

Low-frequency noise in solid-state nanopores

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Abstract

Low-frequency ionic current noise in solid-state nanopores imposes a limitation on the time resolution achieved in translocation experiments. Recently, this $1/f$ noise was described as obeying Hooge's phenomenological relation, where the noise scales inversely with the number of charge carriers present. Here, we consider an alternative model in which the low-frequency noise originates from surface charge fluctuations. We compare the models and show that Hooge's relation gives the best description for the low-frequency noise in solid-state nanopores over the entire salt regime from 10^{-3} to 1.6 M KCl.

1. Introduction

Single molecules passing through electrolyte-filled nanopores cause temporal changes in the conductivity. This technique has been used to detect nucleic acids and to study a wide range of their properties [1–6]. A variety of biological, synthetic and solid-state nanopores are used in these translocation experiments. The latter type (shown in figure 1(a)) is the obvious candidate for device integration and offers the best flexibility in nanopore size and experimental conditions. The temporal resolution for single-molecule translocation experiments is ultimately set by the level of ionic current noise. Fast detection with low noise levels might eventually allow for the detection of local structures along nucleic acids such as single bound proteins, triple-strand structures, individual hairpins, and mismatched bases [5]. Noise studies will not only help to improve and optimize nanopore characteristics, but can also provide detailed information on dynamic processes occurring within the volume of a single pore, and contribute to the understanding of noise sources. The high-frequency ionic current noise in solid-state nanopores is associated with the capacitance of the support chip and as such subjected to engineering improvements [7, 8]. The low-frequency noise in solid-state nanopores is of a $1/f$ spectral character and imposes a fundamental limitation on the detection [7–11]. Figure 1(b) shows the normalized current power spectral density of an individual nanopore. The low-frequency flicker noise in solid-state nanopores was recently found to obey Hooge's phenomenological relation, where the noise power

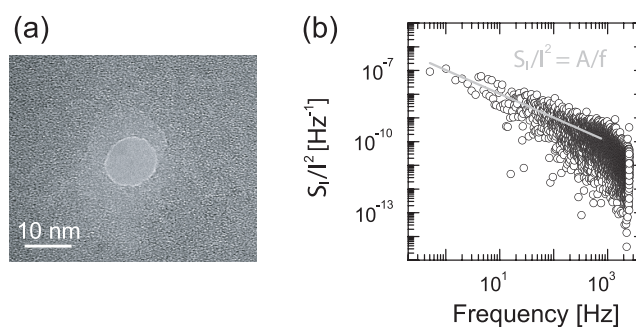


Figure 1. (a) Transmission electron micrograph of a 10.2 nm diameter nanopore. (b) The normalized current power spectral density of an individual nanopore at a salt concentration of 500 mM. The ionic current noise at low frequencies is of a $1/f$ spectral character. The solid line results from a fit of the data to the formula shown.

scales linearly with the inverse of the number of charge carriers [8]. However, surface modifications have resulted in reduced $1/f$ -noise levels in solid-state nanopores [10]. While these results might be explained by improvements in the surface hydrophilicity [12], they raise the question to what extent surface charge fluctuations can be directly responsible for the observed low-frequency noise.

Here, we study low-frequency ionic current fluctuations in fabricated solid-state nanopores. Nanopores with excessive low-frequency noise are not considered [8]. We develop a model, in addition to the Hooge model, in which the low-

frequency noise originates from surface charge fluctuations due to surface charge traps. Subsequently, we compare the predictions from the models to measurements of the noise power in nanopores as a function of salt concentration. The surface charge trap model and Hooge's relation do not scale identically with salt concentration. As a result, their validity can easily be discriminated. We verify that over the entire salt regime probed the noise is best described by Hooge's relation.

Our analysis provides a tool to identify low-frequency noise originating from surface charge fluctuations due to charge traps, and yields insight into different noise mechanisms.

2. Models of the low-frequency current noise

Low-frequency $1/f$ noise spectra are described and compared by the normalized noise power, A , defined as

$$A = S_I \frac{f}{I^2} \quad (1)$$

with S_I the current power spectral density, f the frequency, and I the average current. Hooge's phenomenological relation predicts a linear scaling of the noise power with the inverse number of charge carriers, N_c , given by [13]

$$A_H = \frac{\alpha}{N_c} \quad (2)$$

where α represents the Hooge parameter quantifying the amount of low-frequency noise. Recently, we found that the low-frequency noise in solid-state nanopores is well described by equation (2) using $\alpha = 1.1 \times 10^{-4}$ [8]. Here, we develop an alternative model in which the low-frequency noise in solid-state nanopores originates from surface charge fluctuations.

