Electrochemical response of biased nanoelectrodes in solution

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Novel approaches to DNA sequencing and detection require the measurement of electrical currents between metal probes immersed in ionic solution. Here, we experimentally demonstrate that these systems maintain large background currents with a transient response that decays very slowly in time and noise that increases with ionic concentration. Using a non-equilibrium stochastic model, we obtain an analytical expression for the ionic current that shows these results are due to a fast electrochemical reaction at the electrode surface followed by the slow formation of a diffusion layer. During the latter, ions translocate in the weak electric field generated after the initial rapid screening of the strong fields near the electrode surfaces. Our theoretical results are in very good agreement with experimental findings.

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Single-molecule detection using micro/nano-fluidic devices has recently attracted quite a lot of attention [1–4]. In particular, solid-state nanopores [5–8], in which translocated molecules can be detected by electrical signals [9–11], are expected to become one of the core technologies for next-generation DNA and RNA sequencing. As part of this approach, the tunneling current through nucleotides as they translocate through the nanochannel was recently measured using nanometer gap electrodes made by a mechanically controllable break junction (MCBJ) [12–15]. In addition to information on single nucleotides, the measured electrical signals have contributions from ionic currents due to the presence of the electrolyte solution. Those signals are usually hidden within the inevitable noise in the nanofluidic system. Clarifying the mechanisms responsible for the behavior of these “background” currents is critical to the development of DNA sequencing approaches based on electronic transport. Their study is also of relevance for any nanofluidic technology that employs electrodes in solution, e.g., for the improvement of the energy storage capabilities of electrochemical capacitors [16–19].

In this letter, we experimentally investigate electrical currents generated by electrodes in an electrolyte solution. We find a transient electrical response that decays very slowly and an associated noise that increases with increasing ionic solution concentration. We develop a theoretical understanding of these effects that is in very good agreement with the experimental observations and reveals the rich behavior contained in the electrochemical response.

Figures 1(a) and 1(b) show a schematic illustration and scanning electron microscopy (SEM) image, respectively, of a MCBJ made with Au electrodes. The lithographically defined nano-junction is fabricated on a polyimide-coated phosphor bronze substrate. It consists of 30 nm thick Au/Cr wires of approximately 10 mm end-to-end length and width tapered from 10 µm to 1 µm along the length. We create a pair of nanoelectrodes using a self-
by the potential field, and $R_i$ each species \[22\]:

In our experimental setup, the electrodes are symmetrically placed in a liquid container of 2 mm diameter. Therefore, large surfaces ($\sim 10^{-8}$ m²) of the lead line are exposed to the electrolyte solution, which cause the background current with noises as shown in Fig. 1(c). Here, the electrical response of NaCl solution was measured for various salt concentrations under constant dc voltages at 10 kHz by using a custom-built setup \[16\] (see also supplementary materials). From Figs. 1(c) and 1(d), the transient response includes a rapid increase and subsequent slow decay of the ionic current. Particularly, the current–voltage characteristics and a 1 nF capacitor. Table S1). Assuming an equivalent circuit, this system is defined in an interval of $m = \{+1, -1\}$, where $\rho_i$ is the random force from solvent molecules in external force fields is expressed for all species that contribute to $\phi$. The ionic density and the electrostatic potential should be determined self-consistently to solve the non-linear partial differential equation. Taking into account the effect of noise as shown in the experimental result (Fig. 1(c)), source terms are added and thus Eqs. \[1\] become

$$
\frac{\partial \rho_i}{\partial t} - \frac{z_i e}{\xi_i} \partial_x \left( \frac{d\phi}{dx} \rho_i \right) - D_i \frac{\partial^2 \rho_i}{\partial x^2} = \sum_r f_{ir} \cos(\omega_{ir} t + \varphi_{ir}) \delta(x),
$$

where $f_{ir}$ are constants depending on the current density and noise, and $\varphi_{ir}$ are the phase shifts at $t = 0$. In the numerical solution, $\phi$ depends only on the displacement of ions and thus it is treated as independent of time in the short interval. The smallest time step, which is large enough to represent the stochastic process, should be determined properly to maintain constraints at boundaries and electroneutrality. The source terms represent noise generated at $x = 0$ and induce external flux in the domain. As a first step, we consider Gaussian white noise, although it is known that noises detected in micro/nano-fluidic devices usually show also flicker noise \[23\][25]. The parameters $\omega_{ir}$ and $\varphi_{ir}$ are generated by Gaussian and uniform probability distributions, respectively.

