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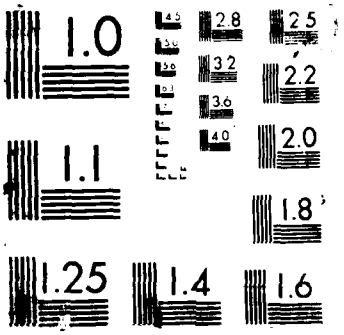
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Conductivity fluctuations observed in single crystal and ceramic sodium, silver, and beta"alumina result from diffusion noise of the mobile ions. Measured noise levels are much greater and the temperature dependence is different than that predicted by the standard expression for diffusion noise, which is attributed to correlation effects between the mobile ions. Effective mobile ion densities calculated from the observed diffusion noise levels are thermally activated and are much smaller than the known density of mobile ions in these materials. The effective ion densities are largest in the case of Na beta"alumina and smallest for Ag beta"alumina.

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DIFFUSION NOISE IN Na, Ag AND Pbβ"ALUMINAS

by

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Abstract

Conductivity fluctuations observed in single crystal and ceramic sodium, silver, and lead β"alumina result from diffusion noise of the mobile ions. Measured noise levels are much greater and the temperature dependence is different than that predicted by the standard expression for diffusion noise, which is attributed to correlation effects between the mobile ions. Effective mobile ion densities calculated from the observed diffusion noise levels are thermally activated and are much smaller than the known density of mobile ions in these materials. The effective ion densities are largest in the case of Naβ"alumina and smallest for Agβ"alumina.

INTRODUCTION

Experimental investigations of electrical fluctuations in single crystal and ceramic sodium[1], silver[2], and lead[3] β"alumina reveal a variety of effects that demonstrate similarities as well as differences between the mobile ion species. In general, these materials exhibit three distinctly different electrical noise processes. In the absence of current and at frequencies greater than about 100 Hz, Nyquist noise corresponding to the bulk sample resistance is observed. this makes it possible, for example, to determine the conductivity as a function of frequency in the absence of possible disturbing influences due to current and imperfect electrodes.

At lower frequencies, noise phenomena attributable to chemical reaction effects at the electrode/electrolyte interface can be observed[4,5]. In the particular instance of mercury or amalgam

electrodes to Naβ"alumina, a reaction characterized by a reaction rate of $6.3x10^2$ sec^{-1} at room temperature is seen. The reaction rate is dominated by diffusion of sodium ions in the electrolyte and is attributed to amalgamation at the interface. At very low frequencies, extending to less than 10^{-4} Hz, reactions related to ion exchange at the interface are observed in all samples[6]. This process usually becomes too small to measure after several hours, suggesting a reaction gone to completion.

In the presence of current, all materials exhibit bulk conductivity fluctuations characteristic of diffusion noise. This directly confirms the view that conductivity in these fast ionic conductors arises from diffusion of the mobile ions. The observed noise levels are much greater and the temperature dependence different than expected from the standard expression for diffusion noise[7]. These discrepancies are attributed to correlation effects between the mobile ions. This work compares experimental observations of diffusion noise in ceramic and single crystal sodium, silver, and lead β"alumina in an effort to understand the variation in correlation effects in the different materials.

EXPERIMENTAL TECHNIQUE

Sodium β"alumina (90.4% Al_2O_3, 8.85% Na_2O, 0.75% Li_2O) ceramic specimens[8] and single crystals[9] approximately 5x5x0.5 mm^3 are converted[10] to Agβ"alumina or Pbβ"alumina by ion exchange in molten 50% $AgNO_3/NaNO_3$ at 300°C for 8 hours or by immersion in molten $PbCl_2$ at 550°C for 24 hours under a partial pressure of oxygen. Weight change of the converted samples indicates essentially complete exchange of silver or lead ions for the mobile sodium ions. The corners of the samples are sealed into the sides of four plastic test tubes containing appropriate liquid electrode materials to provide diagonally opposing corner current contacts and transverse noise contacts. This configuration reduces the possible influence of

contact current noise on conductivity fluctuations observed at the transverse contacts[11].

