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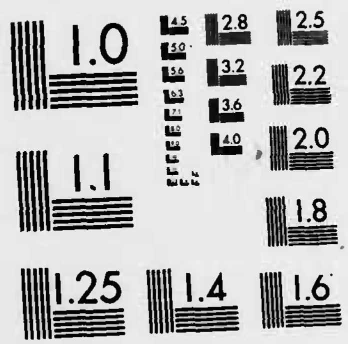

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Conductivity fluctuations in the fast ionic conductors sodium and silver β" alumina ceramic have been observed for the first time in research supported under Contract No. N00014-82-K-0603. The phenomena is not masked by contact noise effects and, indeed, contact current noise itself yields useful experimental data. Noise spectra suggesting relaxation and diffusion processes are found both in the bulk and at the electrodes. This proposal describes a continuation of

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Abstract continued

the research effort which enables a more quantitative interpretation of experimental results in terms of transport properties of the mobile ions. The approach includes study of single crystal specimens and exchange of mobile ions in both ceramic and single crystal samples, as well as extension of these new experimental techniques to other fast ionic conductors such as silver iodide and conducting polymers. One phase of the proposed effort concentrates on the study of molten sodium electrodes to sodium β'' alumina ceramics under destructive breakdown conditions.

Beta''

OFFICE OF NAVAL RESEARCH

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TECHNICAL REPORT NO. 2

ELECTRODE NOISE IN BETA ALUMINAS

by

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ELECTRODE NOISE IN BETA ALUMINAS

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ABSTRACT

Experimental contact noise spectra of Naβ" alumina and Agβ" alumina ceramics at room temperature exceed low frequency thermal noise for both blocking and ohmic electrodes. Contact noise spectra above 10^2 Hertz for ohmic electrodes of sodium amalgam and NaI in propylene carbonate agree with Nyquist noise levels determined from ac impedance measurements, and the low frequency excess noise is shown to be associated with non-equilibrium electrochemical processes. Similar effects are found for ohmic silver amalgam and aqueous $AgNO_3$ electrodes on Agβ" alumina. Greatly increased voltage fluctuations are observed to accompany current in the sample and both contact current noise and bulk granular current noise have similar characteristics. A total dc charge flow of 25 coul/cm^2 at sodium amalgam electrodes to Naβ" alumna increases both contact and current noise many orders of magnitude and can be returned to initial levels by equivalent reverse charge flow. No corresponding changes in conventional experimental measurements, e.g. current-voltage characteristics are detected.

ELECTRODE NOISE IN BETA ALUMINAS

I. Introduction

Although it has long been recognized[1] that equilibrium electrical fluctuations associated with electrochemical contacts can be used to examine electrode properties experimentally, relatively few studies have been reported. On the other hand, faradaic current noise has been commonly used to determine kinetics of electrode reactions such as crystal growth[2] and corrosion[3,4]. Conductivity fluctuations in aqueous ionic conductors have been examined with minimum influence from contact noise by suitable cell design employing large area metal electrodes; in the absence of current, white noise has been observed over the frequency range 1 to 10^4 Hertz in solutions of beryllium sulphate[5], potassium chloride[6] and copper sulphate[7]. Similar Nyquist noise spectra are also observed at glass microelectrode contacts to KCl[8].

Corresponding studies of contacts to solid ionic conductors are rare[9], although Nyquist noise has been observed at colloidal graphite and evaporated lead contacts to lead fluoride[10]. The present work examines voltage fluctuations characteristic of ohmic and blocking contacts to the superionic conductors sodium β'' alumina and silver β'' alumina ceramics[11], both in electrical equilibrium and in the presence of current. These results represent the first reports concerning contact noise of ionic conductors in which the electrical species crossing the electrode - conductor interface is ionic rather than electronic.

II. Experimental Procedure

Polycrystalline ceramic samples[12] of Naβ" alumina and Agβ" alumina approximately 1 cm x 0.5 cm x 0.4 cm are shaped to provide current contacts and transverse potential electrodes. All specimens are baked above 800 °C in air for several hours and subsequently kept dessicated to reduce absorbed moisture. The ends of the sample are sealed with epoxy cement into openings in the sides of plastic test tubes to make contact with various liquid electrode materials inside. Liquid electrodes are found to yield more reproducible noise measurements than other configurations[9], although the present technique limits the study to temperatures near ambient. Conventionally, the same electrode material is used for all contacts to the sample.

Electrical noise is observed with samples connected to the input of a conventional amplifier, tuneable filter and ac voltmeter system. Either a PAR 113 or a specially-constructed low-noise preamplifier[13] employing a FET input stage is used to assure that internal amplifier noise is independent of sample impedance. The system accurately measures Nyquist noise of resistances from 10^4 to 2×10^8 ohms over the frequency interval 10^0 to 10^5 Hertz. Current is supplied to the samples through a 10^5 ohm metallic series resistor to reduce current fluctuations.

III. Contact Noise in Sodium Alumina

Contact noise spectra in the absence of current for gallium, mercury, sodium amalgam, and NaI in propylene carbonate electrodes are shown in Figure 1. Both the gallium and mercury contacts are blocking such that the resistance between contacts exceeds 10^8 ohms. The sodium amalgam and propylene carbonate contacts are ohmic, as illustrated by the current-voltage characteristics in Figure 2.

