SUPPORTING INFORMATION

Strong Electroosmotic Coupling Dominates Ion Conductance of 1.5 Nanometer Diameter Carbon Nanotube Porins

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This supporting information file includes a methods section, two figures, and two tables.
Methods

Continuum modeling using coupled Navier-Stokes and Poisson-Nernst-Planck equations.

The Poisson equation is given by:

\[
\nabla \cdot (\varepsilon \nabla \phi) = -\frac{\rho_e}{\varepsilon_0} \tag{S1}
\]

where \( \varepsilon \) is the relative permittivity of the medium, \( \varepsilon_0 \ (8.85 \times 10^{-12} \text{ C}^2/\text{N.m}^2) \) is the permittivity of the vacuum, \( \phi \) is the electrical potential, and \( \rho_e \) is the net ionic space charge density. \( \rho_e \) is defined as,

\[
\rho_e = F \left( \sum_{i=1}^{m} z_i c_i \right) \tag{S2}
\]

where \( F \) is the Faraday constant, \( m \) is the total number of the ionic species, \( z_i \) is the valence of species \( i \), and \( c_i \) is the concentration of species \( i \).

The transport of each ionic species is given by,

\[
\frac{\partial c_i}{\partial t} = -\nabla \cdot \Gamma_i \tag{S3}
\]

where \( \Gamma_i \) is the total ionic flux vector of species \( i \) and is defined as,

\[
\Gamma_i = -D_i \nabla c_i - \Omega_i z_i F c_i \nabla \phi + c_i \mathbf{u} \tag{S4}
\]

where \( D_i \) is the diffusion constant of species \( i \), \( \Omega_i \) is the ionic mobility, and \( \mathbf{u} \) is the velocity of the fluid. The ionic mobility is related to the diffusion constant by the Einstein's relation, \( \Omega_i = D_i/RT \), where \( R \) is the ideal gas constant, and \( T \) is the thermodynamic temperature. The three terms on the right-hand side of Eq. (S4) describe, respectively, the ionic diffusion, electrical migration, and convective transport. Eqs. (S1-S4) represent the coupled Poisson-Nernst-Planck (PNP) model for electrochemical transport of ionic species in the absence of the fluid velocity (e.g. \( \mathbf{u} = 0 \)).

The electroosmotic flow is described by the incompressible Navier-Stokes and the continuity equation which are given by,

\[
\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} = -\nabla p + \nu \nabla^2 \mathbf{u} + \frac{\rho_e E}{\rho} \tag{S5}
\]

\[
\nabla \cdot \mathbf{u} = 0 \tag{S6}
\]

where \( p \) is the pressure, \( \rho \) and \( \nu \) are, respectively, the density and the kinematic viscosity of the fluid, and \( E \) (= \( -\nabla \phi \)) is the electric field. The PNP equations are coupled to the NS equations by the \( \rho_e E \) term in Eq. (S5). Eqs. (S1) – (S6) represent the fully coupled NS-PNP equations. The contribution of electroosmotic flow to ionic transport can be neglected by not including the NS equations. The total ionic current, \( I \), over the cross-section area of the CNT, \( A \), is computed using the expression,

\[
I = \int_A \sum_{i=1}^{m} z_i F \Gamma_i \, dA. \tag{S7}
\]

The boundary conditions at the CNT walls are given by,

\[
\frac{\partial \mathbf{u}}{\partial n} = 0 \tag{S8}
\]

\[
\mathbf{n} \cdot \Gamma_i = 0 \tag{S9}
\]

\[
\mathbf{n} \cdot \nabla \phi = \frac{\sigma}{\varepsilon_0 \varepsilon_r} \tag{S10}
\]
where \( n \) denotes the unit outward normal vector to the CNT, and \( \sigma \) is the imposed surface charge density. Eqs. (S8) – (S10) correspond to slip velocity condition, zero normal flux of each species to ensure no electric leakage, and an imposed surface charge, respectively. For the conductance simulations, the boundary conditions at both ends of the reservoirs are given by,

