Supporting Information for:
Response Time of Nanofluidic Electrochemical Sensors

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A. Multi-potential-step chronoamperometry

Figure S1 shows an experiment complementary to the one of Figure 3: The bottom electrode was kept at 0.5 V instead of 0 V while the potential of the top electrode was stepped. Current transients were observed when the top electrode potential was stepped to the base level of 0 V, which corresponds to diffusion-limited mass transport. The shape of the transient depended on the potential of the top electrode prior to the potential step, the magnitude of the transient fraction is larger for higher starting potentials. Specifically, when the potential of the top electrode was stepped from 0.4 V, 0.45 V and 0.5 V to 0 V, the current increased to 129 nA, 133 nA and 139 nA, respectively.

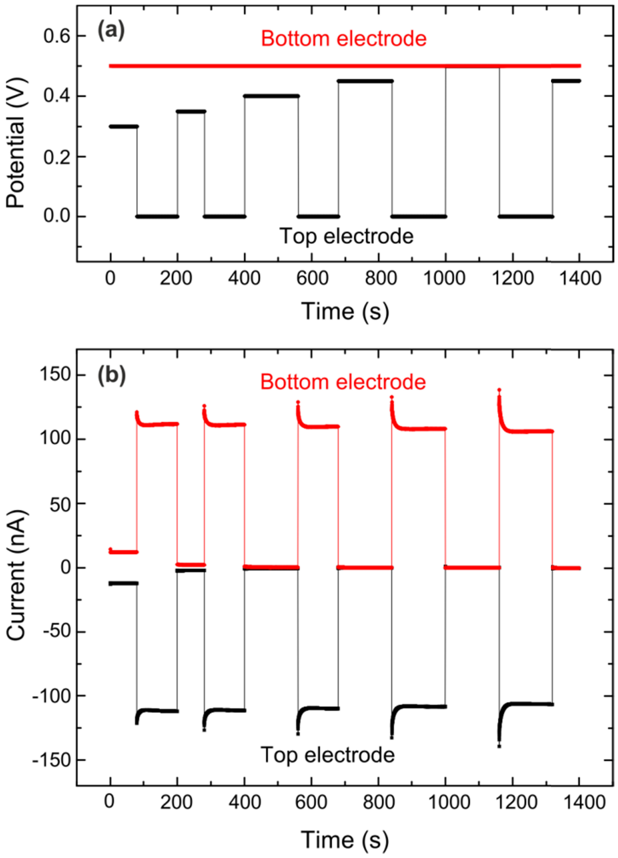

Fig. S1 Multi-potential-step chronoamperometry of a device of type L50H2 filled with an aqueous solution of 1 mM Fc(MOH)$_2$ and 1 M KCl as supporting electrolyte. (a) Potentials applied as a function of time to the top (black) and bottom (red) electrode. (b) Corresponding current-time responses.

B. *RC* charging time of the device

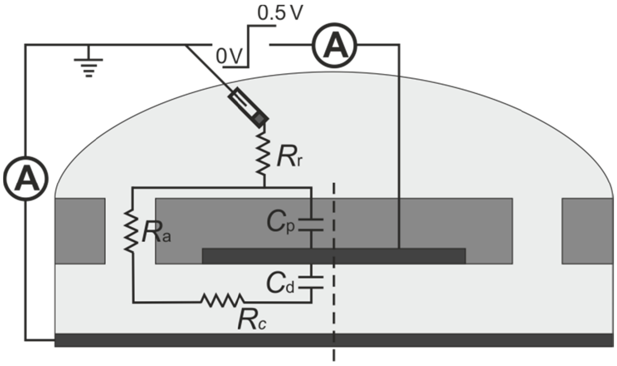

Fig. S2 Equivalent circuit diagram of the nanofluidic system.