The sodium amalgam electrodes[14,15] are prepared by dissolving approximately 5% (by weight) of Na in reagent grade mercury at room temperature. The propylene carbonate electrodes[16] are a 0.5 M solution of NaI, while the silver nitrate contacts are a 5M solution in water. Platinum foil contacts are immersed in the liquid electrodes to connect to the external circuit. These electrode materials all yield linear current-voltage curves, Figure 2, with slopes corresponding to a total sample resistance of 1.2×10^4 ohms in the case of Naβ" alumina and 2.2×10^4 ohms for the Agβ" alumina sample. Silver amalgam contacts to Agβ" alumina are also ohmic, but of high resistance, 3.9×10^6 ohms, and have a tendency to show current-voltage hysteresis. The slight voltage offset of the propylene carbonate data at zero current is enhanced by prolonged currents and may reach values as large as 0.3 volt. The effect appears to translate the curve along the voltage axis, as in Figure 2, with no apparent change in slope.

According to Figure 1, the observed high-frequency noise in the case of ohmic contacts is in rough agreement with Nyquist noise calculated from the measured dc resistance using the familiar Nyquist expression[17,18]

$$S_V = 4kTR_e$$

where S_V is the noise spectral density in volts^2/Hertz, k is Boltzmann's constant, T is the absolute temperature and R_e is the real part of the sample impedance. Conversely, the noise in the case of blocking electrodes greatly exceeds this value. No difference in the observed noise for either type of contact is found when the large area platinum foil contacts are replaced by platinum wire contacts of small area, indicating that the measured noise is characteristic of the electrode-sample interface and/or internal noise of the sample.

The electrical properties of an electrochemical contact may be modeled[1,14] by a faradaic resistance R_C in parallel with a double-layer capacitance C_C. A resistor R_b in series with this combination accounts for the bulk sample resistance, although a more accurate representation could incorporate a distribution of parallel resistance-capacitance values to account for the ceramic nature of the specimen and the effect of grain-grain contacts[16]. The real part of the impedance of the series-parallel combination is easily shown to be

$$R_e = R_b + \frac{R_C}{1 + (\omega R_C C_C)^2} \qquad (2)$$

where ω is the angular frequency. This value may be inserted into Equation (1) to calculate the predicted noise (assuming both contacts are identical) or, conversely, to determine parameters characteristic of the contacts and sample from the observed noise spectra.

Depending somewhat upon the relative values of the parameters, Equations (1) and (2) predict a low-frequency noise plateau characteristic of a resistance equal to $(R_b + R_c)$ and a high frequency noise plateau given by R_b. In the frequency interval between the plateau regions the noise spectrum decreases with a slope of -2 on a log-log plot as used in Figure 1.

Many features of the noise spectra in Figure 1 are similar to this description except that the low frequency noise in the case of ohmic contacts is very much larger than the value calculated from Equations (1) and (2) using the measured value of $(R_b + R_c)$ from the current-voltage curves in Figure 2. It is conceiveable that R_c could be so highly non-linear at very small voltages that $(R_b + R_c)$ is very large under the zero current conditions pertaining to the noise spectra in Figure 1, but this seems artificial and unlikely in view of the good linearity of the experimental current-voltage curves. Because of the blocking nature of the Ga and Hg electrodes, R_c is very large and Equation (2) could apply in these cases. However, as discussed more fully below, the low frequency noise spectra in Figure 1 exceed the noise level of the amplifier input resistance, in violation of Nyquist's law. Thus, both sets of data suggest that the specimens are not in thermodynamic equilibrium, even in the absence of any applied voltage and accompanying current.

The stochastic nature of electrochemical reactions is most easily observed under faradaic conditions. In the simple case of a single reacting species characterized by a reaction rate k, fluctuations in the current are given by[2]

$$S_i = \frac{4I^2}{N} \frac{k}{k^2 + \omega^2} \qquad (3)$$

where S_i is the noise spectral density in Amperes^2/Hertz, I is the current, and N is the total number of the reacting specie. In the absence of current but in a state of chemical non-equilibrium, a noise voltage spectrum related to Equation (3) is observable under appropriate experimental conditions. Note also that the spectral shape of Equation (3) is the same as the second term of Equation (2).

In order to explore this possibility, the noise properties of a second Naβ'' sample cut from the same larger piece as the first sample were examined. The sample was not subjected to dc current (as in current-voltage experiments) to obviate the possibility of an electrochemically-induced non-equilibrium state. The observed contact noise spectra for gallium and sodium amalgam electrodes are shown in Figure 3. The gallium electrode data is taken with two different amplifier input resistances, 2 x 10^8 ohm and 4.7 x 10^6 ohm. The observed contact noise spectrum is sensibly the same for both and is in essential agreement with the gallium noise spectrum in Figure 1. Significantly, the observed noise for both input resistances with the sample removed is much lower than the sample noise at low frequencies and is in good agreement with that calculated from Equation (1) for the known input resistances. These results prove that the gallium electrode sample is not in thermodynamic equilibrium, since the Nyquist noise of two resistances in parallel must be smaller than either one alone. The excess noise is attributed to chemical reactions at the gallium-sample interface.