\[
\begin{align*}
\phi &= V^{DC}, \quad c_i = c_s, \quad n \cdot \nabla u = 0, \quad p = 0 \\
\phi &= 0, \quad c_i = c_s, \quad n \cdot \nabla u = 0, \quad p = 0
\end{align*}
\]  
(S11)

\[
\begin{align*}
\phi &= 0, \quad c_i = c_s, \quad n \cdot \nabla u = 0, \quad p = 0 \\
\phi &= 0, \quad c_i = c_s, \quad n \cdot \nabla u = 0, \quad p = 0
\end{align*}
\]  
(S12)

where \( V^{DC} \) is the applied bias, and \( c_s \) is the ionic concentration. For the selectivity simulations, the boundary conditions at both ends of the reservoirs are given by,

\[
\begin{align*}
\phi &= 0, \quad c_i = c_{\max}, \quad n \cdot \nabla u = 0, \quad p = 0 \\
\phi &= 0, \quad c_i = c_{\min}, \quad n \cdot \nabla u = 0, \quad p = 0
\end{align*}
\]  
(S13)

\[
\begin{align*}
\phi &= 0, \quad c_i = c_{\max}, \quad n \cdot \nabla u = 0, \quad p = 0 \\
\phi &= 0, \quad c_i = c_{\min}, \quad n \cdot \nabla u = 0, \quad p = 0
\end{align*}
\]  
(S14)

The physical properties that are used in solving the NS-PNP are provided in the method section of the main manuscript.

References

**Figure S1.** Meshing of the continuum computational domain. The axisymmetric geometry has two reservoirs ($L = 1 \mu m \times d = 1 \mu m$) and a CNT ($L = 10$ nm $\times d = 1.5$ nm) in the middle.
Figure S2. Mean squared displacement of potassium (red) and chloride (blue) ions as obtained from molecular dynamics simulations inside CNT (11,11).
Data fitting to the CNT pore conductance model in the low surface charge regime. Measured CNTP conductance was fitted to Eq 1 in the main text (see main text for the model parameter descriptions).

Table S1. Fitted parameters of the Equation 1 for the wCNTP conductance at pH=7.5 and pH=3.

<table>
<thead>
<tr>
<th>Model parameters</th>
<th>$\bar{b}$</th>
<th>$\sigma^*/2h$</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH=7.5</td>
<td>1.5 ± 0.8</td>
<td>0.052 ± 0.011</td>
</tr>
<tr>
<td>pH=3</td>
<td>25.5 ± 10.0</td>
<td>0.0019 ± 0.0005</td>
</tr>
</tbody>
</table>

Table S2. The Lennard-Jones parameters and charges. All carbon atoms were fixed, and the surface charge density was imposed only the carbon atoms of the CNT. Lorentz-Berthelot rule was used to obtain the interactions between the unlisted pairs.

<table>
<thead>
<tr>
<th>Interaction</th>
<th>$\sigma$ [Å]</th>
<th>$\epsilon$ [kcal/mol]</th>
<th>Charge</th>
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</thead>
<tbody>
<tr>
<td>O-O$^2$</td>
<td>3.1656</td>
<td>0.1554</td>
<td>-0.8476</td>
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<td>H-H$^2$</td>
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<td>0.0000</td>
<td>0.4238</td>
</tr>
<tr>
<td>Cl-Cl$^2$</td>
<td>4.8305</td>
<td>0.0128</td>
<td>-1.0000</td>
</tr>
<tr>
<td>K-K$^2$</td>
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<td>0.4300</td>
<td>1.0000</td>
</tr>
<tr>
<td>C-O$^1$</td>
<td>3.4360</td>
<td>0.0850</td>
<td>-</td>
</tr>
<tr>
<td>C-H$^1$</td>
<td>2.6900</td>
<td>0.0383</td>
<td>-</td>
</tr>
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