Rescaling $x$, $t$, and $\phi$ to make them dimensionless by

$$
x^* = \frac{x}{L}, \quad t^* = \frac{D_i t}{L^2}, \quad \psi_{ir}^* = \frac{z_i e \phi}{k_B T},
$$

and, considering a unit surface, replacing $\rho_i$ by

$$
n_i^* = \frac{L}{z_i e} \exp \left[ \frac{1}{2} \int_{x^*}^{x^*} \frac{d\psi_{ir}^*}{dx^*} \frac{d\psi_{ir}^*}{dx^*} \right],
$$

Eq. \[2\] becomes

$$
\left[ \frac{\partial}{\partial t^*} + \frac{1}{4} \left( \frac{d\psi_{ir}^*}{dx^*} \right)^2 - \frac{1}{2} \frac{d^2 \psi_{ir}^*}{dx^*^2} - \frac{\partial^2}{\partial x^*^2} \right] n_i^* = e^{\frac{1}{2}} \int_{-L}^{L} \sum_r f_{ir} \cos(\omega_{ir} t^* + \varphi_{ir}) \delta(x^*), \tag{5}
$$

where $f_{ir} = L^2 f_{ir}/z_i e D_i$ and $\omega_{ir} = L^2 \omega_{ir}/D_i$. For the other species, the equation can be derived in the same manner with a difference of factor $D_j/D_i$. Here, $n_i^*$ and $\psi_{ir}^*$ are expanded by the Fourier series: $n_i^*(x^*, t^*) = \sum_k c_{ik}(t^*) e^{ik\pi x^*}$ and $\psi_{ir}^*(x^*) = \sum_k g_{ik} e^{ik\pi x^*}$ where $k = 0, \pm 1, \pm 2, \ldots$. $\delta(x^*)$ is also expanded similarly: $\delta(x^*) = \frac{1}{2\pi} \sum_k e^{ik\pi x^*}$. Each basis function is orthogonal on $x^* \in [-1, 1]$. In this model, a mirror symmetry is assumed at $x^* = 0$ and 1. Ions are adsorbed or reflected at $x^* = 0$...
and the concentrations correspond to those of bulk at 
\( x^* \geq 1 \), conserving the electro-neutrality in \( L \). Based on
the description above, Eq. (5) becomes

\[
\frac{dc_j}{dt^*} + \dot{H}_i c_i = \frac{1}{2} \sum_{r} f_{ir}^* \cos (\omega_{ir}^* t^* + \varphi_{ir}),
\]

where

\[
H_{ikl} = \pi^2 k^2 \delta_{k,l} + \frac{\pi^2}{2} (k - l)^2 g_{ikl} - \frac{\pi^2}{4} \sum_{k_1} k_1 (l - k - k_1) g_{ikl} g_{i(k-l+k_1)}.
\]

\( \psi_i \) are real functions and thus \( \dot{H}_i \) are Hermitian matrices.

For the homogeneous case, we can solve Eq. (6) via its
eigenvalues \( \lambda_j \) and eigenvectors. Using these solutions,
we can also solve the inhomogeneous case. If \( \lambda_j \) are non-
zero then

\[
c_{ik}(t^*) = \frac{1}{2} \sum_{l} u_{ik}^o u_{lj} \left[ \frac{f_{ir}^*}{\lambda_j} (1 - e^{-\lambda_j t^*}) \cos \varphi_{ir=0} + \sum_{r \neq 0} f_{ir}^* I_{ir}(t^*) \right] + \sum_{l} u_{ik}^o u_{lj} c_{il}^0 e^{-\lambda_j t^*},
\]

where \( u_{ik}^o \) are the conjugate transpose of \( u_{jk} \), \( c_{il}^0 \) are constants
determined at the initial condition and

\[
I_{ir}(t^*) = e^{-\lambda_j t^*} \int_0^{t^*} \cos (\omega_{ir}^* t'' + \varphi_{ir}) e^{\lambda_j t''} \, dt''.
\]

At equilibrium, \( \lambda_j \) should be zero because the concentra-
tion is in equilibrium. As a consequence, \( \rho_i \) are obtained
and \( \phi \) is given by solving the Poisson equation in the
steady state (see supplementary materials). Thus, we obtain

\[
j_i(x, t) = \frac{2 \pi e D_e}{L^2} e^{-\frac{z_i e \phi}{k_B T}} f \frac{dx}{\pi} \sum_{k>0} k \text{Im} \left[ c_{ik} e^{ik \pi x / L} \right] - \frac{z_i e D_e}{2k_B T} \frac{d\phi}{dx} \rho_i.
\]

We apply this model to evaluate the ionic current near
a Au electrode in a NaCl solution. At the negatively
charged cathode surface, Na\(^{+}\) is highly concentrated
regardless of anion species. In the numerical analysis, \( L \)
is taken as a constant for each molarity. The range
of applied potentials is according to the practical poten-
tials in aqueous solutions: \( \phi(0) = -0.01 \) to \(-1 \) V
for \( \phi(L) = 0 \) V fixed. The valence is +1 and -1 for
Na\(^{+}\) and Cl\(^-\), respectively. The diffusion coefficients are
known: \( D_{Na^+} = 1.35 \times 10^{-9} \) m\(^2\)/s and \( D_{Cl^-} = 2.03 \times 10^{-9} \)

The dielectric constant and temperature are
set to \( \varepsilon = 78.4 \varepsilon_0 \) [28] where \( \varepsilon_0 \) is the dielectric constant
of vacuum and \( T = 298.15 \) K, respectively. More details

