Coupled effect of dehydration and electrostatic interactions on selective ion transport through charged nanochannels - Supplementary information

Mao Wang,¹ Wenhao Shen,¹ Siyuan Ding,¹ Xue Wang,¹ Zhong Wang,¹ Yugang Wang¹*, and ¹ Feng Liu^{*,1,2}

¹State Key Laboratory of Nuclear Physics and Technology, Peking University, 100871 Beijing, People's Republic of China.

²Center for Quantitative Biology, Peking University, 100871 Beijing, People's Republic of China.

PMF calculation

In order to obtain the energy barriers at the entrance of the CCNT, a potential of mean force (PMF) describing the process of the ion entering the model membrane was generated for Li⁺ ions, Mg²⁺ ions and the CCNT with 0e, -4e, -8e surface charges. First, a harmonic potential was used to steer one cation into the CCNT to gain the initial configuration. An umbrella sampling procedure^{1,2} was used involving 32 separate simulations, spanning the distance from Z = 2.1 nm to Z = 3.7 nm, at 0.05 nm intervals. In each simulation, the position of the ion in the Z direction was restrained using a harmonic potential with a force constant of 5000 kJ mol⁻¹nm⁻². The PMF was generated from the force data obtained in a 2 ns of simulation time, using the weighted histogram analysis method.^{3,4}

Table S1. Non-bonded interaction parameters used in the MD simulation^{5,6}

| Ion | σ (nm) | ε (kJ mol ⁻¹) | q (e) |
|------------------|---------------|---------------------------------------|--|
| Li ⁺ | 0.2870 | 0.00061 | +1 |
| Mg ²⁺ | 0.1630 | 0.00061 | +2 |
| Carbon | 0.3214 | 0.48990 | 0, -0.0119, -0.0238, -0.0357, -0.0476, -0.0595 |
| (channel) | | | (total charges are 0e, -2e, -4e, -6e, -8e, -10e) |



Fig. S1 Dehydration of ions when enter the pore. (a, b) Radial pair distribution function (g(r)) of ions $(Li^+ \text{ left}, Mg^{2+} \text{ right})$ in -4e CCNT (blue), -10e CCNT(orange) and bulk (green). (c, d) Number of coordinate waters of ions $(Li^+ \text{ left}, Mg^{2+} \text{ right})$ in -4e CCNT (blue), -10e CCNT (orange) and bulk (green).



Fig. S2 Number of Li^+ ions (a) and Mg^{2+} ions (b) in the CCNT with surface charges varying from 0 to -10 e during simulations. The number of cations inside the nanopore is dynamically changed with time. With the increase of negative surface charges, the number of cations inside CCNT is increasing.



Fig. S3 Snapshots of the distributions of $Li^+(a)$ ions and Mg^{2+} ions (b) in -10e CCNT. The Mg^{2+} ions are shown in purple, the Li^+ ions are shown in pink. The waters are shown in red (O) and white(H). The Li^+ ions are closer to the charged wall compared with the Mg^{2+} ions.



Fig. S4 Distribution of the distance between the cations and the CCNT wall with different surface charges. The red line indicates the center of the CCNT.



Fig. S5 Axial velocity profiles of Li^+ and Mg^{2+} ions inside CCNT with different surface charges of -4e and -10e. The entrance and exit of the CCNT at Z= 2.9 nm and Z = 4.5 nm. (The error bars represent the standard deviation of velocity within the 0.08 nm wide slice)



Fig. S6 Distributions of orientation angles θ of hydrated water molecules of Li⁺ ions and Mg²⁺ ions inside the CCNT with different charge densities.

Reference

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