Electronic Supplementary Information (ESI)

Gate Modulation of Proton Transport in a Nanopore

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Detailed Derivation of eqn (3) and (5) in the Main Text

The electrical potential, ϕ, within the liquid phase ($0 < r < R_n - \delta_s$) can be described by

$$\frac{1}{r}\frac{d}{dr}\left(r\frac{d\phi}{dr}\right) = -\frac{\rho_e}{\varepsilon_f}, \tag{R1}$$

where ρ_e is the mobile space charge density and can be expressed as

$$\rho_e = \sum_{i=1}^{4} F z_i C_{ic} \exp\left[\frac{z_i F\left(\phi_c - \phi\right)}{RT}\right]. \tag{R2}$$

In the above, ϕ_c is the electric potential at the center of the nanopore, and C_{ic} is the concentration of the i^{th} ionic species at the center of the nanopore, which can be described by,

$$C_{ic} = C_{i0} \exp\left[-\frac{z_i F\left(\phi_c - \phi_0\right)}{RT}\right]. \tag{R3}$$

Here ϕ_0 is the reference potential in the reservoirs far away from the charged nanopore and typically vanishes (i.e., $\phi_0 = 0$). Substituting eqn (R3) and (R2) into eqn (R1) gets

$$\frac{1}{r}\frac{d}{dr}\left(r\frac{d\phi}{dr}\right) = -\frac{1}{\varepsilon_f}\sum_{i=1}^{4} F z_i C_{i0} \exp\left(-\frac{z_i F\phi}{RT}\right), \tag{R4}$$

which is the eqn (3) in the main text. Suppose that $C_{t0} = C_{10} + C_{40} = C_{20} + C_{30}$ is the bulk concentration of net cations (or anions). Due to the electroneutrality of bulk solution (i.e., $C_{t0} = C_{10} + C_{40} = C_{20} + C_{30}$) in the reservoirs far away from the charged nanopore, expanding the right term of eqn (R4) yields

$$
\begin{aligned}
&-\frac{1}{\varepsilon_f}\sum_{i=1}^{4} F z_i C_{i0}\exp\left(-\frac{z_i F\phi}{RT}\right)\\
&=-\frac{F}{\varepsilon_f}\left[z_1 C_{10}\exp\left(-\frac{z_1 F\phi}{RT}\right)+z_2 C_{20}\exp\left(-\frac{z_2 F\phi}{RT}\right)+z_3 C_{30}\exp\left(-\frac{z_3 F\phi}{RT}\right)+z_4 C_{40}\exp\left(-\frac{z_4 F\phi}{RT}\right)\right]\\
&=-\frac{zF}{\varepsilon_f}\left[C_{10}\exp\left(-\frac{zF\phi}{RT}\right)-C_{20}\exp\left(\frac{zF\phi}{RT}\right)-C_{30}\exp\left(\frac{zF\phi}{RT}\right)+C_{40}\exp\left(-\frac{zF\phi}{RT}\right)\right]\\
&=\frac{zF}{\varepsilon_f}\left[\left(C_{20}+C_{30}\right)\exp\left(\frac{zF\phi}{RT}\right)-\left(C_{10}+C_{40}\right)\exp\left(-\frac{zF\phi}{RT}\right)\right]\\
&=\frac{2zFC_{t0}}{\varepsilon_f}\left[\frac{\exp\left(\frac{zF\phi}{RT}\right)-\exp\left(-\frac{zF\phi}{RT}\right)}{2}\right]\\
&=\left(\frac{RT}{zF}\right)\left(\frac{2z^2F^2C_{t0}}{\varepsilon_f RT}\right)\sinh\left(\frac{zF\phi}{RT}\right)\\
&=\frac{RT\kappa^2}{zF}\sinh\left(\frac{zF\phi}{RT}\right)
\end{aligned}
\quad , \text{(R5)}
$$

where $z = z_1 = -z_2 = -z_3 = z_4$ and $\kappa^{-1} = \left(\varepsilon_f RT / 2z^2F^2C_{t0}\right)^{1/2}$ is the Debye length. By substituting eqn (R5) into eqn (R4), we obtain eqn (5) in the main text,

$$
\frac{1}{r}\frac{d}{dr}\left(r\frac{d\phi}{dr}\right)=\frac{RT\kappa^2}{zF}\sinh\left(\frac{zF\phi}{RT}\right). \quad \text{(R6)}
$$

Gate Modulation of the Zeta Potential of the nanopore

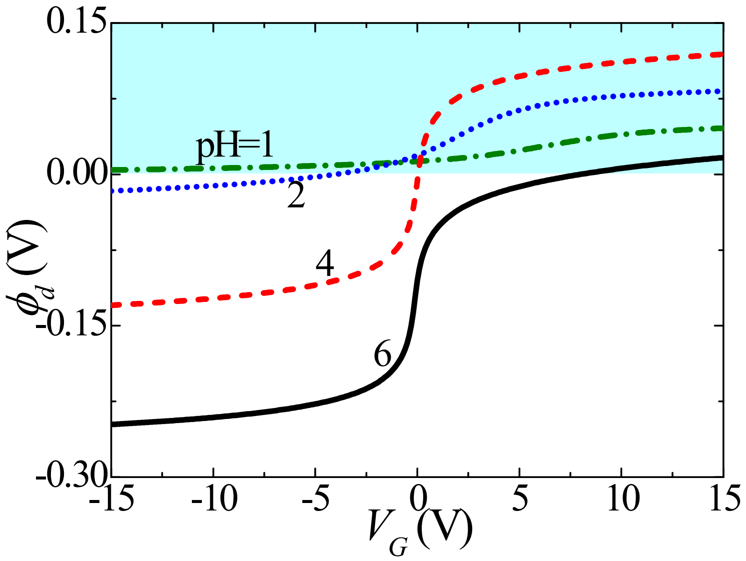

Figure S1. Gate modulation of the zeta potential, ϕ_d, of the nanopore as a function of V_G for various pHs without background salt ($C_{salt} = 0$ mM). The blue region highlights where the modulated ϕ_d is positive.

