a linear function of current through the current electrodes and the conductivity calculated from the observed resistance and sample dimensions (5 ohm-cm) agrees with published values for sodium β" alumina[4].

The non-linear I-V characteristic is ascribed to the interface between a platinum foil used to make contact with the external circuit and the eutectic. The results indicate that an amalgam electrode is ohmic to both the Naβ" and Naβ' ceramic. The amalgam electrodes are more suitable than the eutectic, but the vapor pressure of mercury limits the experimental temperature range.

3. SILVER BETA ALUMINA

Similarly shaped silver β" alumina ceramic samples are provided with aqueous silver nitrate current electrodes since silver amalgam produces a blocking contact. Potential probes of silver paint or silver amalgam exhibit similar noise spectra and both change significantly if the sample is etched in phosphoric acid before electroding.

4. CONTACT NOISE

Noise voltages are observed with a PAR 113 ac-coupled preamplifier, a tunable electronic filter and an ac voltmeter. The system accurately measures the Nyquist noise of known resistors placed at the sample position. Initial measurements have been confined to the frequency range 1 Hz to 10,000 Hz by thermal instability at low frequencies and amplifier noise at high frequencies. Current is supplied to the samples through a noiseless 100,000 ohm series resistor to reduce current fluctuations.

Electrical noise signals observed at the potential probes reflect the quality of the electrical contact, since thermal noise of the resistance associated with a blocking contact is always present. Noise voltages observed in the absence of current are many orders of magnitude in excess of Nyquist noise of the bulk sample and are dependent upon the electrode material at the potential probes, Figure 1. The sodium eutectic mixture exhibits the lowest, and the silver paste electrodes exhibit the highest noise levels. The spectral noise density in these cases varies as f^{-3}. Additional noise accompanying the presence of dc current in the specimen shows the same frequency dependence, although the measurements are difficult because of instabilities in the current contacts.

The observed spectral shape can be accounted for by a simple model in which a distributed contact resistance is shunted by a distributed contact capacitance. This implies that the contacts exhibit 1/f noise, which is not unexpected in view of the polycrystalline nature of these specimens. The conductivity fluctuations indicated by the current dependent noise indicates that a similar model may apply to the bulk phenomenon as well. Alternatively, noise may arise from reaction processes within the sample due to the basically nonequilibrium nature of these materials. The results suggest that the Naβ" ceramic may not be in thermodynamic equilibrium, since white Nyquist is not observed.

The sodium amalgam electrode noise decreases as $f^{-1.6}$, as also shown in Figure 1. A slope of -1.5 is usually associated with diffusion phenomena, so that this noise may be ascribed to such processes, either at the contacts or in the bulk. A remarkable difference is noted in the zero current blocking contact noise spectra for Agβ" ceramic, which shows a $f^{-0.5}$ spectrum, Figure 1. A surface etch treatment in phosphoric acid results in an increased noise level and a $f^{-1.6}$ spectra for both amalgam and silver paste electrodes. A $f^{-1.6}$ spectrum is also observed for the ohmic aqueous contacts at zero current.

5. CURRENT NOISE

Stable two-terminal current noise measurements are observed using the sodium amalgam electrodes, Figure 1. The low frequency slopes are -1.6, which may be associated with ionic diffusion, while the slope of -2.1 at high frequencies suggests a Lorentzian characteristic with a time constant greater than $1/2\pi 300 = 5 \times 10^{-4}$ seconds. The current dependence is $I^{2.5}$, which is somewhat greater than the square law dependence expected for conductivity fluctuations.

Voltage fluctuations in excess of contact noise are observed at the transverse[5] potential contacts in four-terminal specimens of both Naβ" and Naβ" using amalgam electrodes. The spectral density varies approximately as f^{-2} while the current dependence is a power law for Naβ" (exponents range from 1.5 to 3.5) and increases exponentially in the case of Naβ'. This additional noise is associated with conductivity fluctuations in the bulk, including processes occurring at grain-grain contacts.

