Electronic Supplementary Material (ESI) for Soft Matter.

Supplementary Information

Improved ionic current rectification utilizing cylindrical nanochannels coated with polyelectrolyte layers of non-uniform thickness

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Mesh-independence analysis

To demonstrate that the results presented in the present study are mesh-independent, the values of I for various bulk ionic concentrations, nanochannel radii, and concentrations of PEL fixed charges at $V_{app} = -1\text{V}$ calculated by different mesh sizes are listed in Table S1. As is clearly visible in this table, the maximum relative difference between the calculated ionic currents considering different mesh sizes is less than 10^{-4}. This shows that utilizing 104741 mesh elements is sufficient to obtain mesh-independent results.

Table S1. Ionic currents (in the unit of nA) for various bulk ionic concentrations, concentrations of PEL fixed charges, and channel radii calculated by different mesh sizes at $V_{app} = -1$ V and $L = 1000$ nm.

		$R = 10$ nm		$R = 50$ nm	
		Number of mesh elements		Number of mesh elements	
		66112	86274	77424	104741
$\sigma_{PEL} = 1\ \text{mol/m}^3$	$c_0 = 0.1\ \text{mol/m}^3$	-0.0021402	-0.0021402	-0.038607	-0.038606
	$c_0 = 100\ \text{mol/m}^3$	-0.47042	-0.47042	-11.037	-11.037
$\sigma_{PEL} = 20\ \text{mol/m}^3$	$c_0 = 0.1\ \text{mol/m}^3$	-0.0075528	-0.0075528	-0.041946	-0.041945
	$c_0 = 100\ \text{mol/m}^3$	-0.61822	-0.61821	-14.037	-14.037

Model validation

In order to validate the employed numerical model, the obtained results are here compared with the available literature data. Since there is no available data in the literature about the ionic current rectification in the nanoarchitecture proposed in the present study, the employed numerical method is used to solve the governing equations in conical geometry, which has already been studied. In the following, the values of conductance, given as $G = I/V_{app}$, obtained for a conical nanochannel of charged inner surface filled with KCl solution are compared with the corresponding values obtained by the analytical solutions proposed by Steinbock et al. [S1]. The considered conical nanochannel has the following characteristics: base radius, tip radius, and length of nanochannel are equal to 68 nm, 17 nm, and 1000 nm, respectively. Moreover, the surface charge density is set based on the values given in the inset of Fig. 3A in the study of Steinbock et al. [S1], and the conductance is evaluated at a potential bias of -0.8 V, which is consistent with the results provided in the mentioned study. The comparison, performed in Fig. S1 at different bulk ionic concentrations, reveals a good agreement between the results. The deviation between the results at low bulk ionic concentrations may be attributed to the effects of ion concentration polarization, which is important at low c_0 but is neglected in the solutions of Steinbock et al. [S1].

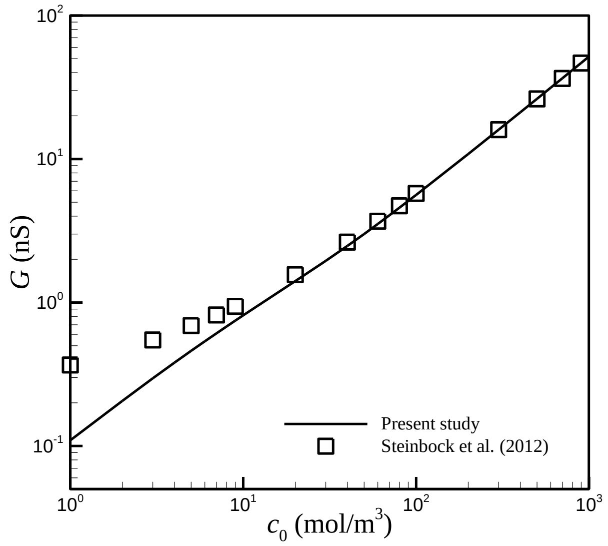

Fig. S1. Comparison between the values of conductance obtained in the present study for a conical nanochannel with a charged inner surface and the corresponding values calculated using the analytical method proposed by Steinbock et al. [S1] at various bulk ionic concentrations.

In the next validation analysis, our developed model is employed to calculate the rectification factors of a conical nanochannel modified by a PEL of 5 nm thickness, which was considered by Hsu et al. [S2]. The electrolyte solution is again KCl while the concentration of fixed charges and base radius, tip radius, and length of the conical nanochannel are, respectively, $116.2\ \mathrm{mol/m^3}$, 98 nm, 10 nm, and 1000 nm. The rectification factors obtained at various bulk ionic concentrations are compared with the numerical results of Hsu et al. [S2] in Fig. S2. As observed, an excellent agreement exists between the results.

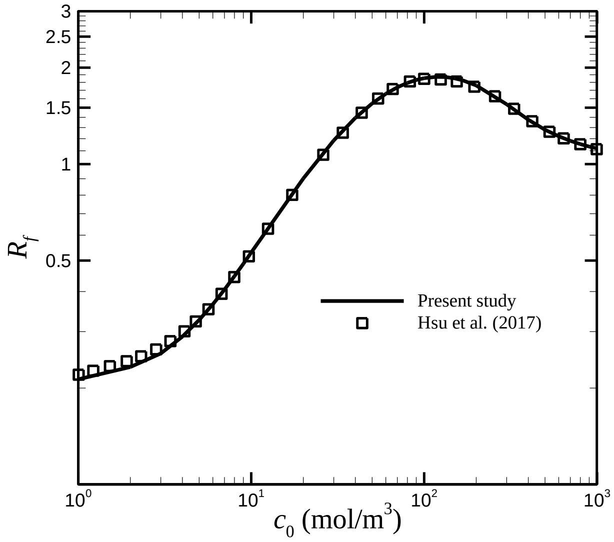

Fig. S2. Comparison between the rectification factors obtained for a conical nanochannel coated with a uniform PEL in the present study and the corresponding numerical results reported by Hsu et al. [S2] at various bulk ionic concentrations.