The much lower noise of the sodium amalgam electrodes precludes a similar experiment in this case. Rather, the noise spectra is observed initially, after four hours, and after 48 hours. As shown in Figure 3, the low frequency noise related to Equation (3) is much reduced, suggesting a chemical reaction gone to completion. Furthermore, the observed noise is in reasonable agreement with Nyquist noise calculated from ac impedance measurements. The overall noise level is increased after 48 hours, suggesting additional chemical effects. If the high frequency noise data are assumed to indicate the bulk resistivity of the ceramic, a value of 4×10^2 ohm-cm, consistant with literature values[19] is obtained.

Similar ageing phenomena are seen with propylene carbonate contacts. The dc sample resistance is increased by a factor of five after several hours and the contact noise level increases correspondingly. The low-frequency noise of the sample with sodium amalgam electrodes subsequently applied is observed to exceed the Nyquist noise of a 10^5 ohm amplifier input resistance and the high frequency noise plateau decreases significantly from 10^2 to 10^4 Hertz. This suggests a distributed resistance-capacitance network associated with grain-grain contacts as seen in ac impedance measurements[16] and that electrode material has penetrated the sample as a result of chemical or electrochemical driving forces.

IV. Contact Noise in Silver Alumina

Related contact noise spectra are observed in Agβ" alumina ceramics, as shown in Figure 4. The slope of the low-frequency portion changes in both cases from -2 corresponding to Equation (3) to -1 after dc current in the sample sufficient to obtain current-voltage characteristics. Here again, electrochemical effects are indicated, which is confirmed by the fact that the low-frequency noise is much greater than Nyquist noise corresponding to the measured dc sample resistance. The change in slope can be accounted for by the conventional explanation[18] for 1/f noise in terms of a distribution of relaxation rates in Equation (3). Also, there is no observable change in current-voltage characteristics equivalent to the differences in the noise spectra.

All of the noise spectra in Figure 4 converge at high frequencies, suggesting a noise level associated with the sample bulk resistance. This value is somewhat below the measured dc resistance for the aqueous sodium nitrate electrodes, which is consistant with a small contact resistance. The room temperature resistivity calculated from sample dimensions is 2.9 x 10^3 ohm cm, which appears to be in agreement with literature values[20].

V. Current Noise

Very significantly increased voltage noise levels are observed accompanying current in the specimen, as illustrated in Figure 5 for a Naβ'' alumina specimen. Essentially identical results are found for Agβ'' alumina. It is noteworthy that the spectra show a slope of -2, in agreement with Equation (3) and that both longitudinal and transverse noise spectra are similar. Since transverse noise can be associated with bulk conductivity fluctuations[21], the data suggest that bulk and contact noise effects are similar. This is consistant with the understanding that bulk conductivity in ceramic specimens is dominated by the resistance of grain-grain contacts[16]. Note also that the zero current noise spectra converge at low frequencies where chemical reaction effects at the contacts dominate, and are different at high frequencies corresponding to the difference in the bulk resistance associated with the geometry of the sample.

Voltage noises observed at both the transverse and longitudinal contacts are porportional to the square of the dc current, as expected for conductivity fluctuations or electrochemical noise described by Equation (3). Transverse noise voltage levels are independent of the value of the series resistance from 10^3 ohms to 10^5 ohms (sample resistance, 10^4 ohms), which is usually sufficient to assure constant-current conditions[22], and ascribe transverse noise to conductivity fluctuations, but bulk electrochemical noise at grain-grain contacts would exhibit similar behavior. Present experimental results are not sufficient to choose between the two explanations. Alternatively, it may be that electrochemical noise is the predominent source of bulk conductivity fluctuations in these ceramic specimens.

Transverse noise using propylene carbonate electrodes is lower than that for sodium amalgam contacts. Presumably this can be ascribed to the penetration of contact material interior to the specimen as noted earlier, and may favor an electrochemical noise explanation for bulk noise.

The sensitivity of experimental contact and current noise spectra to electrochemical effects is dramatically illustrated by Figure 6 in the case of Naβ" alumna with sodium amalgam electrodes. The initial spectrum at zero current is similar to that observed in other specimens. After dc current of 2.5 ma x 30 min = 4.5 coulomb in the sample, both contact and current noise levels are increased dramatically. The current noise spectrum is orders of magnitude greater than before dc current (compare Figure 5) and exhibits a slope of -1 in contrast to -2 in Figure 5. Similarly, the zero current noise level is significantly increased and suggests a minimum reaction rate of approximately 10^3 sec^{-1}, according to Equation (3). Here again the slope of -1 beyond the turnover frequency can be ascribed to a distribution of reaction rates.

Significantly, the specimen can be returned to essentially the starting condition by a reverse current equivalent to the initial charge flow, as also illustrated in Figure 6 for zero current. Of particular significance is the fact that experimental current-voltage characteristics are unchanged by charge flow corresponding to the conditions of Figure 6. This points up the extreme sensitivity of contact noise measurements to electrode conditions compared to conventional experimental techniques.

