Molecular Dynamics Study of Mg^{2+}/Li^{+} Separation via Biomimetic Graphene-based Nanopores: The Role of Dehydration in Second Shell

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Supplemental Material

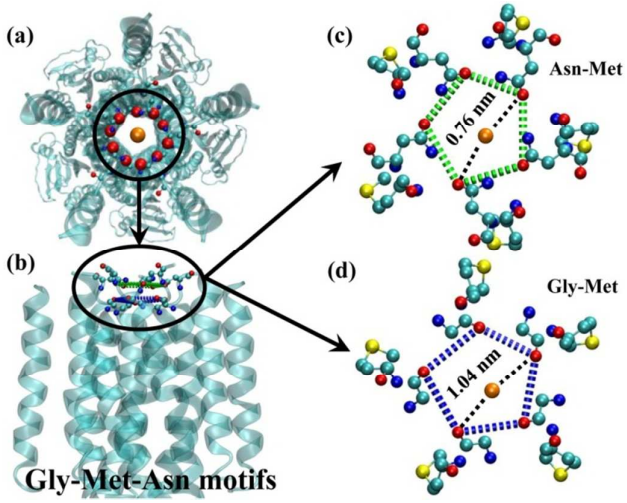

Figure S1. (a), (b) Top and lateral view of selectivity filter structure of the Mg^{2+} channels of CorA. Oxygen atoms in Asn and Gly amino acids are represented as balls colored with red, orange ball represents Mg^{2+}. (c), (d) represents two structural frameworks of CorA selectivity filter, 0.76 and 1.04 nm is the distance of Mg^{2+} center between oxygen atoms in Asn and Gly amino acids, respectively.

1 We provided the system sizes and numbers of atoms detailedly for all the simulation cases studied in **Table S1**.

Table S1. The details of simulation systems

System	Label	N_{Water}	$N_{Mg^{2+}}$	N_{Li^+}	N_{Cl^-}	Box size (/nm^3)
Mixed Solution	4-4-1	2721	13	13	39	4.176×4.254×5.0
	4-4-2	2721	13	13	39	4.176×4.254×5.0
	4-4-3	2721	13	13	39	4.176×4.254×5.0
Single-component Solution ($MgCl_2$)	4-4-1	2747	13	/	26	4.176×4.254×5.0
	4-4-2	2747	13	/	26	4.176×4.254×5.0
	4-4-3	2747	13	/	26	4.176×4.254×5.0
Single-component Solution (LiCl)	4-4-1	2760	/	13	13	4.176×4.254×5.0
	4-4-2	2760	/	13	13	4.176×4.254×5.0
	4-4-3	2760	/	13	13	4.176×4.254×5.0

N_{Water}, $N_{Mg^{2+}}$, N_{Li^+} *and* N_{Cl^-} represents the water, Mg^{2+}, Li^+, and Cl^- numbers in each simulation systems, respectively.

2 We report the Lennard Jones and force field parameters for water, ions and graphene in **Table S2.**

Table S2. The Lennard Jones and force field parameters adopted in this work.

(The Lennard Jones parameters and partial charges for the ions, water molecules, carbon atoms in graphene)

	Atom	σ/nm	ε/KJ mol^{-1}	q/e	Ref
Ions					
	Mg^{2+}	0.211	0.063	2.000	[1]
	Li^{+}	0.213	0.075	1.000	[2]
	Cl^{-}	0.404	0.628	-1.000	[1]
Water					
	OW	0.315	0.636	-0.834	[1]
	HW	0.000	0.000	0.417	[1]
Graphene					
	C	0.355	0.293	0.000	[1]

