

1 **Supporting Information**

2 **Electrokinetic Behavior of Conical Nanopores Functionalized with Two Polyelectrolyte**
3 **Layers: Effect of pH Gradient**

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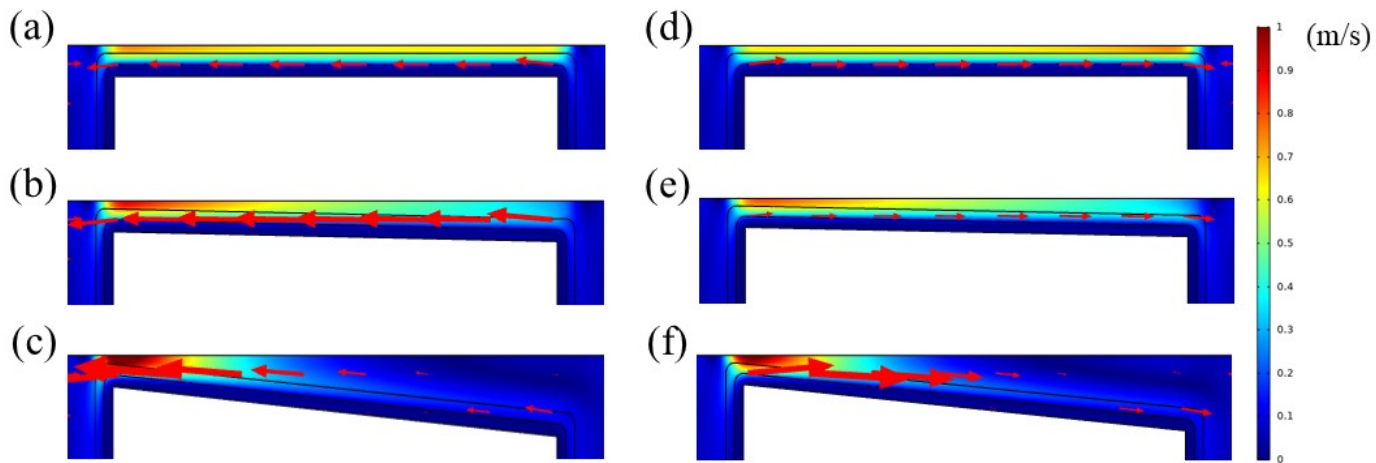
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1 In our study, COMSOL Multiphysics (version 5.4) is used for solving these nonlinear, coupled
 2 governing equations numerically, subject to boundary conditions assumed. The applicability of model
 3 we adopted is verified by fitting the experimental data of Ma *et al.*,¹ where the ionic current through
 4 the polyethylene terephthalate (PET) conical nanopore with modifying double polyelectrolyte (PE)
 5 layer, poly(acrylic acid) (PAA) and poly-L-lysine (PLL), at various level of applied potential bias
 6 (V_{applied}), the half cone angle (θ), and pH gradient applied was recorded.

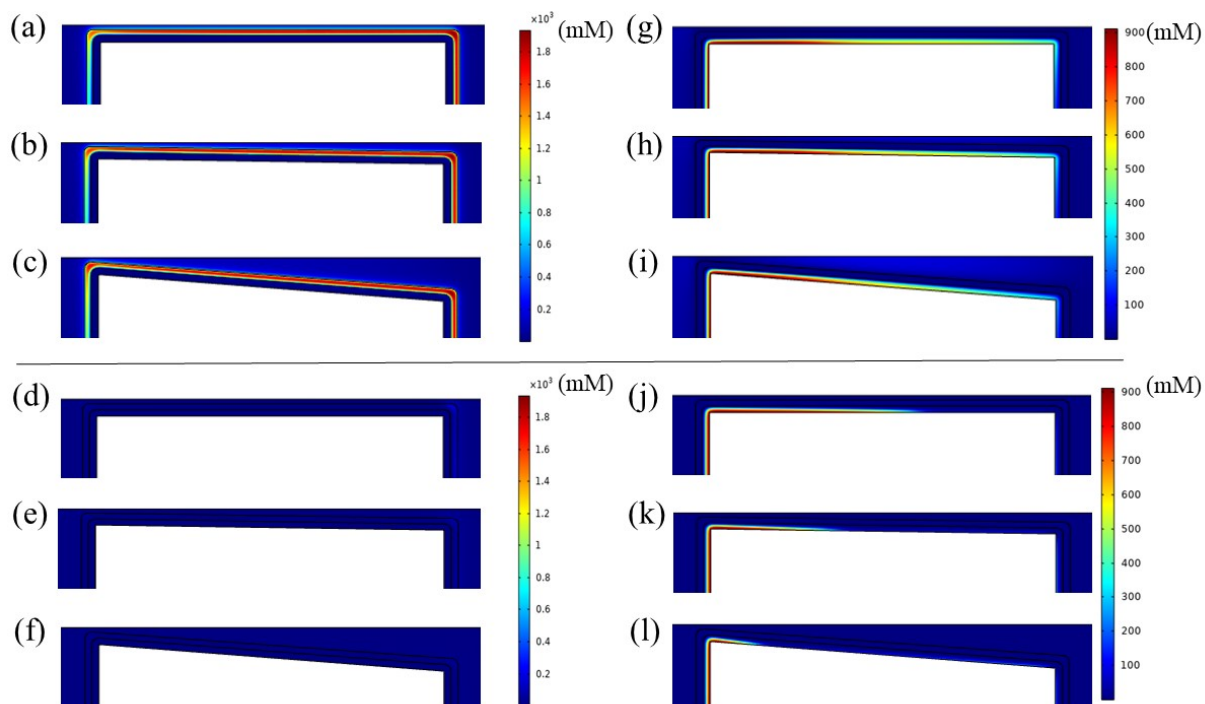
7 S1. Two PE layers



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9 **Fig. S1** Profiles of the flow field in nanopore for various levels of θ at 1 mM NaCl. (a)-(c):
 10 $\text{pH}_i/\text{pH}_b=3/11$, $V_{\text{applied}}=+1$ V, and the levels of θ are 0° , 1° , and 5° , respectively; (d)-(f): $\text{pH}_i/\text{pH}_b=11/3$,
 11 $V_{\text{applied}}=-1$ V, and the levels of θ are 0° , 1° , and 5° , respectively. For the case where $\text{p}K_A=3$ (PAA),
 12 $\text{p}K_B=10$ (PLL), $\Gamma_{A,0} = 2 \times 10^8$ C m⁻³, and $\Gamma_{B,0} = 9.6 \times 10^7$ C m⁻³.