VI. Discussion

These experimental results clearly demonstrate that ohmic, low resistance electrodes to sodium and silver β'' alumina exhibit low contact noise such that Nyquist noise of the sample can be observed. Low frequency contact noise of both ohmic and blocking electrodes is much in excess of Nyquist noise and is attributed to non-equilibrium chemical effects. Measured noise voltages are dramatically increased by current in the sample even in the absence of changes in other experimental data, e.g., current-voltage characteristics. It appears from this that current noise measurements offer an unusually sensitive experimental technique for study of electrode effects.

The shape of experimental current noise spectra (slope of -2) suggests relatively simple electrochemical processes at both the electrodes and grain-grain contacts in favorable cases. It is unfortunate that the present experimental apparatus does not extend the measurements to lower frequencies in order to detect the anticipated low-frequency plateau suggested by Equation (3) and thus permit a more quantitative interpretation which might establish differences or similarities between granular processes compared to electrode effects. Extension of the study to very low frequencies using digital techniques is currently beginning.

Additionally, experimental measurements at higher temperatures may raise characteristic turnover frequencies to the present experimental range, if the electrochemical processes are thermally activated. This is most easily accomplished using molten sodium electrodes in the case of Naβ'' alumina, which may also prove to be chemically simpler than electrode materials examined to date. Furthermore, molten sodium electrodes are of considerable practical interest in connection with device applications of Naβ'' ceramics.

Clearly, grain-grain contact effects can best be established by comparing these experimental results with contact and current noise observed in single crystal samples. Such studies are contemplated after the low-frequency and high-temperature ranges of the experimental apparatus are extended, as discussed above.

VII. Acknowledgments

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FIGURE CAPTIONS

1. Contact noise spectra for blocking and ohmic contacts to Naβ" alumina ceramic. The gallium (Ga) and Mercury (Hg) electrodes are blocking while the sodium amalgam (A) and NaI in propylene carbonate (P) are ohmic.

2. Current-voltage characteristics of Naβ" alumina (open circles) and Agβ" alumina (solid circles) ceramics using sodium amalgam (A), NaI in propylene carbonate (P), and aqueous $AgNO_3$ electrodes.

3. Contact noise spectra for gallium and sodium amalgam electrodes to a second Naβ" alumina ceramic sample. The dashed curves represent the observed Nyquist noise of amplifier input resistances alone and the dot-dash curve is the sample Nyquist noise calculated from ac impedance measurements.

4. Contact noise spectra for silver amalgam (solid circles) and aqueous silver nitrate (open circles) electrodes to Agβ" alumina ceramic before and after dc current in the sample. The dc Nyquist level refers to the silver nitrate electrodes.

5. Current noise spectra for Naβ" alumina ceramic with sodium amalgam electrodes.

6. The effect of dc current on the contact and current noise spectra of Naβ" alumina ceramic with sodium amalgam electrodes.