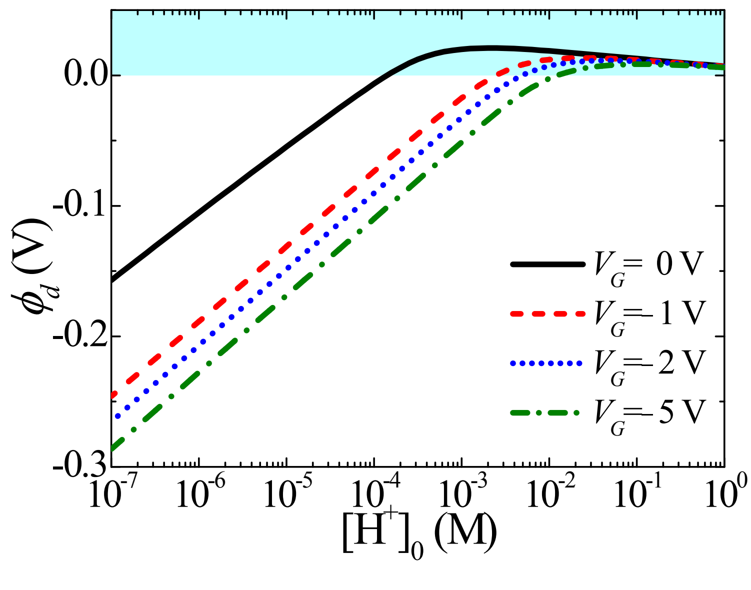

Figure S2. Gate modulation of the zeta potential, ϕ_d, of the nanopore as a function of the molar concentration of protons, $[H^+]_0$, for various levels of V_G without background salt ($C_{salt} = 0$ mM). The blue region highlights where the modulated ϕ_d is positive.

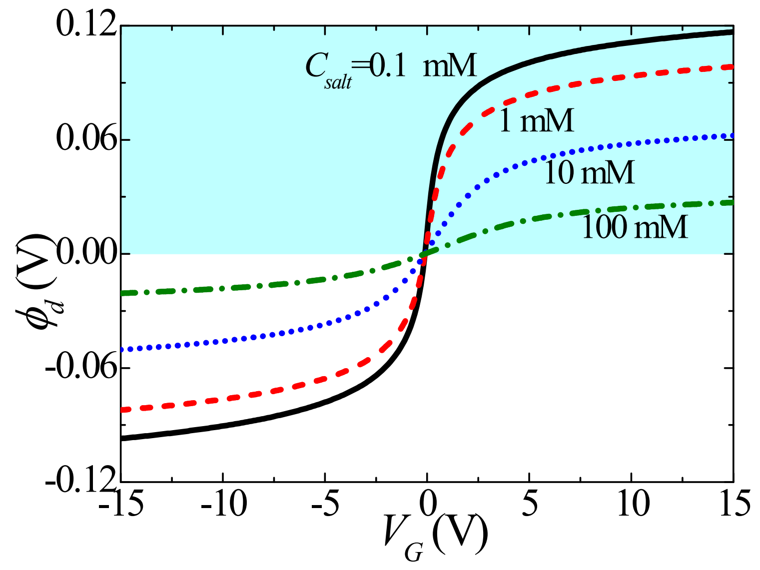

Figure S3. Gate modulation of the zeta potential, ϕ_d, of the nanopore as a function of V_G for various background salt concentrations C_{salt} at $\mathrm{pH} = 3.5$. The blue region highlights where the modulated ϕ_d is positive.

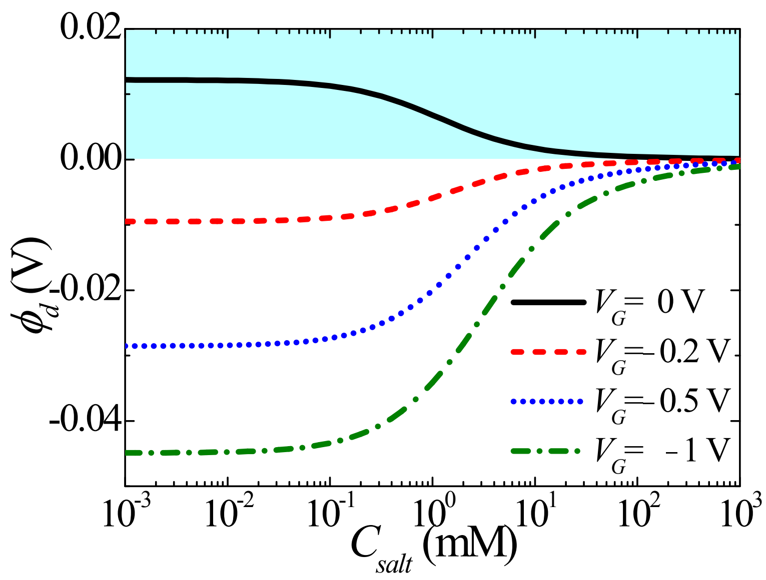

Figure S4. Gate modulation of the zeta potential, ϕ_d, of the nanopore as a function of the background salt concentration C_{salt} for various levels of V_G at $\mathrm{pH} = 3.5$. The blue region highlights where the modulated ϕ_d is positive.