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Current noise in mixed-ion Na/Ag Beta"alumina ceramics is characteristic of conductivity fluctuations due to diffusion noise of the mobile ions as previously observed in Na, Ag, and Pb Beta"alumina single-ion conductors and for mixed-ion Na/Ca Beta"alumina. The measured diffusion noise levels are greater for current injection of Ag ions from $AgNO_3$ solution electrodes. Room temperature conductivities calculated from thermal noise measurements are the same for both Na and Ag electrodes and show a strong mixed alkali effect. Correlation effects between the mobile ions are the same for both Na and Ag ion injection and are strongest near the 50/50 concentration ratio.

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TECHNICAL REPORT NO. 21

# CURRENT AND THERMAL NOISE IN MIXED Na/Ag β''ALUMINA

by

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Prepared for publication in
Solid State Ionics

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March 1989



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# CURRENT AND THERMAL NOISE IN MIXED Na/Ag β''ALUMINA

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## ABSTRACT

Current noise in mixed-ion Na/Ag β''alumina ceramics is characteristic of conductivity fluctuations due to diffusion noise of the mobile ions as previously observed in Na, Ag, and Pb β''alumina single-ion conductors and for mixed-ion Na/Ca β''alumina. The measured diffusion noise levels are greater for current injection of Ag ions from $AgNO_3$ solution electrodes. Room temperature conductivities calculated from thermal noise measurements are the same for both Na and Ag electrodes and show a strong mixed alkali effect. Correlation effects between the mobile ions are the same for both Na and Ag ion injection and are strongest near the 50/50 concentration ratio.

## INTRODUCTION

Conductivity fluctuations arising from diffusion noise of the mobile ions have been reported for sodium[1], silver[2], and lead[3] β''alumina and for mixed-ion conduction in Na/Ca β''alumina[4]. In all cases, the observed noise levels are much greater than predicted by the standard expression for diffusion noise[5]. This is attributed to ordering and correlation effects between the mobile ions, which have been detected in crystal structure studies[6].

Diffusion noise observed in mixed-ion Na/Ca β''alumina is much greater when Na ions are injected at sodium solution electrodes compared to when Ca ions are injected using calcium solution electrodes[4]. The results can be interpreted to indicate greater ion-ion correlations in the former case. A large effect might be anticipated in view of the four orders of magnitude smaller room temperature conductivity of Ca β''alumina and also because of the mixture of monovalent and divalent mobile ions in the structure.

The present work examines the conductivity and conductivity fluctuations in mixed-ion Na/Ag β''alumina over a range of Na/Ag compositions for comparison with the Na/Ca results. In this case the room temperature conductivities of the single ion species differ by only one order of magnitude and both ion species are singly charged. As in the previous work, the ease with which the mobile ions can be exchanged in the structure[7] makes the experiments possible.

## EXPERIMENTAL TECHNIQUE

Ceramic specimens of Na β''alumina approximately 1.1 x 1.1 x 0.1 $cm^3$ are ion exchanged by immersion in 50/50 $AgNO_3$ at 300°C for eight hours. The extent of the exchange of silver ions for sodium ions in the structure is determined from the increase in sample weight. The longest exchange time is sufficient to replace essentially all of the sodium ions with silver ions.

In order to carry out the noise measurements the corners of the square samples are cemented into the sides of four plastic test tubes containing suitable electrode solutions. Sodium β''alumina samples are provided with four electrodes consisting of a 0.5M solution of NaI in propylene carbonate and Ag β''alumina samples use four contacts of a saturated solution of $AgNO_3$ in glycerin. For mixed-ion samples diagonal corners are provided with the NaI solution and the $AgNO_3$ solution respectively. This arrangement makes it possible to measure conductivity fluctuations at transverse electrodes with the current contacts injecting either sodium or silver ions into the sample and to compare thermal (i.e., Nyquist) noise levels using either type of electrode material.