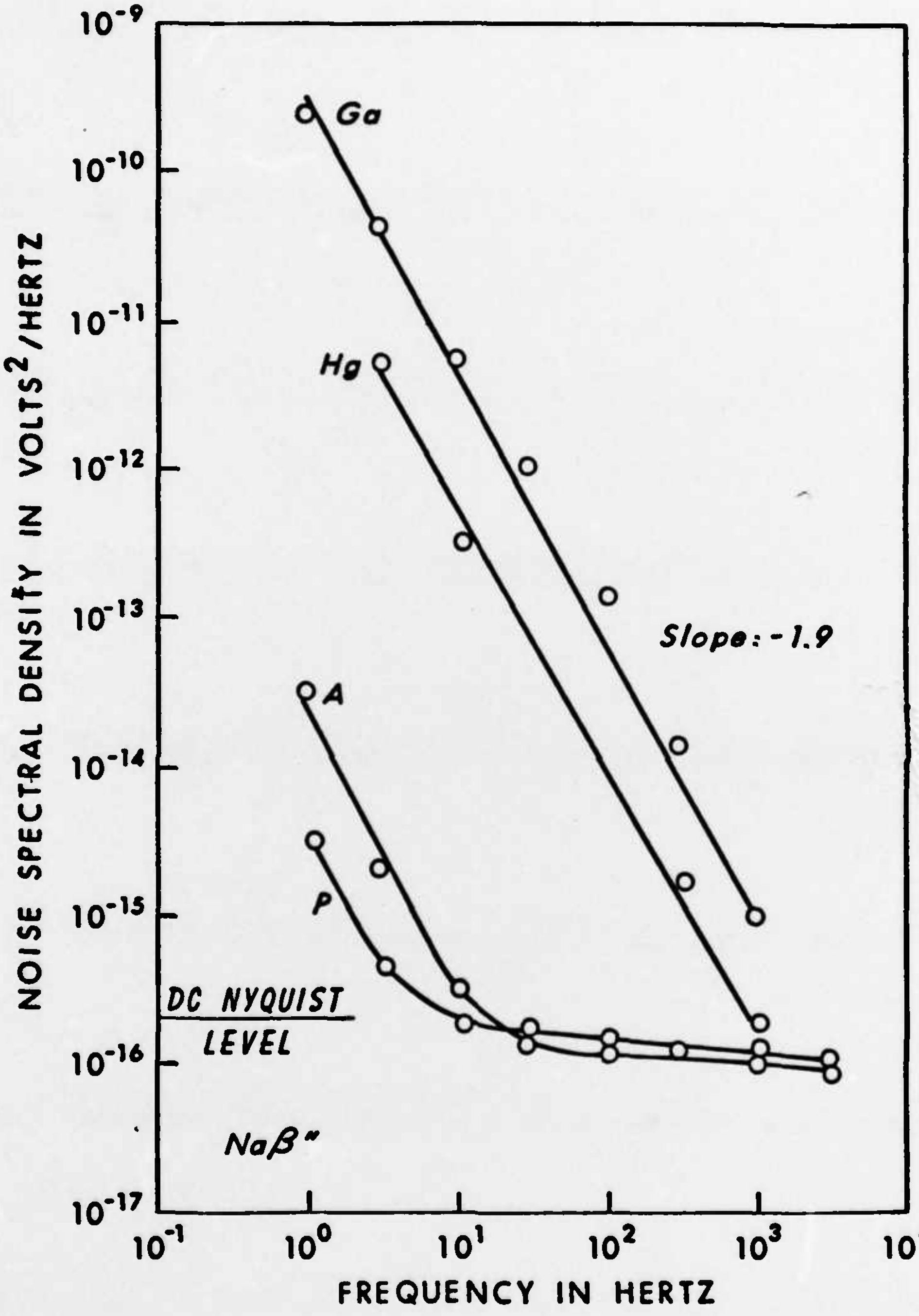

Figure 1. Contact noise spectra for blocking and ohmic contacts to Naβ" alumina ceramic. The gallium (Ga) and Mercury (Hg) electrodes are blocking while the sodium amalgam (A) and NaI in propylene carbonate (P) are ohmic.

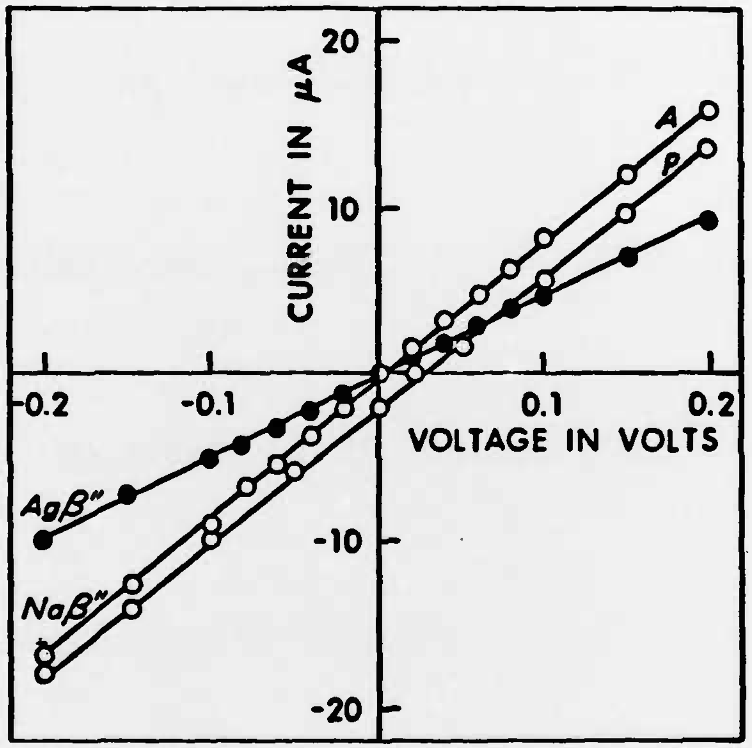

Figure 2. Current-voltage characteristics of Naβ" alumina (open circles) and Agβ" alumina (solid circles) ceramics using sodium amalgam (A), NaI in propylene carbonate (P), and aqueous $AgNO_3$ electrodes.