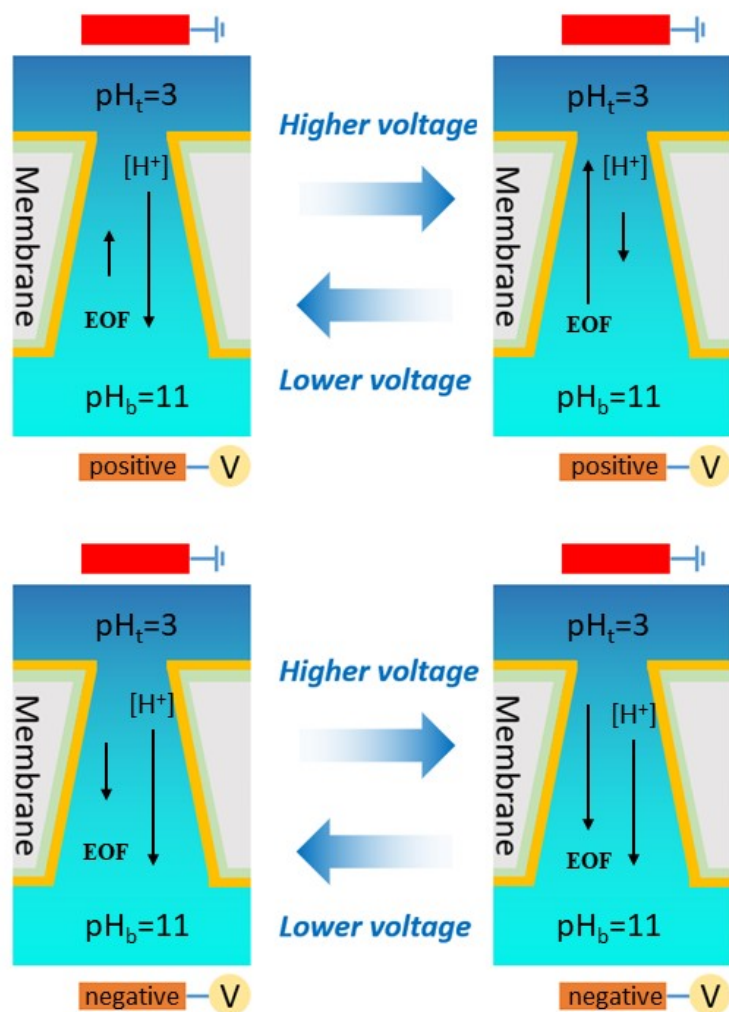
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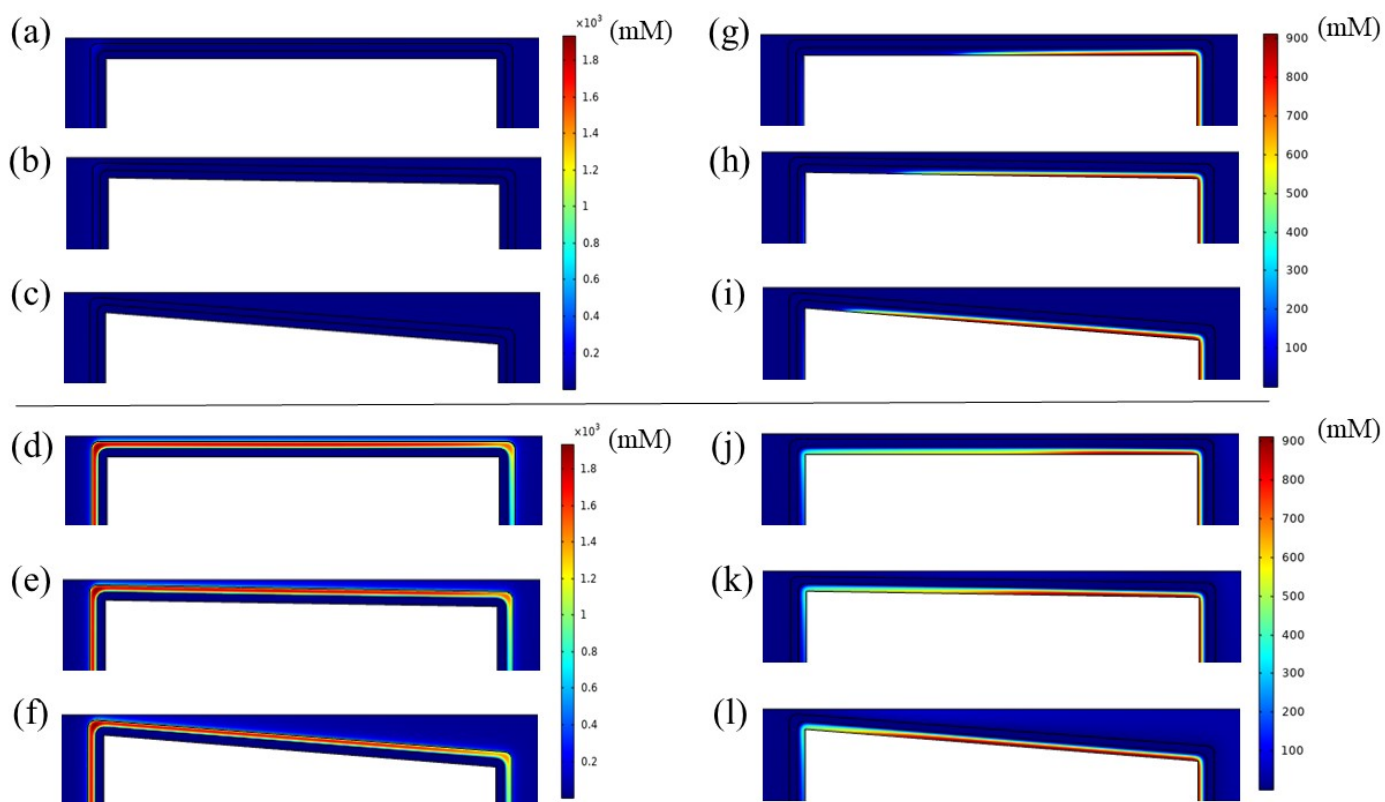
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2 **Fig. S2** Axial variation of concentration for various levels of θ at 1 mM NaCl. (a)-(f): concentration
 3 profiles for cations (Na^+ and H^+), and the levels of θ are 0° , 1° , 5° , 0° , 1° , and 5° , respectively; (g)-(l):
 4 concentration profiles for anions (Cl^- and OH^-), and the levels of θ are 0° , 1° , 5° , 0° , 1° , and 5° ,
 5 respectively. (a)-(c) and (g)-(i): $V_{\text{applied}} = +1$ V; (d)-(f) and (j)-(l): $V_{\text{applied}} = -1$ V. For the case where
 6 $\text{pH}_t/\text{pH}_b = 3/11$, $\text{p}K_A = 3$ (PAA), $\text{p}K_B = 10$ (PLL), $\Gamma_{A,0} = 2 \times 10^8 \text{ C m}^{-3}$, and $\Gamma_{B,0} = 9.6 \times 10^7 \text{ C m}^{-3}$.