Low noise, ohmic contacts are provided by 0.5M NaI propylene carbonate solution, 5M $AgNO_3$ aqueous solution, or saturated aqueous $Pb(NO_3)$ in the four test tubes. In each case, contact noise is negligible after aging for several hours. Transverse noise voltages are measured with a PAR 113 preamplifier and a digital FFT PC analyzer[12].

DIFFUSION NOISE IN β"ALUMINA

In one dimension, the standard expression for the noise voltage spectral density, S(V,f,T), of conductivity fluctuations due to diffusion is[7]

$$\frac{S(V,f,T)}{V^2} = 2\,\frac{\langle \Delta N^2 \rangle}{N^2}\left(\frac{2D}{L^2}\right)^{1/2} [1-\exp(-r)(\cos r+\sin r)]\,\omega^{-3/2}$$

$$r = L(\omega/2D)^{1/2} \qquad (1)$$

Where $\langle \Delta N^2 \rangle$ is the total variance and N the average number of diffusing ions, D is the diffusion constant, L is the sample length, and V is the voltage across the sample. At frequencies well above the characteristic frequency, $2D/L^2$ (given by r=1), the expression reduces to

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

Where Poisson statistics $\langle \Delta N^2 \rangle = N$, are assumed. Equation (2) is an example of the so-called universal -3/2 power law characteristic of diffusion[13].

Experimental results[1,2,3] are in agreement with Equations (1) and (2), except that observed noise voltages are very much greater and the temperature dependence is different than predicted, if N is determined

by the known density of mobile ions, about 10^{21}ions/cm^3. Since the standard expression is derived assuming independent diffusing entities[13], this is evidence for correlations between the mobile ions in β"alumina.

Literature reports of diffusion noise due to proton diffusion in thin niobium films[14] show good quantitative agreement with Equation (1) at proton densities equivalent to the mobile ion concentrations in the β"aluminas. This important result indicates that it is not the large mobile ion density per se that leads to deviations from Equation (1).

There are two significant differences between proton diffusion in niobium and mobile ion diffusion in β"alumina: the protons are not part of the crystal structure of the metal, and conduction electrons in the metal shield coulombic interactions between the ions. Thus protons in niobium may diffuse independently, whereas the mobile ions in the β"aluminas are coupled by host lattice interactions and by inter-ionic forces, both of which can lead to correlations between the mobile ions.

It is convenient to compare experimental results for the several samples by calculating an effective ion density using Equation (2). As illustrated in Figure 1, the results are similar but not identical. In particular, the calculated effective ion densities are much smaller in all cases than the known density of mobile ions. The effective ion densities are all thermally activated with small, but not identical, activation energies such that the densities increases with temperature. Also, single crystals have larger effective ion densities than the corresponding ceramic samples.

It is tempting to identify the calculated effective ion density with the density of ordered regions determined from x-ray and neutron crystal structure analysis[15]. A simple application of this idea does not lead to quantitative agreement with detailed x-ray structure analysis[16], however. The similarity in experimental results shown in

Figure 1 is somewhat surprising in view of the differences in mobile ion ordering in the different materials[15,16]. Sodium and lead ions exhibit ordering in two dimensions with room temperature coherence lengths of 70 A° and 200 A°, respectively, while silver ions have some three-dimensional order and a much smaller coherence length, 10 A°.

As previously reported, experimental diffusion noise measurements in silver and lead β"alumina are quite reproducible [2,3], whereas Naβ"alumina samples tend to change with time and current[1]. an example of this behavior for two Naβ"alumina ceramic samples is illustrated in Figure 2. Three successive experimental runs on each of these samples yields smaller calculated effective ion densities. This may suggest a change in ordering caused by current or by injection and removal of mobile ions from the electrodes.

Clearly, a fuller understanding of these experimental results awaits an improved analytical treatment of diffusion noise which takes into account correlation effects between the diffusing ions. The standard treatment[13] relies on classical Debye-Huckel theory to be equivalent to the assumption of charge neutrality, which may not prove to be adequate in the present circumstances.