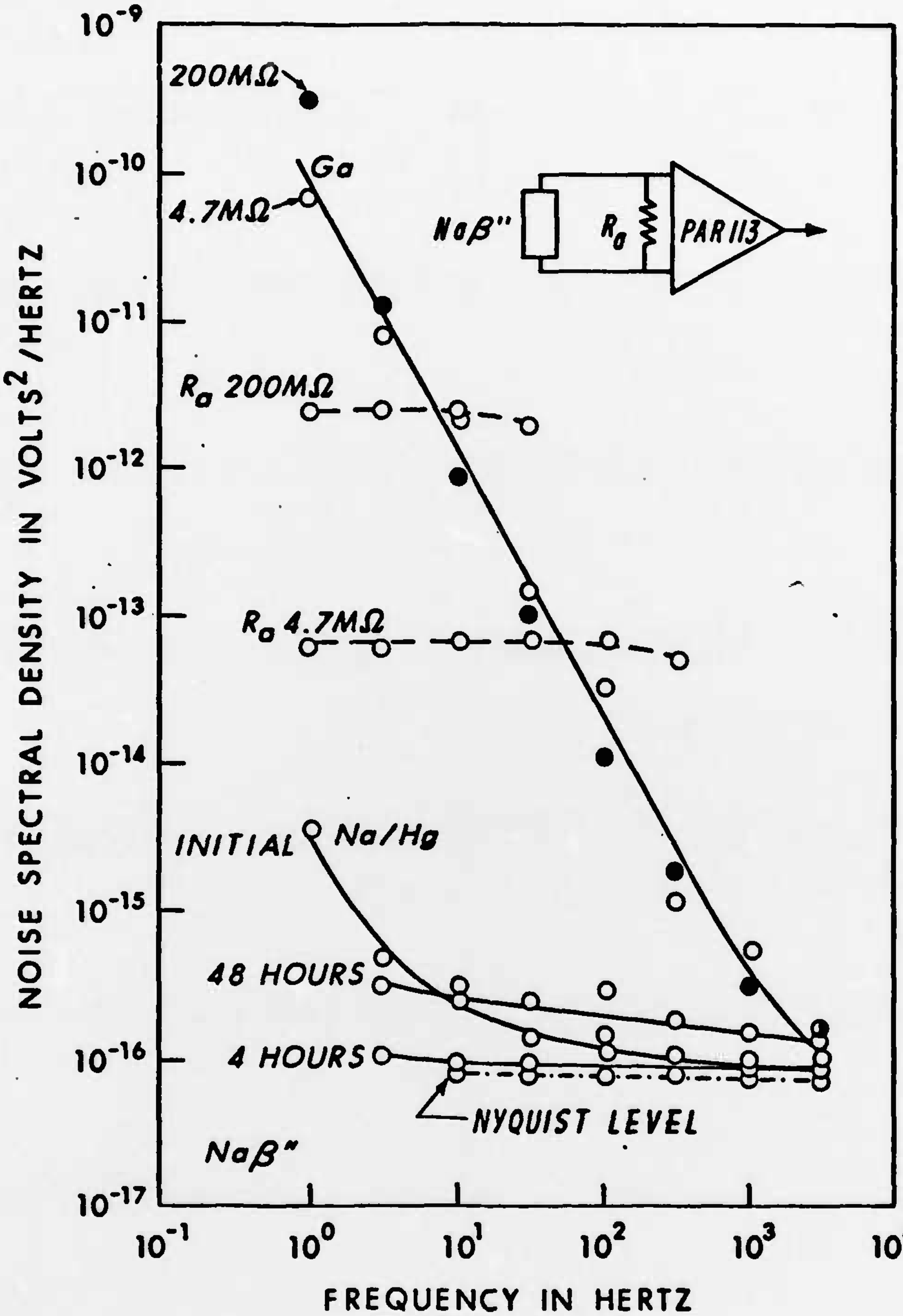

Figure 3. Contact noise spectra for gallium and sodium amalgam electrodes to a second Naβ" alumina ceramic sample. The dashed curves represent the observed Nyquist noise of amplifier input resistance alone and the dot-dash curve is the sample Nyquist noise calculated from ac impedance measurements.