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 2 **Fig. S3** Schematic representation of the competition and synergy between EOF and the $[H^+]$ induced
 3 by ∇pH at different levels of V_{applied} at $pH_t/pH_b=3/11$.
 4

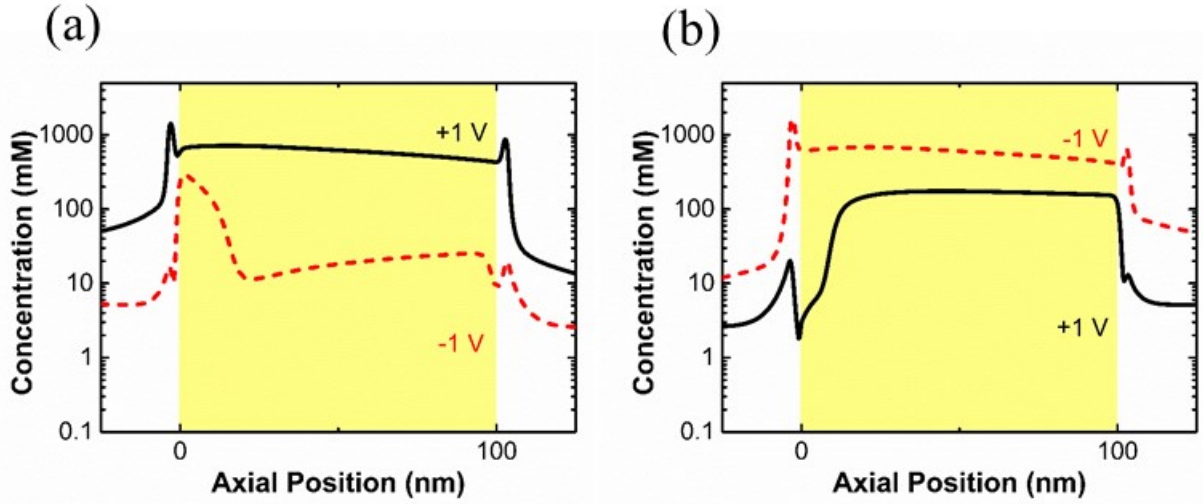


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2 **Fig. S4** Axial variation of concentration for various levels of θ at 1 mM NaCl. (a)-(f): concentration
 3 profiles for cations (Na^+ and H^+), and the levels of θ are 0° , 1° , 5° , 0° , 1° , and 5° , respectively; (g)-(l):
 4 concentration profiles for anions (Cl^- and OH^-), and the levels of θ are 0° , 1° , 5° , 0° , 1° , and 5° ,
 5 respectively. (a)-(c) and (g)-(i): $V_{\text{applied}} = +1$ V; (d)-(f) and (j)-(l): $V_{\text{applied}} = -1$ V. For the case where
 6 $\text{pH}_t/\text{pH}_b = 11/3$, $\text{p}K_A = 3$ (PAA), $\text{p}K_B = 10$ (PLL), $\Gamma_{A,0} = 2 \times 10^8$ C m $^{-3}$, and $\Gamma_{B,0} = 9.6 \times 10^7$ C m $^{-3}$.