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FIGURE CAPTIONS

Figure 1. Calculated effective mobile ion density from experimental diffusion noise measurements for single crystal and ceramic sodium silver, and lead β"alumina.

Figure 2. Effective mobile ion density for successive experiments on two Naβ"alumina ceramic samples.

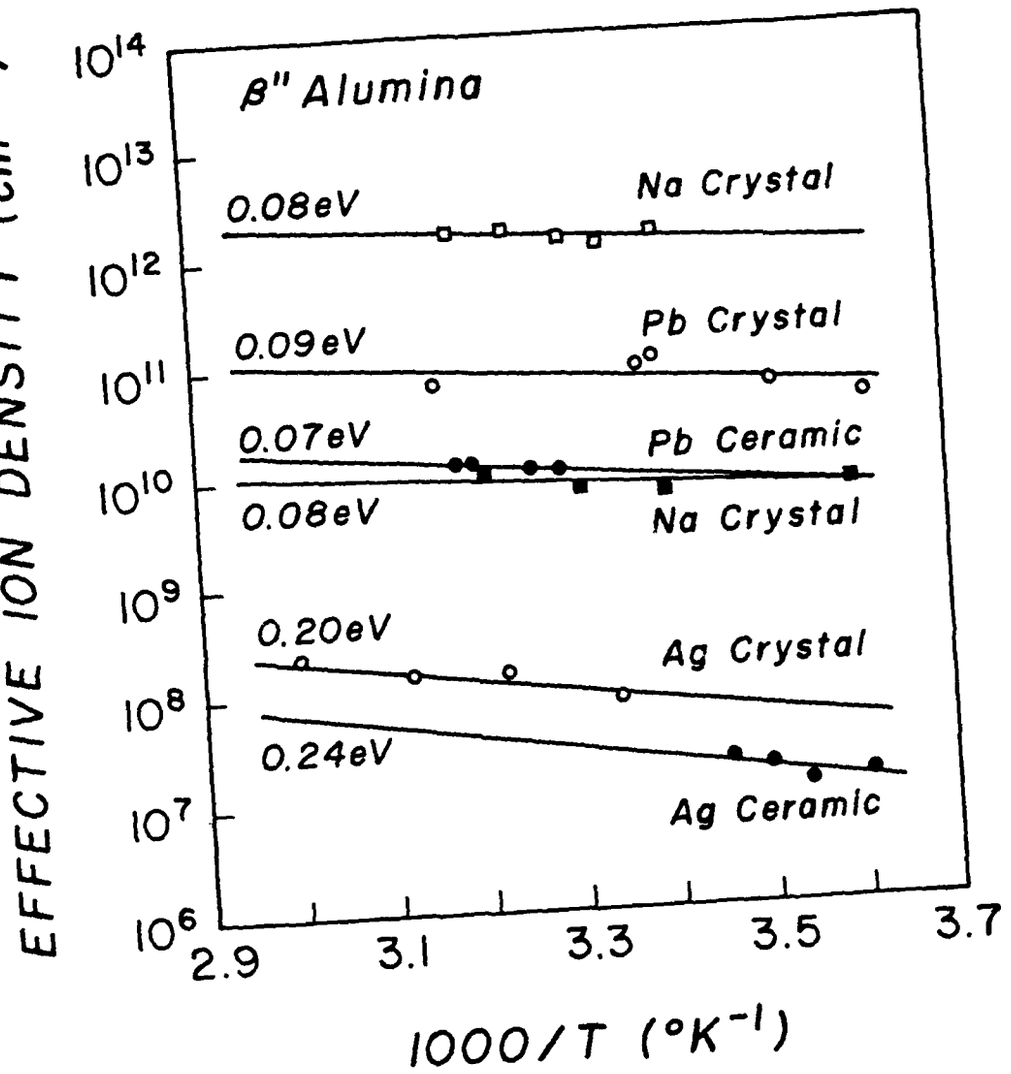
β" Alumina
Na Crystal
0.08eV
Pb Crystal
0.09eV
Pb Ceramic
0.07eV
Na Crystal
0.08eV
Ag Crystal
0.20eV
Ag Ceramic
0.24eV
EFFECTIVE ION DENSITY (cm⁻³)
10¹⁴
10¹³
10¹²
10¹¹
10¹⁰
10⁹
10⁸
10⁷
10⁶
2.9
3.1
3.3
3.5
3.7
1000/T (°K⁻¹)