Ion flux under a constant electric field between reservoirs of given concentrations

Consider charged particles of valence $Z = 1$ in one spatial dimension in an electrostatic potential $\psi(z)$ that varies linearly between $z = 0$ and $z = z_1$. We set $\psi(z = 0) = 0$ and $\psi(z = z_1) = \psi_H$. The particle concentrations at the domain boundaries are given as $c(z = 0) = c_L$ and $c(z = z_1) = c_H$. The particle flux is given by the Nernst-Planck equation. In the absence of a flow field, we obtain

$$J = -D\frac{\mathrm{d}c}{\mathrm{d}z} - \eta c\frac{\mathrm{d}\psi}{\mathrm{d}z}, \tag{S1}$$

where $\eta = FD/\bar{R}T$ denotes the electrophoretic mobility. In a steady-state situation, the flux must be constant, i.e.

$$D\frac{\mathrm{d}c}{\mathrm{d}z} + \eta c\frac{\psi_H}{z_1} = -J_0. \tag{S2}$$

The general solution of this equation is given by

$$c(z) = \alpha\exp\left(-\frac{\eta\psi_H}{Dz_1}z\right) - \frac{z_1}{\eta\psi_H}J_0, \tag{S3}$$

with a coefficient α. After determining the unknown coefficient via the boundary conditions, we obtain

$$J_0 = \frac{\eta\psi_H}{z_1}\left[\frac{c_L - c_H}{1 - \exp(-\eta\psi_H/D)} - c_L\right]. \tag{S4}$$

From that, Eq. (8) of the main text is obtained by equating the ion currents in the two parts of the model domain.

Ion flux in a model potential consisting of two sections with constant electric fields

From Eq. (8) of the main text, the unknown ion concentration at the point of minimal electrostatic potential can be determined as

$$c_J = c_0 \frac{\frac{V_1}{z_1}\frac{1}{1-\exp(-V_1\eta/D)} + \frac{V_2}{z_2}\frac{1}{1-\exp(-V_2\eta/D)}}{\frac{V_1}{z_1}\frac{\exp(-V_1\eta/D)}{1-\exp(-V_1\eta/D)} + \frac{V_2}{z_2}\frac{\exp(-V_2\eta/D)}{1-\exp(-V_2\eta/D)}}. \tag{S5}$$

Applying Eq. (S4) to either of the two sections in Figure 4b and substituting for c_J from Eq. (S5), Eq. (9) of the main text is obtained after some algebra.

Rectification behavior of the model potential

To study the rectification behavior of the model potential consisting of two sections with constant electric fields, we examine under which conditions the current in one direction is larger than the current in the opposite direction. To this end, we consider the inequality $-J(V_1, V_2) > J(V_2, V_1)$. Utilizing Eq. (9), one can show, after some straightforward algebra, that

$$-J(V_1,V_2) > J(V_2,V_1) \Leftrightarrow (z_1 - z_2)\left\{\frac{1}{V_1}\exp\left(\frac{-V_2\eta}{D}\right)\left[1-\exp\left(\frac{-V_1\eta}{D}\right)\right] - \frac{1}{V_2}\exp\left(\frac{-V_1\eta}{D}\right)\left[1-\exp\left(\frac{-V_2\eta}{D}\right)\right]\right\} < 0. \tag{S6}$$

In the following, without loss of generality we assume that $V_2 > V_1$. Further, we consider a potential difference small compared to the thermal potential, i.e. $V_2 = V_1 + \delta$, with $F\delta/(\bar{R}T) \ll 1$. Then, via Taylor expansion of $\exp(-\delta\eta/D)$ up to first order in the argument, we obtain for the inequality Eq. (S6)

$$(z_1 - z_2)\left\{\frac{1}{V_1}\exp\left(\frac{-V_2\eta}{D}\right)\left[1-\exp\left(\frac{-V_1\eta}{D}\right)\right] - \frac{1}{V_2}\exp\left(\frac{-V_1\eta}{D}\right)\left[1-\exp\left(\frac{-V_2\eta}{D}\right)\right]\right\} \approx \delta(z_2 - z_1)\left[\frac{\exp\left(-\frac{V_1\eta}{D}\right)}{V_1}\right]^2\left[1 - \frac{1-\frac{V_1\eta}{D}}{\exp\left(-\frac{V_1\eta}{D}\right)}\right] < 0. \tag{S7}$$

Since $1 - V_1\,\eta/D \; \leq \exp(-V_1\,\eta/D)$, the inequality becomes

$$-J(V_1,V_2) > J(V_2,V_1) \Leftrightarrow z_2 < z_1. \tag{S8}$$

This result is in qualitative agreement with the rectification behavior obtained in the numerical simulations.

References

S1. L. J. Steinbock, A. Lucas, O. Otto and U. F. Keyser, *Electrophoresis*, 2012, **33**, 3480-3487.

S2. J.-P. Hsu, H.-H. Wu, C.-Y. Lin and S. Tseng, *Physical Chemistry Chemical Physics*, 2017, **19**, 5351-5360.