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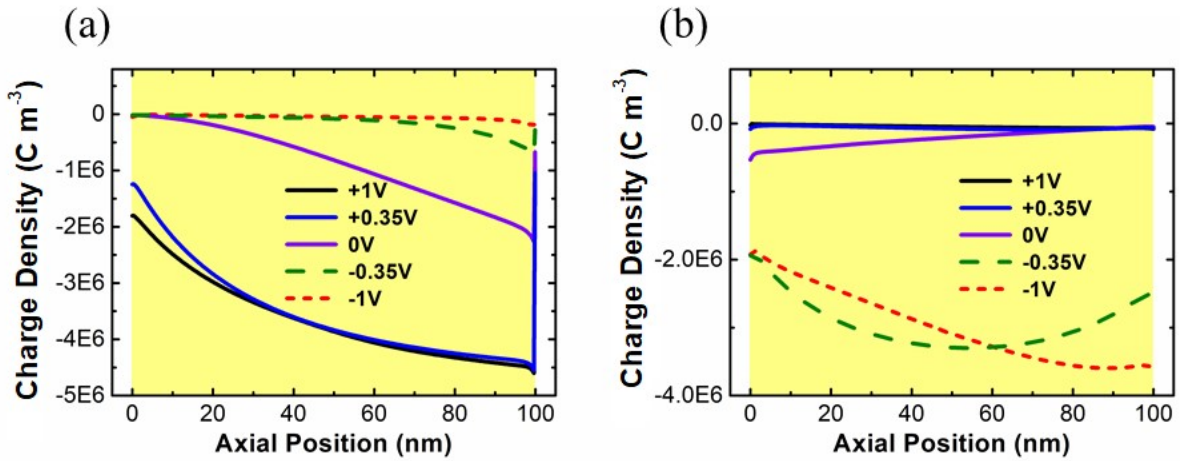


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3 **Fig. S5** Axial variation in the cross-sectional total averaged concentration at $\theta=5^\circ$. (a) $\text{pH}_t/\text{pH}_b=3/11$;
 4 (b) $\text{pH}_t/\text{pH}_b=11/3$. For the case where 1 mM NaCl, $\text{p}K_A=3$ (PAA), $\text{p}K_B=10$ (PLL), $\Gamma_{A,0} = 2 \times 10^8 \text{ C m}^{-3}$,
 5 and $\Gamma_{B,0} = 9.6 \times 10^7 \text{ C m}^{-3}$. The nanopore tip (base) is located at 0 nm (100 nm). The yellow region
 6 denotes nanopore interior.

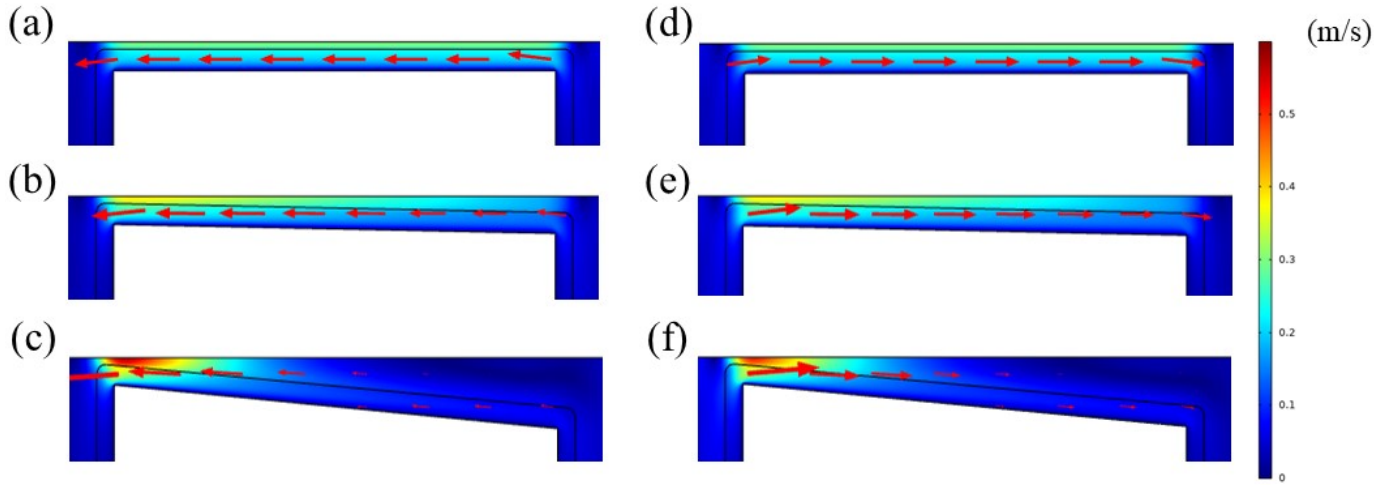
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8 S2. One mixed PE layer



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10 **Fig. S6** Axial variation of the net fixed space charge density at $\theta=5^\circ$. (a) $\text{pH}_t/\text{pH}_b=3/11$;
 11 $\text{pH}_t/\text{pH}_b=11/3$. For the case where 1 mM NaCl, $\text{p}K_A=3$ (PAA), $\text{p}K_B=10$ (PLL), $\Gamma_{A,0} = 1 \times 10^8 \text{ C m}^{-3}$,
 12 and $\Gamma_{B,0} = 4.8 \times 10^7 \text{ C m}^{-3}$. The nanopore tip (base) is located at 0 nm (100 nm). The yellow region
 13 denotes nanopore interior.