Figure 1

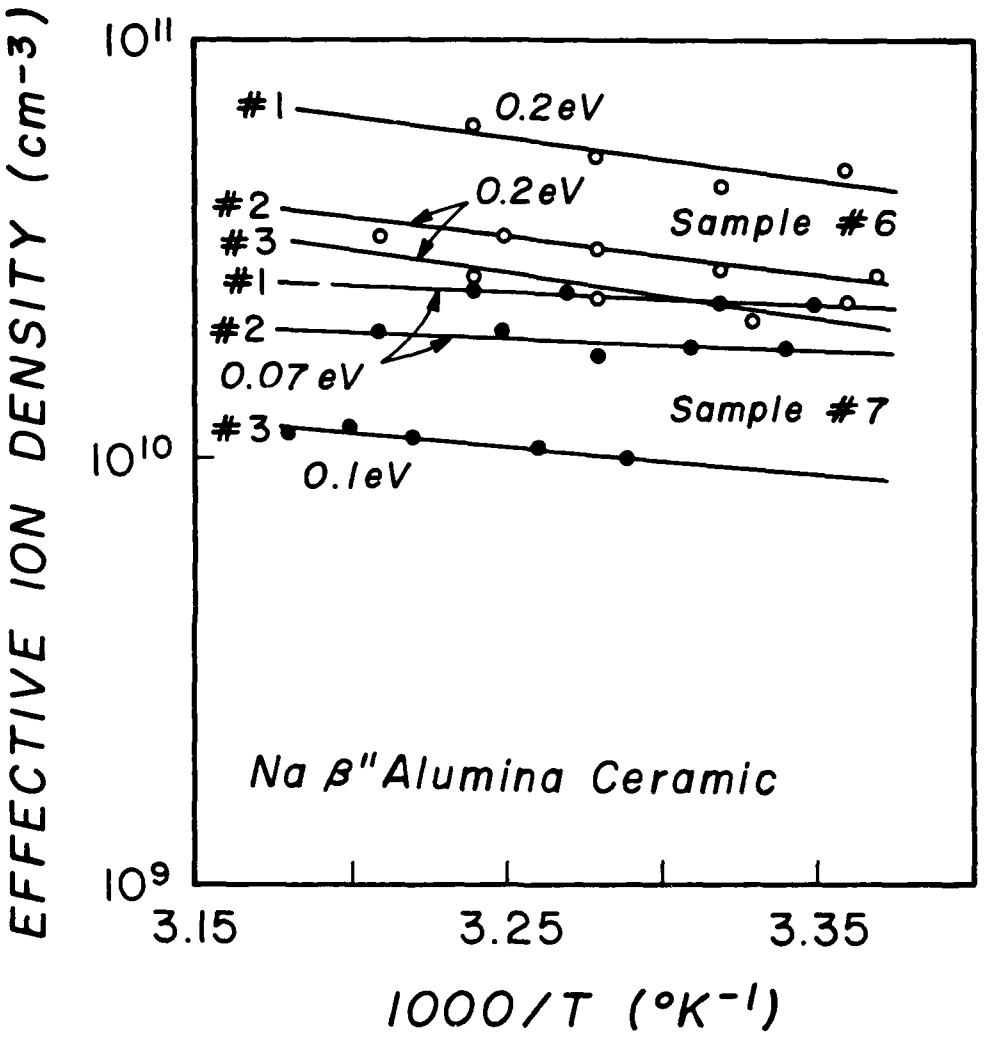
EFFECTIVE ION DENSITY (cm-3)
10^11
10^10
10^9
#1
0.2eV
#2
0.2eV
#3
Sample #6
#1
#2
0.07 eV
Sample #7
#3
0.1eV
Na β"Alumina Ceramic
3.15
3.25
3.35
1000/T (°K^-1)

Figure 2

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