A PAR 113 preamplifier and a digital FFT analyzer are used in the noise measurements. The electrode solutions have low contact noise after ageing for several hours such that Nyquist noise corresponding to the sample resistance can be detected at frequencies above about 100 Hz. All measurements are carried out at room temperature.

## EXPERIMENTAL RESULTS

Current noise and Nyquist noise spectra for a mixed-ion specimen having a 58% Ag mobile ion composition, shown in Figure 1, are similar to those for the single-ion species conductors[1,2,3]. In the absence of current the measured noise increases at low frequencies because of residual contact noise[9] and decreases at high frequencies because of stray capacitance effects. Conductivities determined from the Nyquist noise levels at intermediate frequencies agree with literature values for Naβ''alumina ceramics. The measured Nyquist noise for the mixed-ion sample is the same for both electrode materials.

The current noise spectra increase as the square of the current and vary as $f^{-3/2}$, both characteristic of diffusion noise[5]. The observed noise is greater when current contacts inject sodium ions into the sample (e.g., transverse silver solution electrodes) compared to injection of silver ions. This is the same as found for Na/Ca mixed-ion diffusion noise[4].

The general features illustrated in Figure 1 are repeated for the full range of Na/Ag compositions, Figure 2. The conductivity goes through a minimum with increasing silver ion content, presumably because of the mixed alkali effect[10], and the relative current noise power density, $S(V,1)/V^2$, at a frequency of one Hertz and for the applied dc voltage V, goes through a corresponding maximum. Except for the 32% Ag composition sample, the current noise level is greater for current injection at the NaI solution electrodes.

## DISCUSSION

The precipitous drop in conductivity for small concentrations of silver ions and the conductivity minimum at silver-rich concentrations are in agreement with the mixed alkali effect[10,11]. The effect is explained by interaction between pairs of the different kinds of ions that leads to an increase in the activation energy for conduction, hence lowering the conductivity at a given temperature. The magnitude of the interaction increases with increasing mass difference of the two ions, which is confirmed by the deep minimum shown in Figure 2 for Na/Ag mixtures compared to a shallow[12] or missing[4] minimum in the case of Na/Ca mixtures.

The standard expression for the noise voltage spectral density, $S(V,\omega)$, due to conductivity fluctuations arising from diffusion of the current carriers is[5]

$$\frac{S(V,f,T)}{V^2} = \frac{2}{N}\left[\frac{2D}{L^2}\right]^{1/2} \omega^{-3/2} \tag{1}$$

where T is the temperature, N is the number of diffusing ions, D is the diffusion constant, L is the sample length and $\omega$ is the angular frequency. Equation (1) assumes Poisson statistics and applies above a characteristic frequency given by $2D/L^2$.

As noted previously[1,2,3] Equation (1) predicts noise levels many orders of magnitude smaller than observed, even though the other features are confirmed experimentally. The discrepancy is attributed to correlation effects between the mobile ions since the analysis leading to this result assumes independent diffusing entities.

It is helpful to compute an effective ion density from the experimental data using Equation (1). Diffusion constants for mixed-ion Na/Ag β''alumina are not available, so it is assumed that the variation in conductivity with composition given in Figure (2) is due to changes in an effective diffusion constant that can be calculated from the Einstein relation

$$D = (kT/e)\mu = (kT/ne^2)\,\sigma \tag{2}$$

where k is Boltzmann's constant, e is the electronic charge, μ is the ionic mobility, σ is the conductivity, and n is the mobile ion density, about $10^{21}cm^{-3}$ in the β''aluminas.

The results of this calculation are illustrated in Figure 3. The effective ion density passes through a minimum at intermediate concentrations and is about the same for injection of either ion species. This is in distinct contrast to the case of Na/Ca mixtures[4] in which the effective ion density decreases monotonically with increasing calcium content and is much greater in the case of calcium ion injection. Using the rather naive assumption that a small effective ion density implies large ion-ion interactions, the present results indicate that the interactions are largest for ion concentration ratios near the 50/50 composition, as would be expected from the mixed alkali effect.