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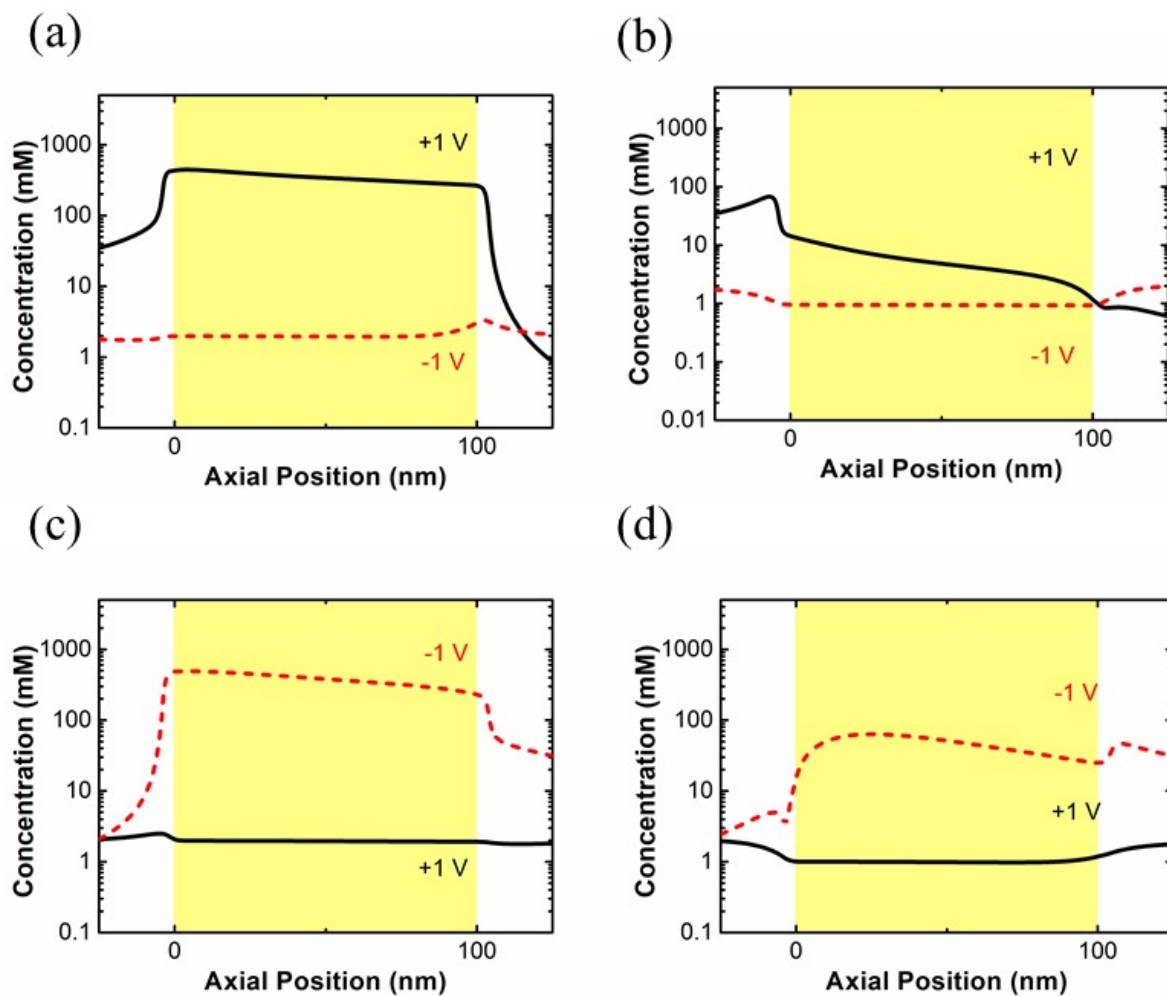
2 **Fig. S7** Profiles of the flow field in nanopore for various levels of θ at 1 mM NaCl. (a)-(c):
 3 $\text{pH}_t/\text{pH}_b=3/11$, $V_{\text{applied}}=+1$ V, and the levels of θ are 0° , 1° , and 5° , respectively; (d)-(f): $\text{pH}_t/\text{pH}_b=11/3$,
 4 $V_{\text{applied}}=-1$ V, and the levels of θ are 0° , 1° , and 5° , respectively. For the case where $\text{p}K_A=3$ (PAA),
 5 $\text{p}K_B=10$ (PLL), $\Gamma_{A,0} = 1 \times 10^8$ C m $^{-3}$, and $\Gamma_{B,0} = 4.8 \times 10^7$ C m $^{-3}$.

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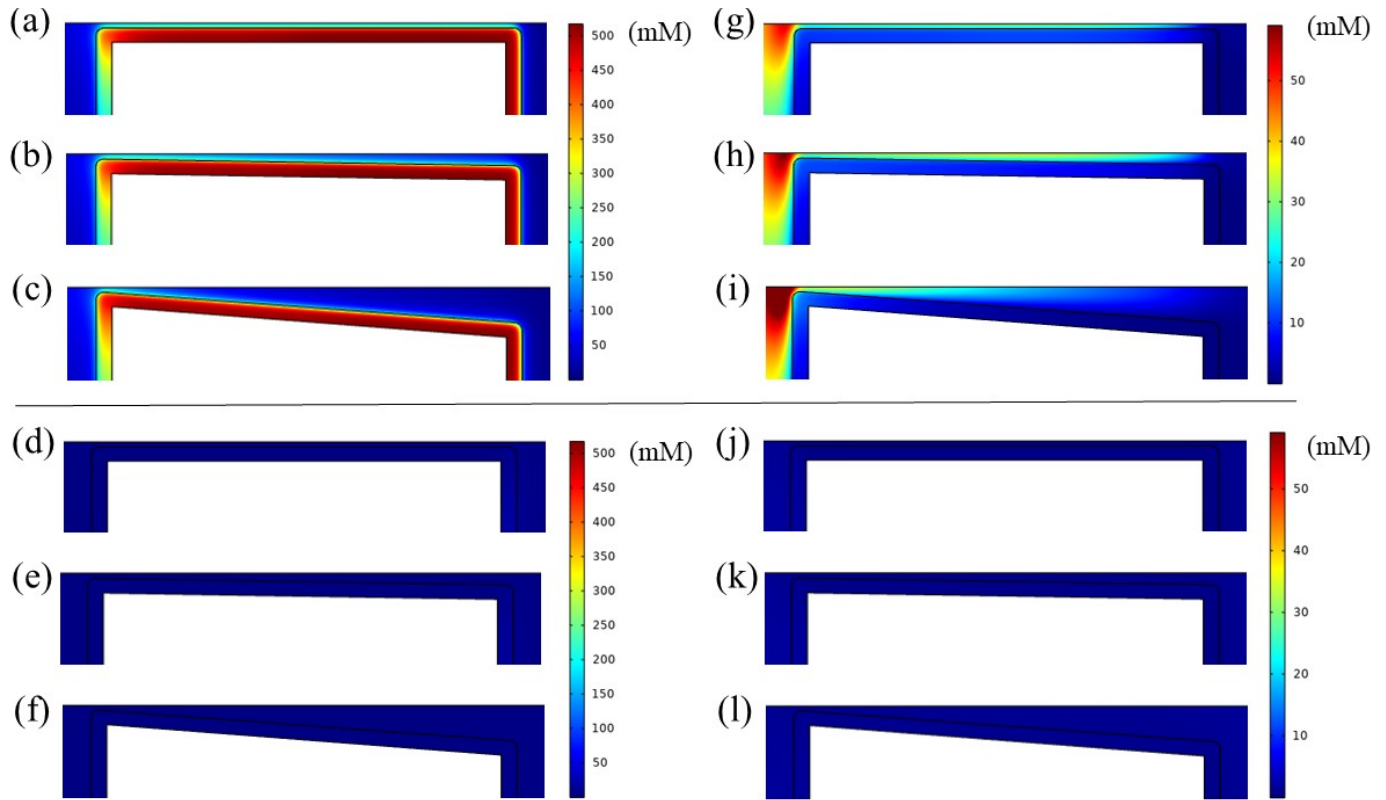
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2 **Fig. S8** Axial variation in the cross-sectional averaged concentration of cations (Na^+ and H^+) and
 3 anions (Cl^- and OH^-) at $\theta=5^\circ$. (a) and (b): $\text{pH}_t/\text{pH}_b=3/11$; (c) and (d): $\text{pH}_t/\text{pH}_b=11/3$. (a) and (c):
 4 concentration profiles for cations; (b) and (d): concentration profiles for anions. For the case where 1
 5 mM NaCl, $\text{p}K_A=3$ (PAA), $\text{p}K_B=10$ (PLL), $\Gamma_{A,0} = 1 \times 10^8 \text{ C m}^{-3}$, and $\Gamma_{B,0} = 4.8 \times 10^7 \text{ C m}^{-3}$. The nanopore
 6 tip (base) is located at 0 nm (100 nm). The yellow region denotes nanopore interior.