Here we estimate the *RC* charging time when stepping the potential of the top electrode (geometry of the device of type L50H2 is used). The equivalent circuit for this case is shown in Figure S2. The various parameters in Figure S2, as well as estimates for their numerical values, are as follows :

C_p	This represents the capacitance between bulk solution and the electrode across its protective passivation layer. The passivation layer consists of 90 nm/325 nm/90 nm thick SiO_2/SiN/SiO_2. The total capacitance is therefore given by the individual capacitances contributed by these three layers connected in series. Using a relative permittivity of $\varepsilon_r = 7$ for PECVD SiN, $\varepsilon_r = 5$ for PECVD SiO_2, and an area A ≈ 1000 μm^2 (including 350 μm^2 for the top electrode itself and about 650 μm^2 for its contacting wire exposed to solution) yields a total capacitance $C_p \approx 0.1$ pF.
C_d	This represents the ionic double layer capacitance. At a given potential, the double layer capacitance per unit area is typically in the range of 10 to 40 μF/cm^2.[†] Using A = 175 μm^2, which is half of the top electrode area (for a symmetric device with two access holes), yields C_d in the range of 18 to 70 pF.
R_a	The resistance of the cylindrical access hole is given by $l/\kappa\pi r^2$ = 16 kΩ, where l = 505 nm is the depth of the access hole, r = 1 μm is its radius, and κ is the conductivity of the solution, which is 10.2 $\Omega^{-1}m^{-1}$ for 1 M KCl at 20°C. The spreading resistance in the vicinity of the entrance hole contributes an additional resistance $1/4\kappa r$ = 25 kΩ, for a total access resistance R_a = 41 kΩ.
R_r	The resistance of the bulk solution, R_r, is dominated by the spreading resistance in the region near the device. A rough estimate is $R_r = 1/4\kappa L$ = 500 Ω, which indicates that it can be neglected.
R_c	The resistance of (half of) the nanochannel, R_c, is equal to $L/\kappa hW$ = 7.6 MΩ, where L = 27 μm is half of the length of the nanochannel, h = 70 nm and W = 5 μm are the height and width of the nanochannel, respectively.

[†] A. J. Bard, L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, Wiley: New York, 2001.

The above indicates that the capacitance of the passivation layer is utterly negligible compared to the double-layer capacitance, despite the additional area relevant for C_p. Similarly, the resistance in series with the double layer capacitance is dominated by the nanochannel itself by virtue of its small cross-sectional area. An upper bound for the dominant RC time constant is therefore estimated as $\tau = (R_r + R_a + R_c)\ C_d = 0.53$ ms. This is orders of magnitude shorter than the transients observed in the experiments, indicating that the latter have a different origin. A corresponding calculation for the bottom electrode yields a similarly short RC time constant.

In addition to estimating the RC time constant, we measured the current response of a device of type L50H1 filled with only supporting electrolyte to the potential steps applied as in Figure 3(a). Keeping the potential of bottom electrode at 0 V, without any redox species present in the nanochannel, positive or negative current spikes were observed at the top electrode when its potential was stepped upward or downward, respectively. The transients lasted ~0.2 s, significantly shorter than those observed in the experiments with redox molecules. This shows that the slow response in the latter experiments was not caused by charging effects. To understand the difference between the observed response and the numerical estimate of the RC time given above, note that besides RC charging, dielectric relaxation of the passivation material (SiO_2/SiN/SiO_2)[1,2,3] also contributes to (and in fact dominates) the measured current.