2.1. Surface charge fluctuations

We consider the charge fluctuations of the nanopore surface as arising from charge traps. The surface of the solid-state nanopores under consideration consists of an oxide layer. Charge traps present within the surface layer have a fluctuating charge state that can affect the ionic current through a solid-state nanopore. The frequency characteristics of the charge fluctuations obey a $1/f$ spectral dependence, when assuming a constant trap concentration and an exponentially decreasing ion penetration probability through the oxide layer, and independent charge traps [14]. We can express the amount of surface charge fluctuations due to surface charge traps, δq_t , and its power spectral density, $S_{q,t}$, as

$$\delta q_t = \gamma F(t) \quad (3)$$

$$S_{q,t} = \frac{\gamma^2}{f} \quad (4)$$

where γ is a proportionality constant reflecting the strength of fluctuations and $F(t)$ is a dimensionless noise function with a $1/f$ power spectrum [15].

2.2. Ionic current fluctuations

We can use the expression for the surface charge power spectral density, S_q , developed above to calculate its effect on the ionic current through nanopores. The normalized current noise power of equation (1) in terms of surface charge fluctuations is now simply given by

$$A = \left(\frac{\partial I}{\partial q} \right)^2 S_q \frac{f}{I^2}. \quad (5)$$

Assuming a cylindrical nanopore geometry, we can now express the noise power in terms of the surface charge density

$$A = \left(\frac{1}{\pi dL} \right)^2 \left(\frac{\partial I}{\partial \sigma} \right)^2 S_q \frac{f}{I^2} = \left(\frac{1}{\pi dL} \right)^2 \left(\frac{\partial G}{\partial \sigma} \right)^2 S_q \frac{f}{G^2} \quad (6)$$

where d is the diameter, L is the length, and G is the conductance of the nanopore. To calculate the noise power, the dependency of the ionic conductance (or current) through the nanopore on the amount of surface charge density must thus be known.

We have previously developed a model which successfully describes the ionic conductance, G , through cylindrical nanopores in a monovalent KCl salt solution in terms of the pores' surface charge density

$$G = \frac{\pi d^2}{4L} \left((\mu_k + \mu_{cl}) n_{kcl} e + \mu_k \frac{4\sigma}{d} \right) \quad (7)$$

where n_{kcl} is the number density of potassium and chloride ions in solution, and μ_k and μ_{cl} are their respective electrophoretic mobilities [16]. The first term in between brackets accounts for the contribution of the bulk concentration of ions inside the nanopore whereas the second term accounts for the contribution of the positive counterions shielding the negative nanopore surface charge. The nanopore access resistance is not taken into account. The model for the ionic current through nanopores accurately describes the data over salt concentrations spanning six orders of magnitude when the surface reactivity is taken into account [16]. The surface charge density is then dependent on the bulk concentration of ions in solution [17]. From equation (7) it follows that

$$\left(\frac{\partial G}{\partial \sigma} \right) = \frac{\pi d}{L} \mu_k. \quad (8)$$

Combining equations (4), (6), and (8), we obtain the current noise power due to surface charge fluctuations originating from surface charge traps:

$$A_t = \left(\frac{\mu_+ \gamma}{GL^2} \right)^2. \quad (9)$$

The value of μ_+ is given by the mobility of the used potassium ions, $\mu_k = 7.6 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$. This leaves the measurable conductance, G , and γ/L as the only remaining unknown parameters.

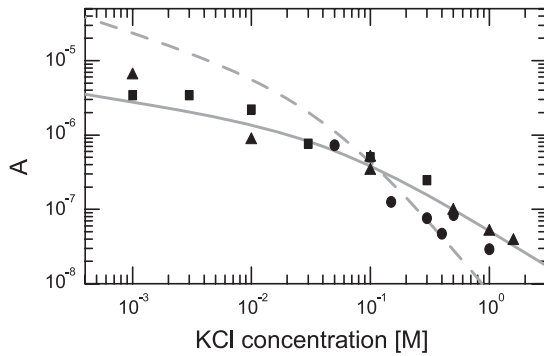


Figure 2. Noise power of three nanopores with similar diameters from salt concentrations of 1 mM up to 1.6 M. The dashed line is a fit to the noise power data from the charge traps model. Hooge's relation is shown by the solid line which clearly gives the better description of the noise power over the salt range probed.