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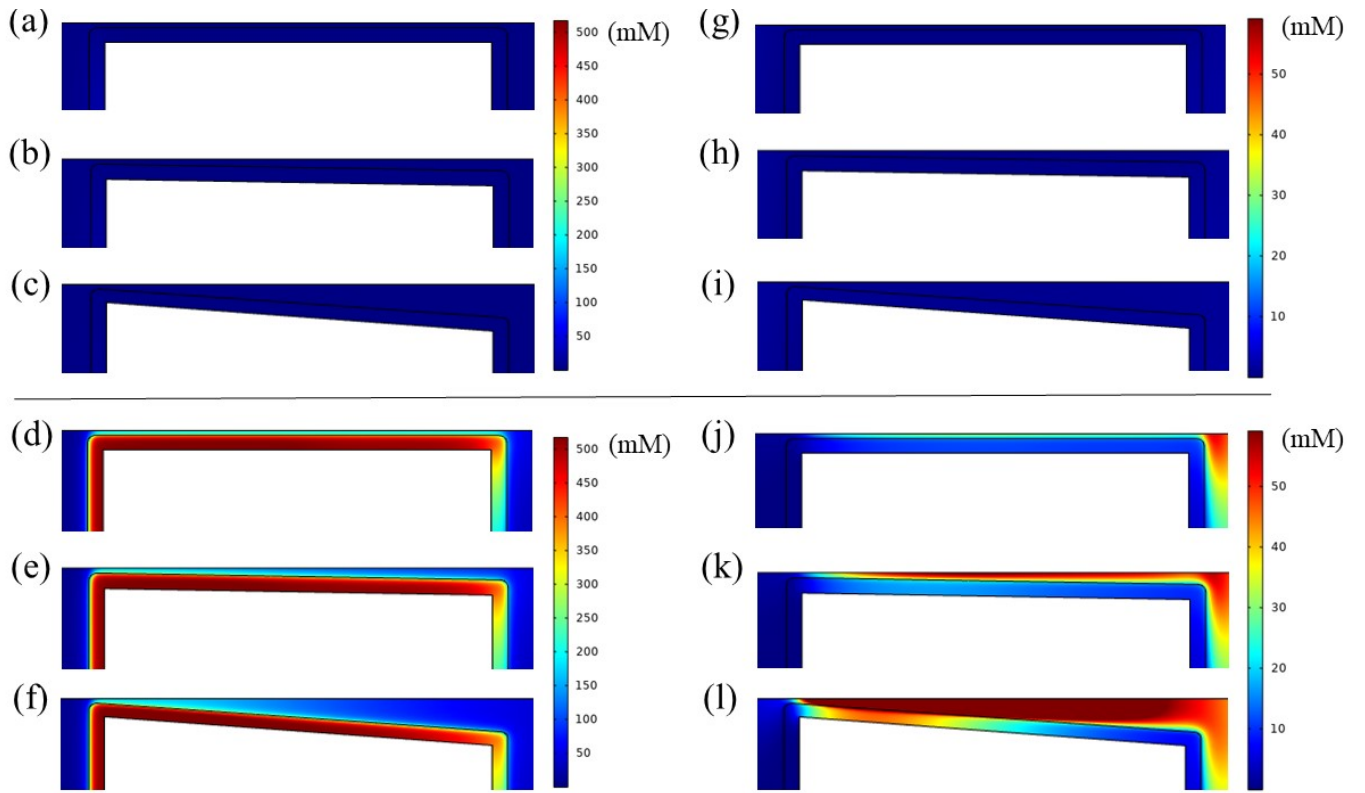


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2 **Fig. S9** Axial variation of concentration for various levels of θ at 1 mM NaCl. (a)-(f): concentration
 3 profiles for cations (Na^+ and H^+), and the levels of θ are 0° , 1° , 5° , 0° , 1° , and 5° , respectively; (g)-
 4 (l): concentration profiles for anions (Cl^- and OH^-), and the levels of θ are 0° , 1° , 5° , 0° , 1° , and 5° ,
 5 respectively. (a)-(c) and (g)-(i): $V_{\text{applied}} = +1$ V; (d)-(f) and (j)-(l): $V_{\text{applied}} = -1$ V. For the case where
 6 $\text{pH}_t/\text{pH}_b = 3/11$, $\text{p}K_A = 3$ (PAA), $\text{p}K_B = 10$ (PLL), $\Gamma_{A,0} = 1 \times 10^8 \text{ C m}^{-3}$, and $\Gamma_{B,0} = 4.8 \times 10^7 \text{ C m}^{-3}$.