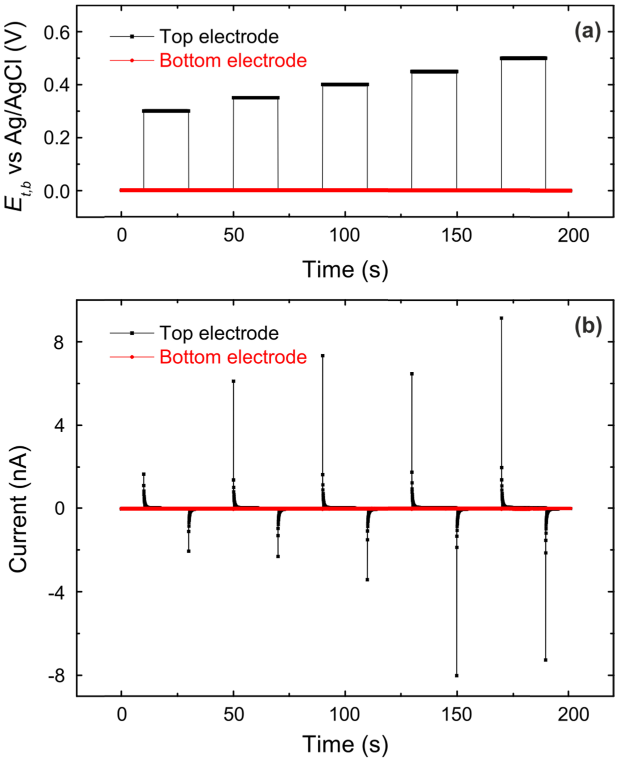

Fig. S3 Transient response of a device of type L50H1 filled with only supporting electrolyte of 1 M KCl. (a) Potentials applied as a function of time to the top (black) and bottom (red) electrode. (b) Corresponding current-time responses.

[1] D. Krapf, M. Wu, R. M. M. Smeets, H. W. Zandbergen, C. Dekker, and S. G. Lemay, *Nano Lett.*, 2006, **6**(1), 105-109.

[2] A. K. Jonscher, *Nature*, 1977, **267**, 673-679.

[3] S. Westerlund, L. Ekstam, *IEEE Trans. Dielectr. Insul.*, 1994, **1**(5), 826-839.

C. Determination of the transient response

We obtained the expression for the transient response of the current, equation (3), as a purely phenomenological fit to the numerically determined diffusion of molecules into the channel.

The one-dimensional diffusion equation,

$$\frac{\partial c(x,t)}{\partial t} = D\frac{\partial^2 c(x,t)}{\partial x^2},$$

was solved numerically along the length L of a nanochannel using the following initial and boundary conditions:
– Initially, no redox active molecules are present in the channel. Hence, the starting condition for $t = 0$ is

$$c(x, 0) = 0 \text{ for } 0 < x < L.$$

– The bulk concentration at the edge of the nanochannel that is connected to the reservoir is kept constant at c_b for all times t:

$$c(x = 0, t) = c(x = L, t) = c_b.$$

– For $t > 0$, molecules start to diffuse into the nanochannel from both ends until the concentration equilibrates to $c(x, t) = c_b$ at time $t \rightarrow \infty$.

The total number of molecules present in the channel was determined by integrating the numerical solution $c(x, t)$ along the channel length for all time steps t:

$$N(t) = \int_0^L c(x,t)\mathrm{d}x$$

This numerical solution $N(t)$ was phenomenologically fitted to the analytical expression

$$N(t) = c_b\, L \operatorname{erf}\left(2.97\,\left(\frac{D\,t}{L^2}\right)^{0.6}\right),$$

which does not deviate more than 3% from the numerical solution for all time t (Figure S3).

If molecules are initially present in the nanochannel, i.e. $N(t = 0) \neq c_b L$, the expression for $N(t)$ is modified to

$$N(t) = N(0) + \left(c_b L - N(0)\right) \operatorname{erf}\left(2.97\,\left(\frac{D\,t}{L^2}\right)^{0.6}\right).$$

Since the faradaic current is proportional to the concentration of molecules in the channel, the current $i(t)$ can be be expressed as

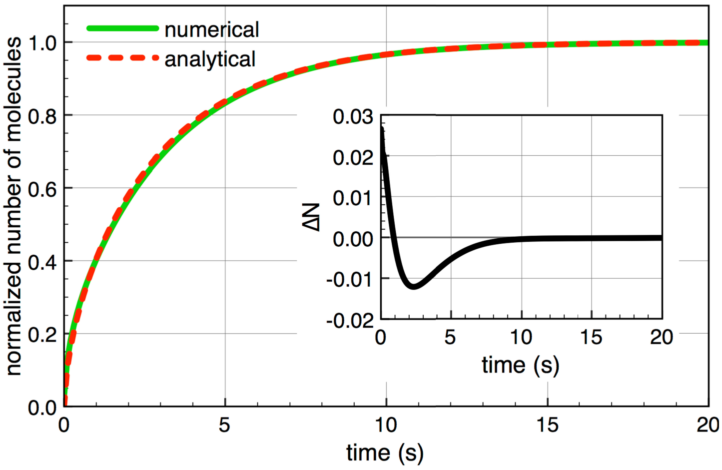

Fig. S4 Comparison of the normalized numerical solution for *N(t)* (green line) and the analytical expression (dashed red line) for a 10 µm long device with two access holes using $D_{\mathrm{eff}} = 8 \times 10^{-7}$ cm²/s for both curves. Inset: Difference of the numerical solution and analytical expression.