3. Comparison of models to the experimental data

The measurements are performed using single solid-state nanopores fabricated in thin 20 nm low-stress SiN membranes covered by 20 nm sputtered SiO₂ on each side. The details of the solid-state nanopore fabrication are described elsewhere [18]. The nanopores are mounted into the setup using a microfluidic flow cell. Solutions of different salt concentrations are prepared by adding 18 MΩ cm Milli-Q filtered water (Millipore) to a stock solution of 1 M KCl with 20 mM TRIS-HCl buffer at pH = 7.5. We record ionic currents using Ag/AgCl electrodes connected to an amplifier (Axopatch 200B, Axon Instruments) and power spectra result from ≈2 s of current recordings using Labview (National Instruments). The normalized noise power, A , is extracted by fitting the normalized current power spectral density at low frequencies to A/f (see equation (1)), as shown in figure 1(b).

We now compare the models developed above to measurements of the low-frequency noise power in solid-state nanopores as a function of salt concentration [8]. The conductance of the nanopores is well described using equation (7), assuming an average nanopore diameter of $d = 9.3$ nm and a nanopore length of $L = 25$ nm. We use the conductance, G , and the determined length of the nanopore, L , in equation (9).

Figure 2 shows the current noise power of the nanopores as a function of salt concentration. The best fits to the data of the charge trap model (equation (9)) is shown by the dashed line. We obtain $\gamma = 3.1 \times 10^{-20}$ C for the single fit parameter.

The surface-charge-fluctuation model predicts an increase in noise power when the salt concentration is decreased. However, the model does not closely follow the trend measured in solid-state nanopores. In particular, it fails to give a valid description at high-salt concentrations ($\gtrsim 0.1$ M). Figure 2 also shows the noise power calculated from Hooge's relation, indicated by the solid line. Here we have used the determined value of the nanopore length and the surface charge value adopted from literature to calculate the number of charge carriers, N_c , present inside the nanopore. The Hooge parameter is given by $\alpha = (1.1 \pm 0.1) \times 10^{-4}$ [8]. In contrast to the

developed surface charge model, Hooge's phenomenological relation gives a good description of the measured low-frequency noise.

4. Discussion and conclusions

The surface-charge-fluctuation model developed above can in principle yield different values of γ for different nanopores. However, we find that the value deduced is comparable for all three nanopores analysed in figure 2. The assumption of a constant surface charge density for the nanopores does also not improve the comparison to the measurements. Indeed, Hooge's relation gives a better description of the low-frequency current noise in solid-state nanopores over the whole salt range probed. Obviously, this does not exclude a possible surface charge fluctuation contribution to the overall measured ionic current noise.

In the low-salt regime ($n_{\text{kcl}} \ll \frac{2\sigma}{ed}$), the conductance as well as the number of charge carriers inside the nanopores are dominated by the counter ions screening the nanopore surface charge. Consequently, they both scale with the surface charge density of the nanopore, i.e. $G, N_c \sim \sigma$. The charge trap model of equation (9) and Hooge's relation of equation (2) exhibit a different scaling with $A_t \sim 1/\sigma^2$ and $A_H \sim 1/\sigma$. The different scaling relations for the charge trap model versus the Hooge model can easily be identified by inspection of the model curves shown in figure 2. Hooge's relation give a better description of the measured noise power in the low-salt regime. In the high-salt regime ($n_{\text{kcl}} \gg \frac{2\sigma}{ed}$), the conductance and the number of charge carriers are dominated by the contribution of the bulk concentration of ions inside the nanopore. In this regime, G as well as N_c scale with the ion number density in solution, i.e., $G, N_c \sim n_{\text{kcl}}$. From equation (9) we find $A_t \sim 1/n_{\text{kcl}}^2$. In contrast, Hooge's relation (equation (2)) scales as $A_H \sim 1/n_{\text{kcl}}$. This qualitatively explains the rapid decrease of the noise power with increasing salt concentrations for the surface-charge-fluctuation model in this regime (see figure 2). This rapid decrease is not supported by the measurements and Hooge's relation clearly gives a better description of the data in the high-salt regime.

In summary, we have developed a model for the low-frequency current noise in solid-state nanopores in terms of surface charge fluctuations. The model is compared to noise data of nanopores at different salt concentrations, as well as with Hooge's relation. The charge trap model fails to account for the data in the low as well as the high-salt regime. We conclude that the low-frequency noise of solid-state nanopores is best described by the number of charge carriers as expressed in Hooge's relation and that surface charge fluctuations due to charge traps are relatively unimportant.

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