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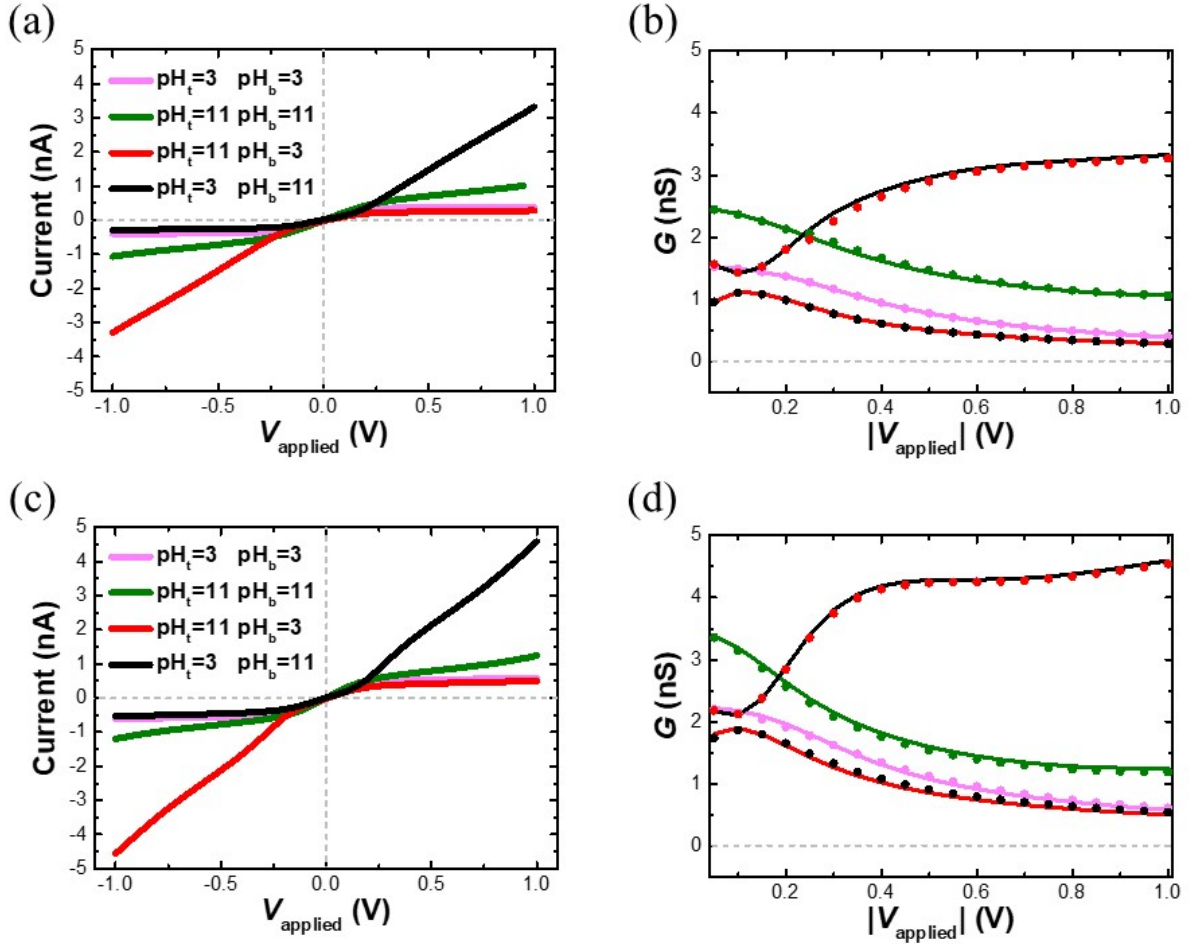
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2 **Fig. S10** Axial variation of concentration for various levels of θ at 1 mM NaCl. (a)-(f): concentration
 3 profiles for cations (Na^+ and H^+), and the levels of θ are 0° , 1° , 5° , 0° , 1° , and 5° , respectively; (g)-(l):
 4 concentration profiles for anions (Cl^- and OH^-), and the levels of θ are 0° , 1° , 5° , 0° , 1° , and 5° ,
 5 respectively. (a)-(c) and (g)-(i): $V_{\text{applied}} = +1$ V; (d)-(f) and (j)-(l): $V_{\text{applied}} = -1$ V. For the case where
 6 $\text{pH}_t/\text{pH}_b = 11/3$, $\text{p}K_A = 3$ (PAA), $\text{p}K_B = 10$ (PLL), $\Gamma_{A,0} = 1 \times 10^8 \text{ C m}^{-3}$, and $\Gamma_{B,0} = 4.8 \times 10^7 \text{ C m}^{-3}$.