$$i(t) = i(0) + \left(i_{ss} - i(0)\right) \operatorname{erf}\left(2.97 \left(\frac{D\,t}{L^2}\right)^{0.6}\right),$$

where $i(0)$ is the current at $t = 0$ and i_{ss} is the steady-state current.

For the case of a device with one access hole, molecules can only diffuse into the nanochannel from one end. This corresponds to starting conditions

$$c(x, 0) = 0 \text{ for } x > 0,$$

$$c(x, 0) = c_r \text{ for } x \leq 0,$$

and the boundary conditions

$$c(x=0, t) = c_b,$$

$$\frac{\partial c(x=L,t)}{\partial x} = 0.$$

The numerical solution of the diffusion equation under these conditions is well described by

$$N(t) = c_b\, L \operatorname{erf}\left(2.97 \times 0.60 \left(\frac{D\,t}{L^2}\right)^{0.6}\right),$$

and the solution for the diffusion with $N(0)$ molecules present in the channel at $t = 0$ is

$$N(t) = N(0) + (c_b L - N(0)) \operatorname{erf}\left(2.97 \times 0.60 \left(\frac{D\,t}{L^2}\right)^{0.6}\right).$$

Correspondingly, the current is equal to

$$i(t) = i(0) + \left(i_{ss} - i(0)\right) \operatorname{erf}\left(2.97 \times 0.60 \left(\frac{D\,t}{L^2}\right)^{0.6}\right).$$

D. Multi-potential-step chronoamperometry exhibiting opposite tendencies

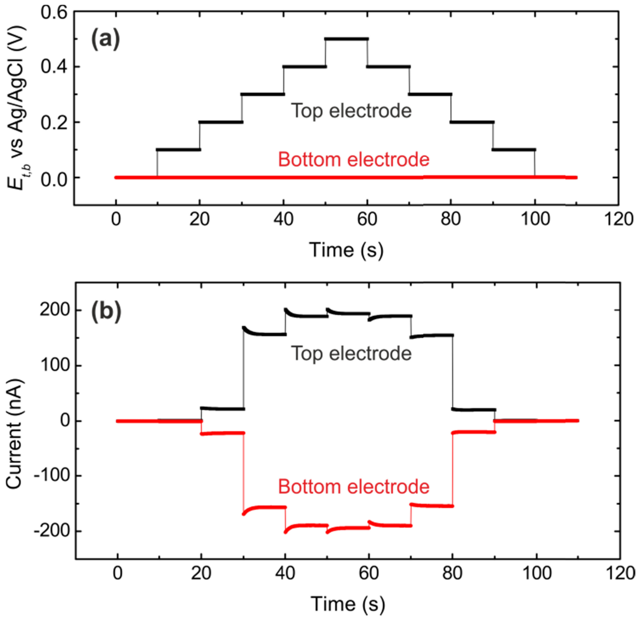

Fig. S5 Multi-potential-step chronoamperometry of a device of type L50H1 filled with an aqueous solution of 1.5 mM $Fc(MOH)_2$ and 1 M KCl as supporting electrolyte exhibiting tendencies opposite to Figure 2 and 3. (a) Potentials applied as a function of time to the top (black) and bottom (red) electrode. (b) Corresponding current-time response.

Occasionally it was observed that a device whose Cr sacrificial layer was freshly etched exhibited opposite tendencies to those shown in Figure 2 and 3, as shown in Figure S4. When the potential of the oxidizing electrode was stepped up while that of the reducing electrode was maintained at 0 V, the current jumped to a value higher than i_{ss} and gradually returned to the steady-state value; the current fell below i_{ss} when the potential was stepped downwards, then increased again during the transient.