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Converting external potential fluctuations into nonzero time-average electric currents using a single nanopore

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The possibility of taking advantage of a fluctuating environment for energy and information transduction is a significant challenge in biological and artificial nanostructures. We demonstrate here directional electrical transduction from fluctuating external signals using a single nanopore of conical shape immersed in an ionic aqueous solution. To this end, we characterize experimentally the average output currents obtained by the electrical rectification of zero time-average input potentials. The transformation of external potential fluctuations into nonzero time-average responses using a single nanopore in liquid state is of fundamental significance for biology and nanophysics. This energy and information conversion constitutes also a significant step towards macroscopic scaling using multipore membranes. © *2015 AIP Publishing LLC*.
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Spatial flows of energy and information coexist with ambient noise in most biological processes. For instance, enzymes allow directional free energy transduction from fluctuating external signals,[1–5] and the protein ion channels in cell membranes may convert noisy chemical and electrical signals into net fluxes.[6–9] Most biological systems have developed mechanisms to overcome (or even take advantage) of noise and fluctuations instead of trying to avoid them.[10] However, noise is generally perceived as an obstacle for developing applications at the nanoscale. It is then important to develop and demonstrate methods that allow the conversion of fluctuating external signals into directional average responses.

Fluctuations will usually dominate the behavior of nanosystems in the absence of high external fields that may overwhelm them. The biological mechanisms that allow natural systems to exploit noise (in particular, ratchet and rectification phenomena[11–13]) can inspire useful strategies also for artificial nanostructures.[14,15] Following previous work by Siwy and Fuliński,[16,17] we demonstrated recently the conversion of periodic electrical signals of zero time-average into net currents with an asymmetric nanopore functionalized with amino acid groups[18] and a (symmetric) cylindrical pore asymmetrically blocked by a nanoparticle.[19] Moreover, we showed the pumping of potassium ions against an external concentration gradient for the case of the bacterial porin *OmpF* (outer membrane protein F) channel of *Escherichia coli* using periodic potentials.[8]

We demonstrate experimentally here that significant average currents can be obtained from fluctuating external potentials using a single conical nanopore immersed in an aqueous electrolyte solution. This pore mimics the rectifying properties observed in the current-potential curves of ion channels.[6,8,20] Because of the generic nature of the model, the results obtained should be of interest to both biological and artificial systems (e.g., the rectification of electrical fluctuations is significant for the averaging of low frequency electric fields in cells[21,22] and multipore membranes are useful in energy transduction and storage applications[23,24]).

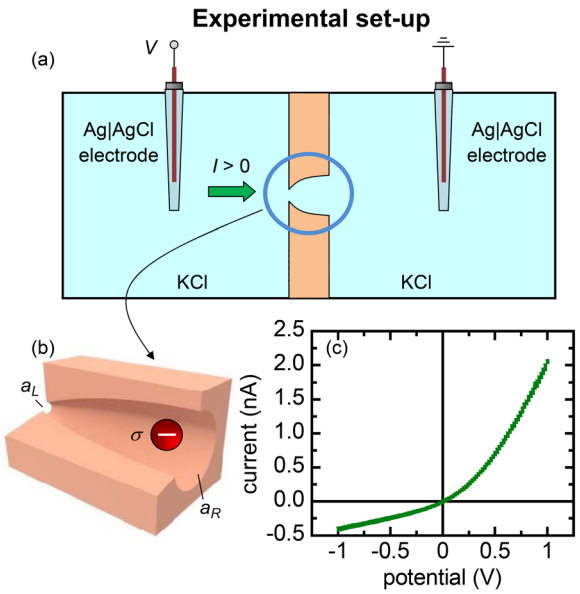

FIG. 1. Scheme of the experimental set-up (a). Single asymmetric nanopore with ionized carboxylate residues obtained by track-etching (b). Experimental *I-V* curve for a single nanopore (c). Using a Poisson-Nernst-Planck model,[23] the pore radii $a_L \approx 10$ nm (tip) and $a_R \approx 190$ nm (base) and the fixed charge concentration $\sigma = -0.4e$ nm^{-2} are obtained from the comparison of the experimental *I–V* curves with the theoretical results.

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Figure 1 shows the scheme of the experimental set-up used for the ionic current measurements. The polymer film contains a single conical pore having a nanoscale tip radius fabricated through asymmetric track-etching procedures.[25] The single-pore membrane separates the two identical electrolyte (0.1 M KCl) aqueous solutions. A couple of Ag|AgCl electrodes in the external cell solutions are used to apply the external electric potential V, and a pico-ammeter measures the electric current I passing through the system. In our experimental conditions, the pore wall contains ionized carboxylate residues which impart negative fixed charges to the pore surface (Fig. 1(b)). Complete experimental details can be found elsewhere.[25] The current entering the pore through the small opening experiences an electrical resistance lower than that entering the pore through the wide opening.[25] As a result, the steady-state current-potential (I-V) curves[25] show current rectification. It means that high and low conducting states are obtained for positive and negative applied potentials, respectively; Fig. 1(c). This ion current rectification is described by the ratio $r(V) \equiv |I(V)/I(-V)|$. Comparison of the experimental I-V curves with the theoretical results obtained using a Poisson-Nernst-Planck model[23] allows for the determination of the pore radii a_L (tip) and a_R (base) and the surface concentration σ of fixed charge, which are $a_L \approx 10\,\text{nm}$, $a_L \approx 190\,\text{nm}$, and $\sigma = -0.4e\ \text{nm}^{-2}$, where e is the elementary charge.