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2 **S3. Symmetric pH solution**

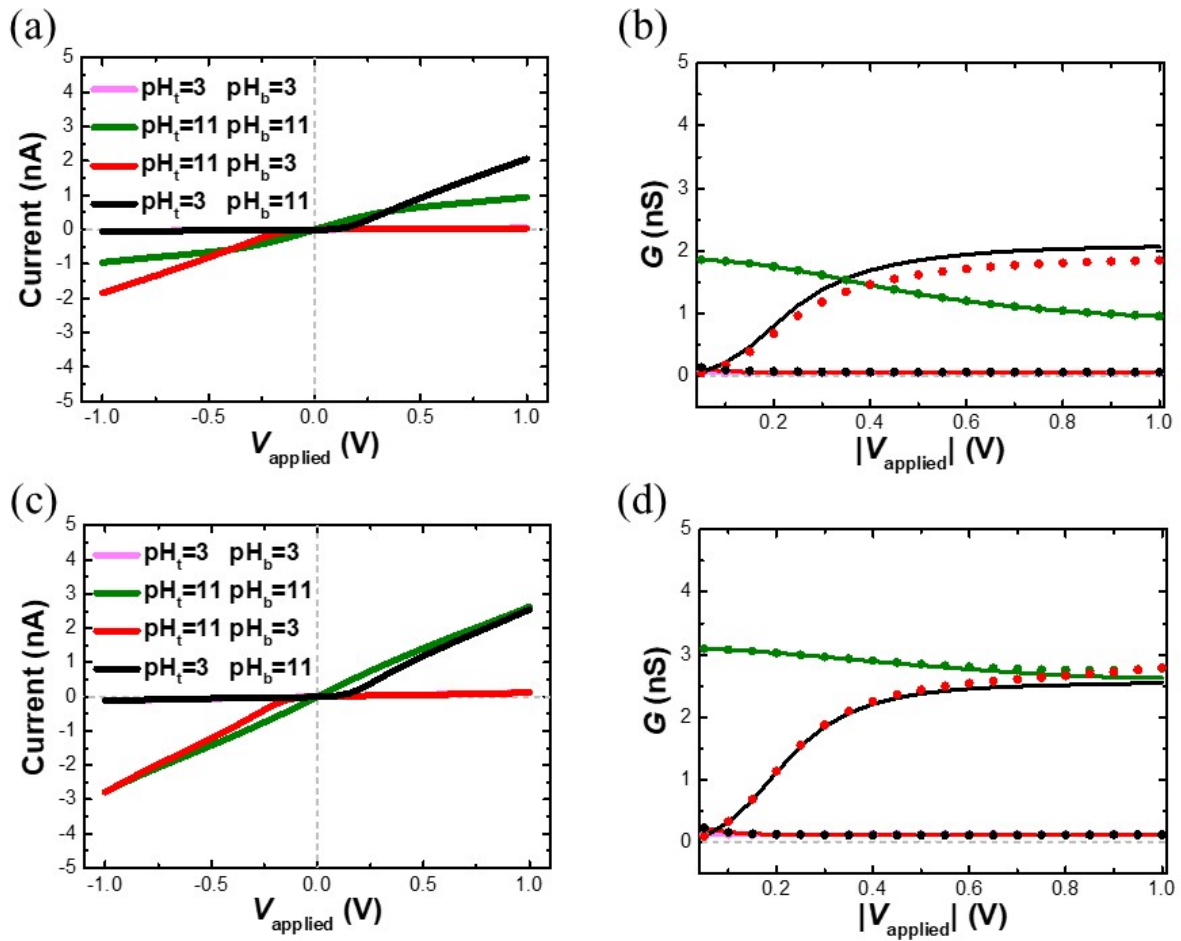


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4 **Fig. S11** Simulated I - V curves, (a) and (c), and G - V curves, (b) and (d), for various composition of
 5 pH_t/pH_b in the case of two PE layers. (a) and (b): $\theta=0^\circ$; (c) and (d): $\theta=5^\circ$. For the case where 1 mM
 6 NaCl, $pK_A=3$ (PAA), $pK_B=10$ (PLL), $\Gamma_{A,0} = 2 \times 10^8 \text{ C m}^{-3}$, and $\Gamma_{B,0} = 9.6 \times 10^7 \text{ C m}^{-3}$. Solid curves:
 7 $V_{\text{applied}} > 0$; discrete symbols: $V_{\text{applied}} < 0$. Pink curves: pH_t/pH_b=3/3; green curves: pH_t/pH_b=11/11; red
 8 curves: pH_t/pH_b=11/3; black curves: pH_t/pH_b=3/11.

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2 **Fig. S12** Simulated I - V curves, (a) and (c), and G - V curves, (b) and (d), for various composition of
 3 pH_t/pH_b in the case of one mixed PE layer. (a) and (b): $\theta=0^\circ$; (c) and (d): $\theta=5^\circ$. For the case where 1
 4 mM NaCl, $\text{p}K_A=3$ (PAA), $\text{p}K_B=10$ (PLL), $\Gamma_{A,0} = 1 \times 10^8 \text{ C m}^{-3}$, and $\Gamma_{B,0} = 4.8 \times 10^7 \text{ C m}^{-3}$. Solid curves:
 5 $V_{\text{applied}} > 0$; discrete symbols: $V_{\text{applied}} < 0$. Pink curves: $\text{pH}_t/\text{pH}_b=3/3$; green curves: $\text{pH}_t/\text{pH}_b=11/11$; red
 6 curves: $\text{pH}_t/\text{pH}_b=11/3$; black curves: $\text{pH}_t/\text{pH}_b=3/11$.

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9 We investigate the symmetric pH solution in the same system. As shown in Fig. S11 and

10 S12, the ion current rectification (ICR) characteristics only occurs in asymmetric pH gradient

11 applied in the case of two PE layer and one mixed PE layer. In the situation of asymmetric pH

12 gradient applied, the electroosmotic flow will drive the different pH solution from the reservoir

13 into or out of the nanopore with the electric potential applied and make the fixed charge density

1 change. This behavior make the fixed charge density become negative or neutral in the
2 nanopore and produce the enrichment and depletion of ions in specific V_{applied} . In symmetric
3 pH solution, the concentration of hydrogen ions separates averaged in nanopore when the
4 electric potential applied, and the fixed charge density almost the same in opposite V_{applied} . This
5 behavior make the current become symmetric and the ICR behavior do not exist in symmetric
6 pH solution.

7

8 **Reference**

9 1 T.-J. Liu, T. Ma, C.-Y. Lin, S. Balme and J.-P. Hsu, *J. Phys. Chem. Lett.*, 2021, **12**,
10 11858-11864.

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