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## FIGURE CAPTIONS

1. Nyquist noise and current noise of a mixed Na/Ag β''alumina ceramic at a 58% concentration of silver ions.

2. Conductivity and relative current noise power of mixed Na/Ag β''alumina as a function of silver ion content.

3. Effective ion density of mixed Na/Ag β''alumina as a function of the concentration of silver ions for both sodium ion injection and silver ion injection.

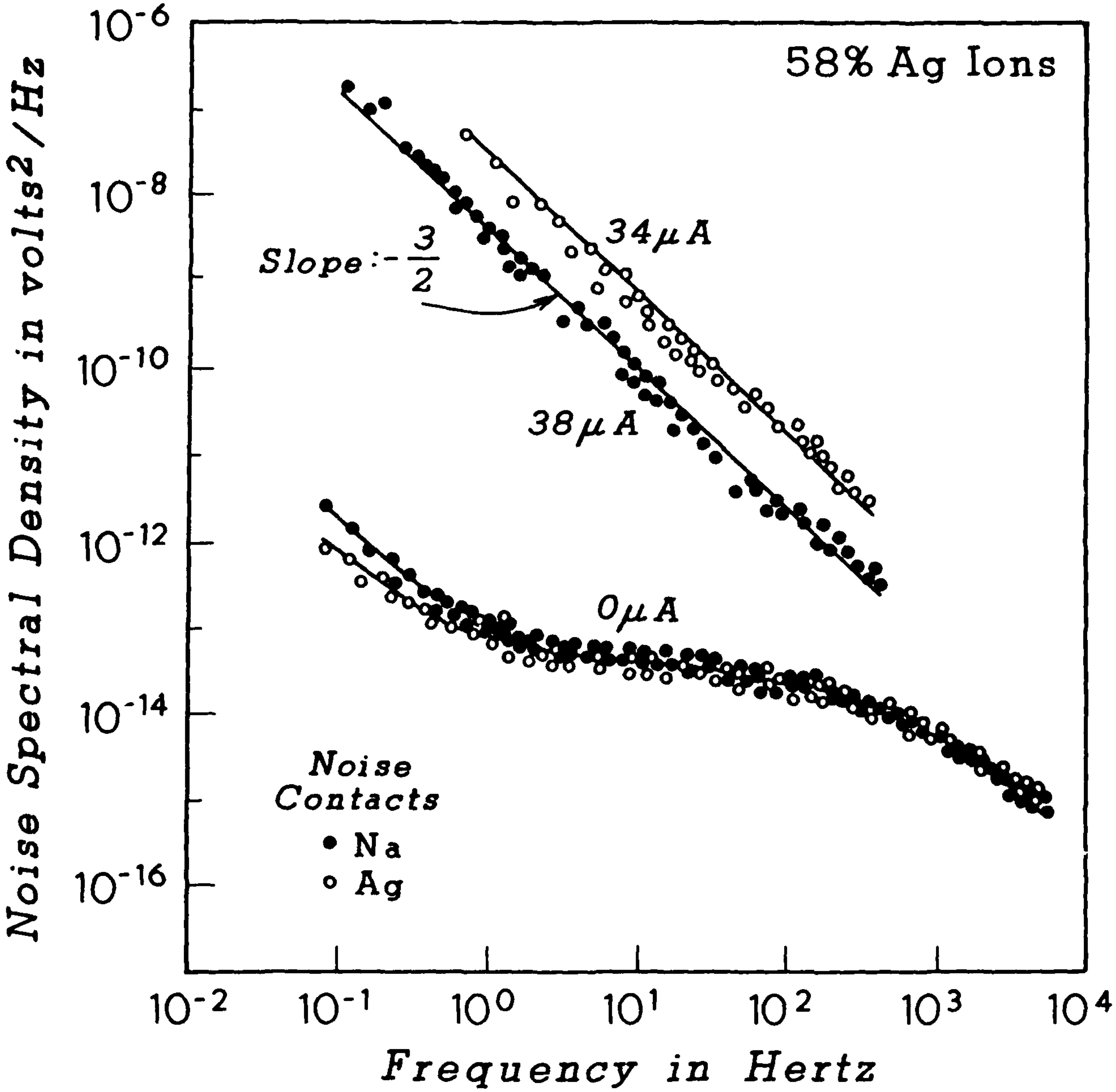
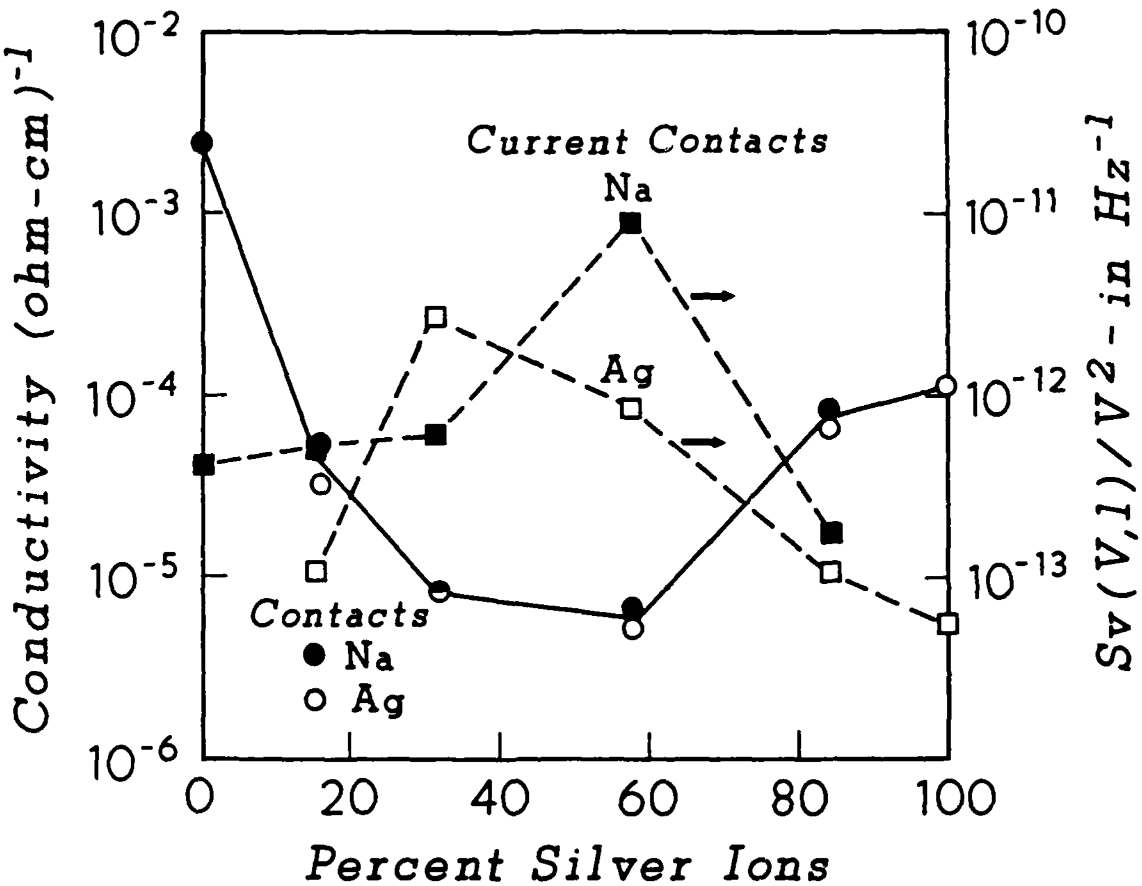