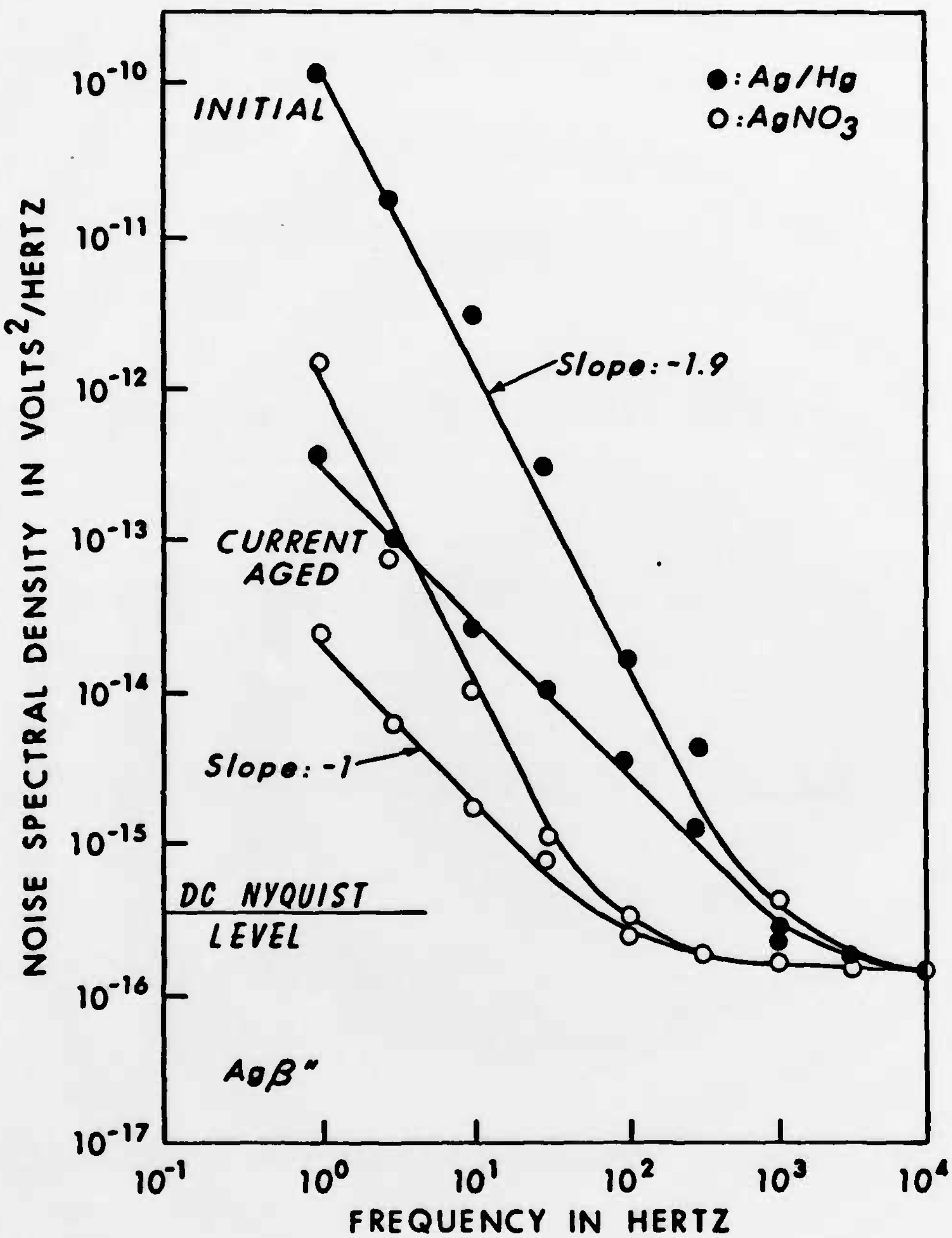

Figure 4. Contact noise spectra for silver amalgam (solid circles) and aqueous silver nitrate (open circles) electrodes to Agβ" alumina ceramic before and after dc current in the sample. The dc Nyquist level refers to the silver nitrate electrodes.