When a time-dependent potential $V(t)$ is introduced, the system responds with an electric current $I(t)$. For the system to show no time delay with respect to $V(t)$, the external signal period τ should be much longer than the characteristic response time of the system; this condition is approximately valid for nanostructures such as ion channels[8] and nanopores[18] because of the small volumes involved provided that low frequency signals are considered (see, e.g., Fig. 3 of Ref. 8 and Fig. 1 of Ref. 18). When the input potential $V(t)$ has zero time average, $\langle V \rangle = 0$, the output average current $\langle I \rangle$ can be different from zero because of the pore rectification described above. To simulate a broad range of external fluctuating signals, we have used the following waveforms[4] for the input potential: a Gaussian-distributed amplitude with constant lifetime (see Fig. 2 for typical time traces and distributions), a random telegraph noise (RTN) of constant amplitude with Gaussian-distributed lifetime (see Fig. 3), a Gaussian-distributed amplitude and lifetime (see Fig. 3), and finally white noise (see Fig. 4). All these input potentials verify that $\langle V \rangle = 0$.

Figures 2(a)–2(d) show the typical results obtained when the fluctuating external potential has constant lifetime (4.4 s) and a Gaussian-distributed potential amplitude (Fig. 2(a)). Since $r > 1$ for the pore of Fig. 1(c), the distribution of measured currents shifts to positive values and the average current is 0.25 nA (Fig. 2(d)) when most of the potential amplitudes are less than 0.5 V.

Figures 3(a) and 3(b) correspond to an input signal with constant potential amplitude and Gaussian-distributed lifetime, while Figs. 3(c) and 3(d) correspond to an input signal where both the potential amplitude and the lifetime are Gaussian-distributed. In the case of the RTN signal (Figs. 3(a) and 3(b)), the average current can be estimated as[13] $\langle I \rangle = \frac{|I(+1\,\text{V}) + I(-1\,\text{V})|}{2} = 0.86\,\text{nA}$ to be compared with the value $\langle I \rangle = 0.21\,\text{nA}$ obtained for the case of Figs. 3(c) and 3(d) (see also the case of Figs. 2(a) and 2(b)). Note that the lifetimes of the driving voltage signals used here are higher than the times required for the formation of the high and low conductance regimes (see Refs. 8 and 18 for a detailed discussion). As a result, the average currents measured are not influenced by the (random) pulse lifetime because the instantaneous current is slave (no time delay) of the potential. The currents are then dictated by the potential amplitude distribution only.

Figure 4 shows finally the case of white noise potentials (a) and currents (b), together with sample distributions of input (c) and output signals (d). Because all potential values are now equally probable, the average current is defined as

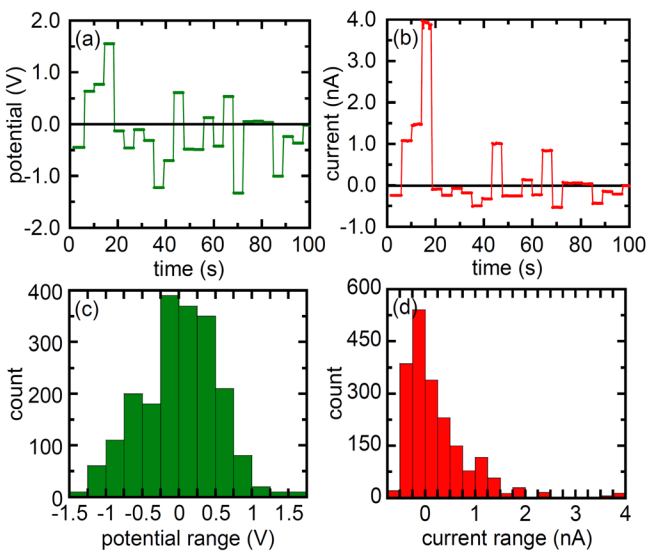

FIG. 2. Fluctuating input signal with a Gaussian-distributed potential amplitude and a constant lifetime (a) and measured output current (b). Gaussian distribution of potential amplitudes (c) and experimental distribution of output currents (d).