58% Ag Ions
34 μA
38 μA
0 μA
Slope: - 3/2
Noise Contacts
• Na
○ Ag
Noise Spectral Density in volts²/Hz
Frequency in Hertz
10⁻⁶
10⁻⁸
10⁻¹⁰
10⁻¹²
10⁻¹⁴
10⁻¹⁶
10⁻²
10⁻¹
10⁰
10¹
10²
10³
10⁴

Figure 1



$10^{-2}$
$10^{-3}$
$10^{-4}$
$10^{-5}$
$10^{-6}$
$10^{-10}$
$10^{-11}$
$10^{-12}$
$10^{-13}$
Conductivity (ohm-cm)$^{-1}$
$S_v(V,1)/V^2$ - in $Hz^{-1}$
Current Contacts
Na
Ag
Contacts
Na
Ag
0
20
40
60
80
100
Percent Silver Ions


Figure 2

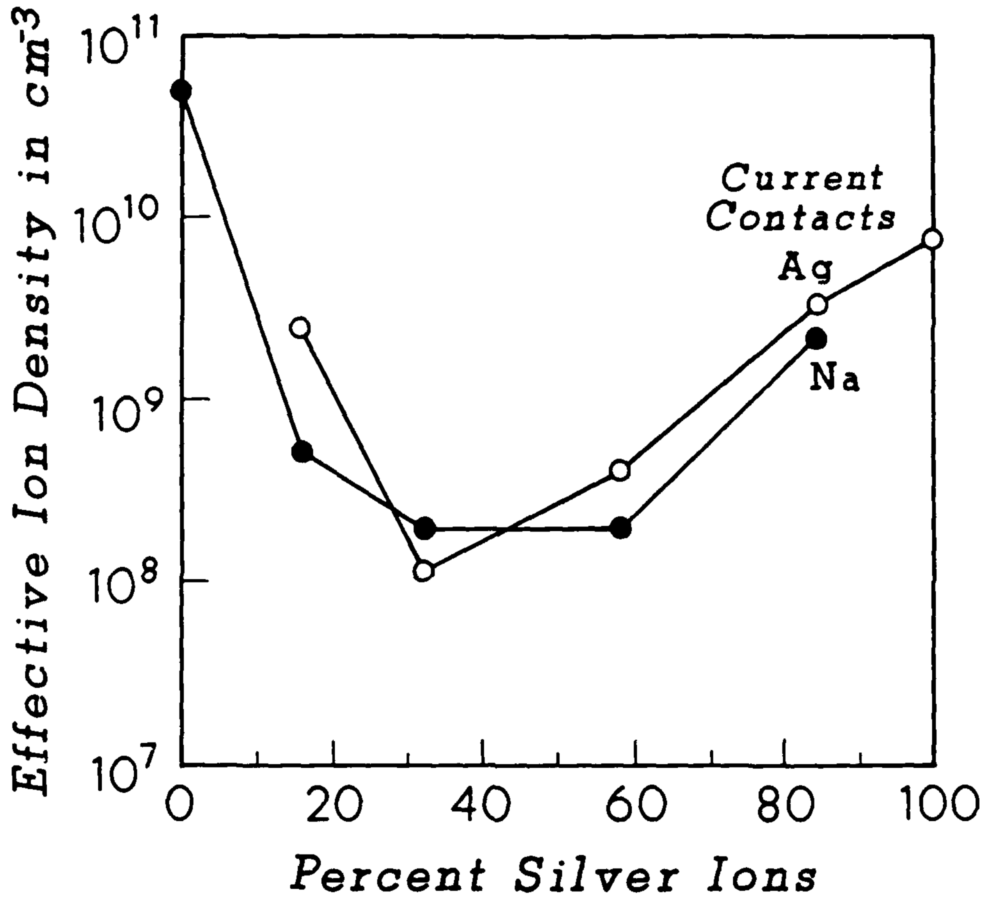

Effective Ion Density in cm$^{-3}$
$10^{11}$
$10^{10}$
$10^{9}$
$10^{8}$
$10^{7}$
0
20
40
60
80
100
Percent Silver Ions
Current Contacts
Ag
Na

Figure 3