Figure 2 shows \( \tau \) for Na\(^{+}\) and Cl\(^-\) as a function of the
ratio of \( V = \phi(L) - \phi(0) \) to \( L \) for the molarity of 1, 10, 50,
and 100 mM, where \( V/L \) merely expresses a fraction of
the applied potential and the length, but not the electric
field in the system. It is found that \( \tau \) tends to be propor-
tional to \( (V/L)^2 \) where \( \zeta = -2.15 \) for Na\(^{+}\) and \( -2.05 \) for
Cl\(^-\) resulting from the fits of the computational data at
1 mM. It can then be predicted that \( \tau \propto (V/L)^{-2} \) at the
dilute limit, since the second term on the left-hand side
of Eq. (5) becomes dominant as \( \tau \) far away from the electrode. The magnitude of \( \tau \) is expected to be on the order of 1 s for the electric field of
10\(^3\) V/m. For comparison, \( \tau \) evaluated from our exper-
imental results (Fig. 1(c)) is also presented in Fig. 2. In order to evalu-
ate \( \tau \) from the experimental results, the \( \tau \) is fixed at 1.57
nm taking into account the longest length of the electric
field line in the system (see Supplementary materials). The
theoretical evaluations are then in close agreement
with the experimental results. Furthermore, the series of
\( \tau \) resulting from the 200 mM solution is expected to show
negative gradient if the \( L \) becomes large with increasing
the applied potential.

On the other hand, the above model cannot treat
chemical reactions and the charge transfer explicitly. In
order to replicate constant currents at long time and noises with respect to the electrochemical reactions [21], we then apply source terms for Na$^+$. Figure 3 shows current density and normalized number density of each species obtained from 10, 50, 100, and 200 mM NaCl solutions as a function of time. Source terms — to represent the Gaussian white noise — are added to Eq. (2).

The zeroth source term $f_{Na^+_r=0}$ is applied only for Na$^+$ in order to determine the current density at the steady state. We set $f_{Na^+_r=0} = -\alpha n_0 D(\phi(L) - \phi(0))/Lk_BT$ based on the Nernst–Einstein relation, where $n_0$ is the number density of bulk and $\alpha$ is a constant. In addition, the amplitude of the noise is determined to be proportional to square root of the bulk density based on the surface charge density [22] such that $f_{Na^+_r} = \beta \sqrt{n_0}$ with a constant $\beta$ common for each molarity. $f_{Na^+_r}$ is determined from a fraction of $f_{Na^+_r=0}$ for 10 mM such that $\beta = f_{Na^+_r=0}/\alpha \sqrt{n_0}$. We perform computations for a case of $\alpha = 1$, $\beta = 100$, $L = 40$ nm, and $V = 0.3$ V. The total ionic current density is evaluated as $\sum_j (j_1(x \to 0) - j_1(x \to L))$. As shown in Fig. 3(a), rapid increases and subsequent decays in the net current density are observed at the moment when the electric potential is applied. The time constant of Na$^+$ tends to become large as the molarity increases as shown in the inset of Fig. 3(a). $\tau \sim 0.1$ $\mu$s, obtained from $L = 40$ nm and $V = 0.3$ V ($V/L \sim 10^7$ V/m), closely corresponds to the result from Fig. 2. This trend is in close agreement with the experimental results (Fig. 1(c)). Cl$^-$ also shows large $\tau$, but does not contribute to the current density at the cathode side due to the extremely low density near the surface. As shown in Fig. 3(b), the response in the current density is obviously caused by the prominent increase and subsequent decrease of Na$^+$ at the surface. Furthermore, the effect of noise tends to be relatively weaker as the molarity increases. This is a reason why the noise is suppressed due to the highly screened surface.

Figure 4(a) shows density distributions of Na$^+$ at $t = 1.0$ $\mu$s. For each concentration, a minimum peak of Na$^+$ is found near the surface. This peak implies that part of the ions tends to adsorb on the electrode surface and the others separate forming density gradients. In the case of Cl$^-$ as shown in Fig. 4(b), the concentration is depleted near the electrode surface and approaches its bulk density as $x$ increases. Due to these distributions, the electrostatic potentials show extremely steep gradients near the electrode surface, as shown in Fig. 4(c). It is found that the cathode surface is strongly screened by Na$^+$ and this tendency is apparent as the molarity increases. In the 100 mM solution, the strength of the electric field is two orders of magnitude different between both ends. Despite the strong screening, however, weak fields also seem to exist widely in the solution, which is inevitable to induce ionic current due to transport of electrolytes. The above discussion can be applied to the anode side, although results may exhibit small differences due to the different diffusion coefficient of Na$^+$ and Cl$^-$. In conclusion, we have reported a combined experimental and theoretical study of electrical currents of electrodes in solution. We have shown that this current is the result of different processes. In particular the long duration of the initial current response is due to the diffusion layer formation where ions respond to the weak electric fields remaining after the rapid screening at the electrode surface. These are relevant for DNA sequencing approaches presently pursued as well as electrochemical capacitors for high energy density storage.

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