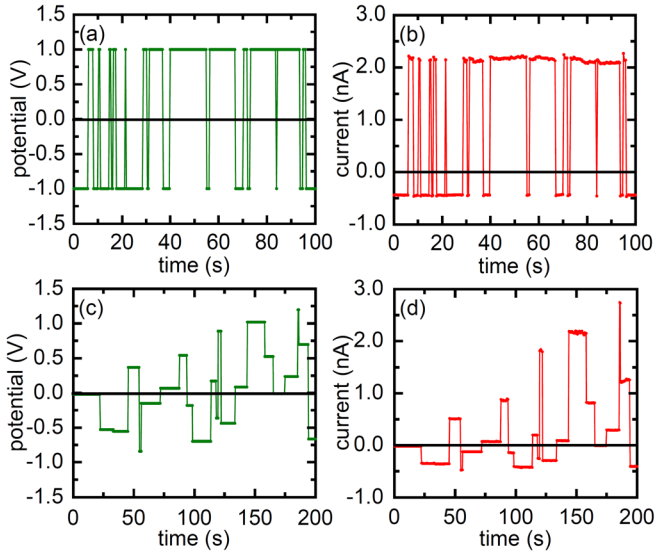

FIG. 3. Fluctuating input signal with constant potential amplitude (1 V) and Gaussian-distributed lifetime (a) and measured output current (b). Fluctuating input signal with Gaussian-distributed potential amplitude and lifetime (c) and measured output current (d).

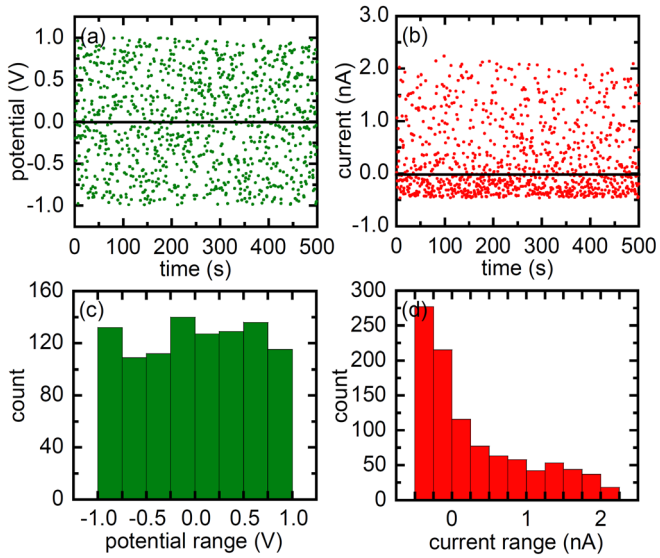

FIG. 4. White noise input signal (a) and measured output current (b). Distribution of fluctuating input potentials (c) and measured output currents (d).

the area limited by the *I-V* curve, and the potential axis between −1 V and +1 V divided by the peak to peak value of the potential. The average current $\langle I \rangle = 0.30$ nA for the results of Fig. 4.

To better demonstrate the experimental robustness and significance of the reported nanoscale effect, Figs. 5(a) and 5(b) show three different zero-average potentials (a) together with the respective nonzero currents $\langle I \rangle$ plotted as a function of the input amplitude (b). Significant currents are obtained for potential amplitudes higher than 0.1 V. The maximum values of $\langle I \rangle$ are obtained for the square signal (this is also the case of the RTN signal in Fig. 3) because of its characteristic high rectification ratio.[23] Note also that this ratio increases with the potential amplitude. The other two signals give essentially the same average current because the triangle signal can be considered as a time reordering of the white noise signal, and this reordering does not change the value of $\langle I \rangle$.

In summary, we have demonstrated directional electrical transduction (net currents $\langle I \rangle$) from fluctuating external signals (potential $V(t)$) of zero time-average using a single nanoscale pore which acts as a soft matter version of the solid-state diode.[26–28] The correlation between the state of a system and its environmental fluctuations does not allow systematic extraction of electrical energy from *equilibrium* random fluctuations. On the contrary, we have shown experimentally using a nanoscale liquid state device that, as expected, this is not the case of *non-equilibrium* fluctuations uncorrelated to the system state. Because the single nanopore shows rectifying properties similar to those observed in the ion channels of the cell membrane,[6,8,20] the results may also have biological implications for the conversion of fluctuating ambient signals into directional energy and information fluxes.[1,9,10,21] Indeed, improving the rectification characteristics of the pore (or, alternatively, using a multipore membrane) should give significant net currents for potential amplitudes less than 0.1 V.

The results also suggest that asymmetric pores could be used for electrochemical charge storage[23,24] using similar concepts as those developed here. The pore should work as a

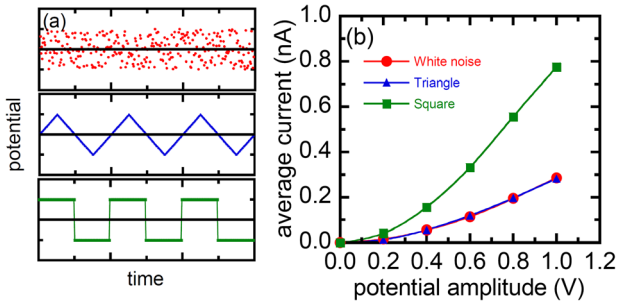

FIG. 5. Schemes of zero-average potentials (a) and their corresponding average currents as a function of the input potential amplitude (b).

voltage-controlled current source when connected to an external load capacitor, allowing the conversion between the net current caused by the fluctuating external potential and the output voltage. Additional work along these lines is now in progress.

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