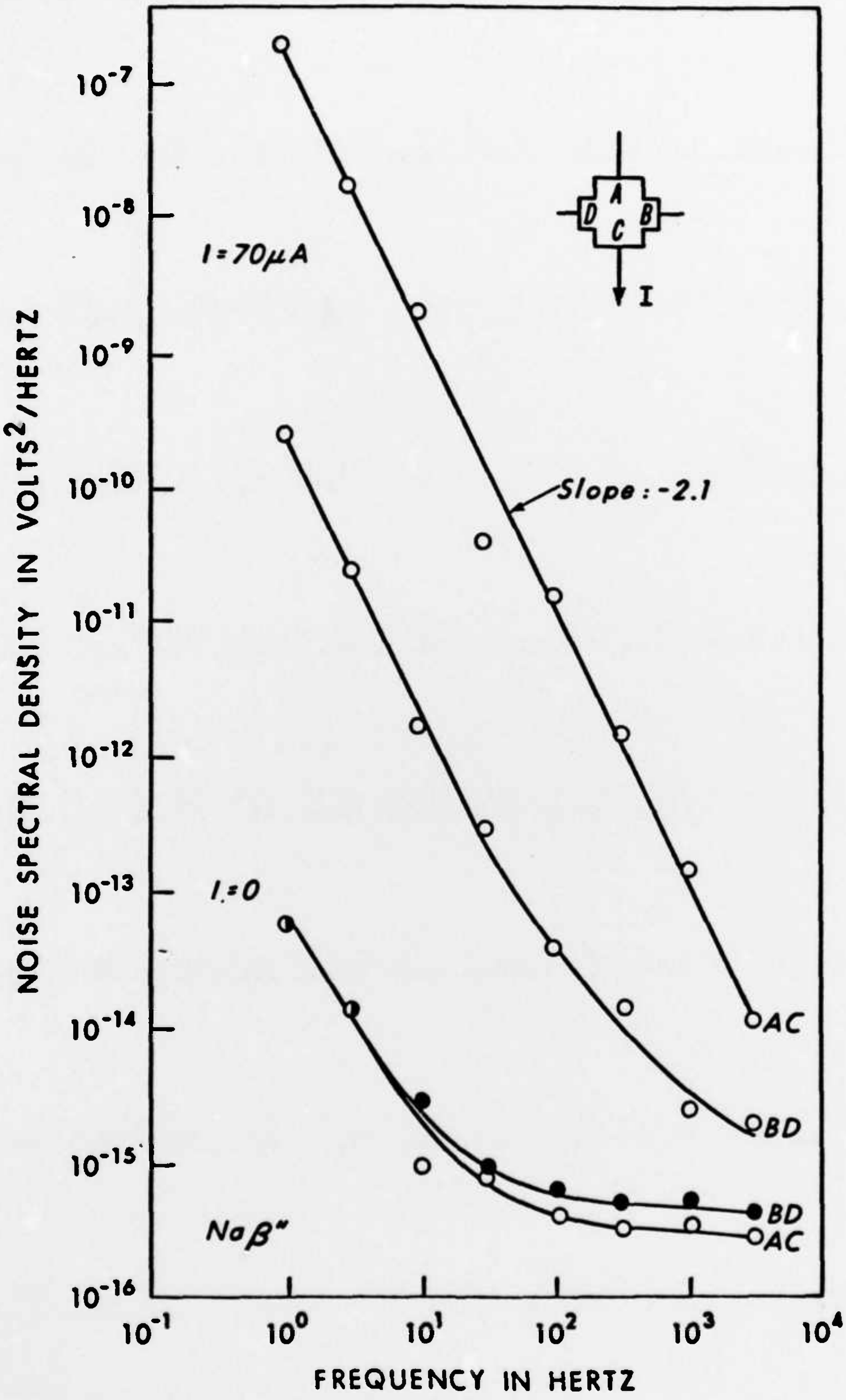

Figure 5. Current noise spectra for Naβ" alumina ceramic with sodium amalgam electrodes.

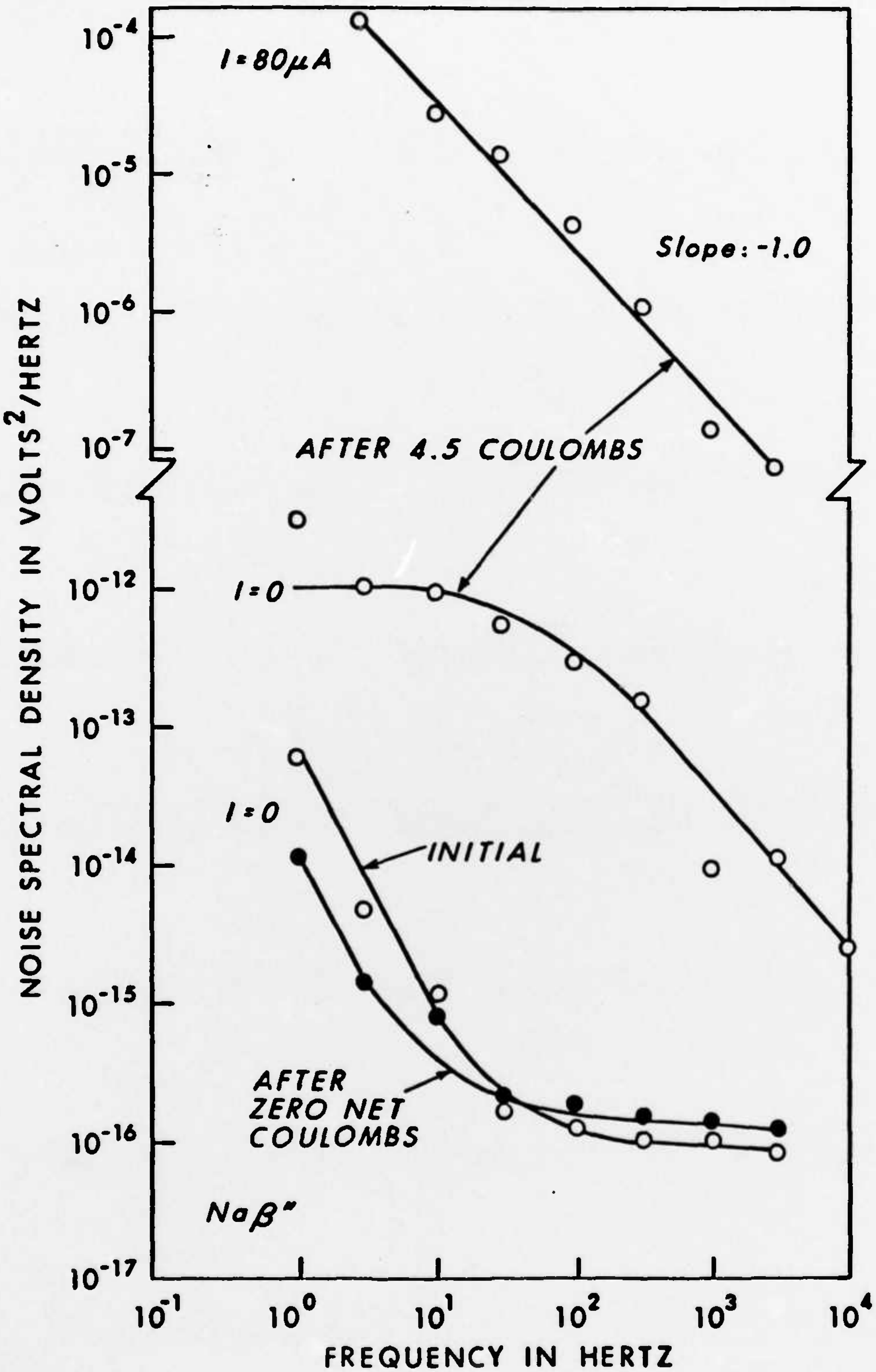

Figure 6. The effect of dc current on the contact and current noise spectra of Naβ" alumina ceramic with sodium amalgam electrodes.

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