6. CONCLUSIONS

These experimental results show that the voltage fluctuations at electrical contacts to superionic conductors exhibit a rich variety of characteristics. Both conducting and blocking contacts to Naβ" ceramic have an f^{-3} spectral density, while ohmic contact current noise suggests both diffusion and Lorentzian processes. In favorable cases, suitable contacts can be devised to observe bulk conductivity fluctuations. The contact and bulk noise properties of Naβ' and Naβ" alumina appear to be quite similar and both are very different from Agβ" alumina. Fuller interpretation of the experimental results awaits additional data, and in particular extension of the measurements to very low frequencies in order to observe possible low frequency plateaus.[6].

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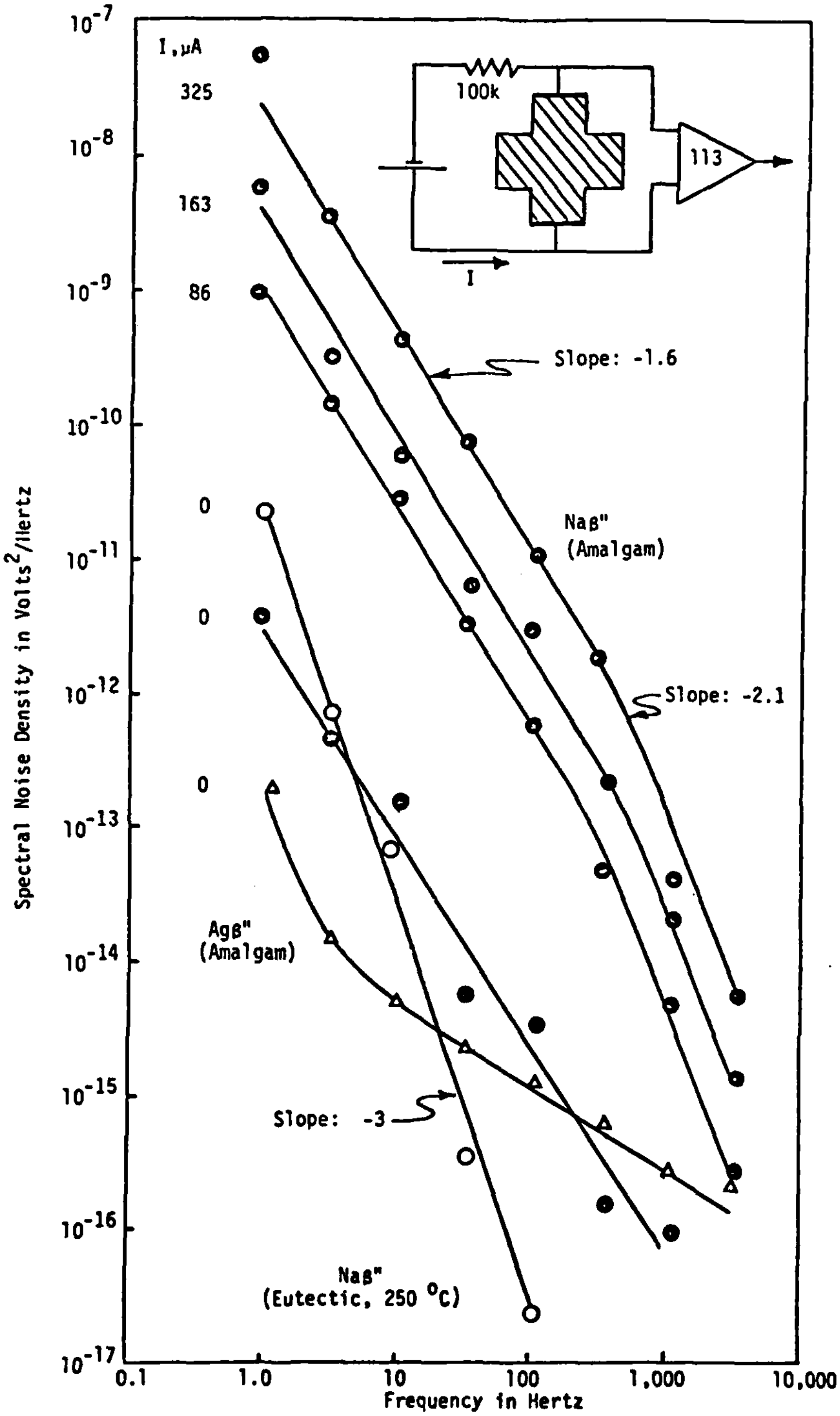

Figure 1 : Noise spectra of contacts to Naβ" and Agβ" ceramics.

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