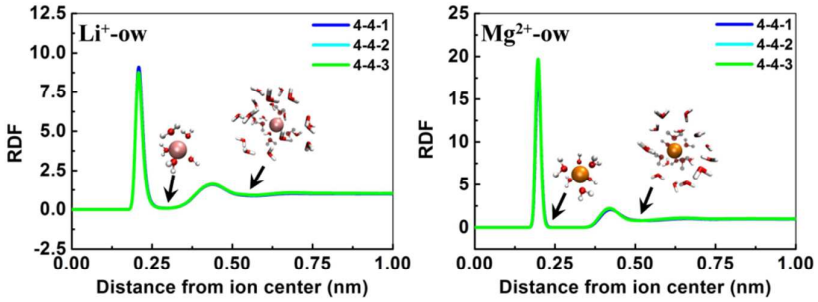

Figure S2: The radial distribution function of water molecules around Li^{+} and Mg^{2+}. The first and second minimum from the center is taken to be the ions first and second hydration radii. The insert snapshots show the ion first and second hydration shell around Li^{+} and Mg^{2+}.

3 Details of the calculated the potential of mean force

The potential of mean force (PMF) for ions to permeate graphene nanopores was calculated along the reaction coordinate by umbrella sampling.[3] The reaction coordinate was defined as the z-component distance between ions and the center of the graphene nanopores. Referring to the methods used by Kang et al.[4], the umbrella sampling was only performed for the reaction coordinates from -1.5 nm to 0.3 nm, and the PMF for the 0–1.5 nm generated from that for -1.5 nm to 0 nm by symmetry, based on the principle of free energy. Therefore, the total reaction coordinates ranged from -1.5 nm to 1.5 nm. The width of the umbrella window was 0.05 nm for the reaction coordinates varying from -1.5 nm to -0.5 nm, and 0.02 nm for -0.5 nm to 0.3 nm to enhance the sampling around the graphene nanopore. A biasing potential of 11368 kJ mol^{-1} nm^2 was implemented in the z-coordinate of the ion in each window. Each window was sampled for 8 ns. The first 3 ns in each umbrella simulation was utilized to reach equilibrium and the last 5 ns of data used the weighted histogram analysis method (WHAM)[5,6] to obtain the final PMF profile.

Figure S3a,b shows the plotted histograms of the configurations within the umbrella sampling windows. These histograms reasonably overlapped between windows, indicating that the entire reaction coordinate was properly sampled. To evaluate the convergence of PMF curves, we further analyzed the PMF sampled between 3–5 ns, 3–6 ns, and 3–7 ns per window for comparison with the result of that sampled between 3–8 ns, as illustrated in **Figure S3**c,d. There was no obvious difference in the peak and valley positions between the curves, and the profiles gradually overlapped along the reaction coordinate.

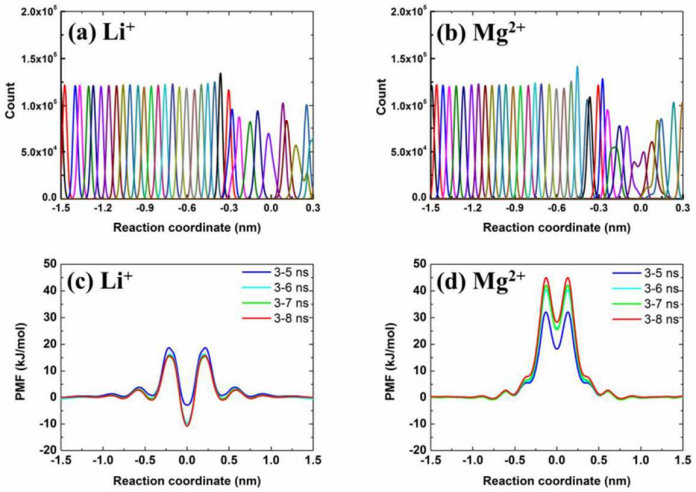

Figure S3. (a) and (b) Histograms of the configurations within the umbrella sampling windows for Li^+ and Mg^{2+}. PMF profiles of (c) Li^+ and (d) Mg^{2+} between different sampling interval.

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