Programmable Cation Migration in Unipolar 2D Ion Channels via Dynamic Debye Length

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Methods

Preparation and exfoliation of GO nanosheets: Graphene oxide was obtained by the improved Hummers method combined with ultrasonication and centrifugation. A total of 200 mg of 80-mesh graphite was weighed, followed by the addition of 10 mL concentrated H_2SO_4 and 1.2 g KMnO₄. After stirring at room temperature and at 35-40 °C for 2 hours, 28 mL water was slowly added. Finally, hydrogen peroxide (H_2O_2) was added to consume the excess KMnO₄ in the system, leading to the production of graphene oxide. The obtained graphene oxide was washed with water and centrifuged until the pH exceeded 6. It was then sonicated for 7 minutes, and the dispersion was subjected to lowspeed centrifugation three times for 10 minutes each, until no black particles remained. The supernatant was then centrifuged at high speed for 10 minutes, and the bottom precipitate was dispersed in an aqueous solution, thus obtaining graphene oxide monolayers.

Preparation of GO membrane: The GO membrane was produced by vacuum filtration of a GO dispersion with a concentration of 0.03 mg/mL onto a polyethersulfone (PES) membrane (diameter 47 mm, pore size 0.22 μm).

Characterization methods: The thickness of the GO nanosheets was characterized using atomic force microscopy (AFM) on a Multi-Mode 8 SPM microscope (Bruker, Bremen, Germany). Scanning electron microscopy (SEM) images was carried out on an Apreo S SEM (Thermo Fisher Scientific, Brno, The Czech Republic). The GO membrane was embrittled by liquid nitrogen, and the crosssection was adhered to a sample stage for gold sputtering before being placed in the SEM chamber for observation. XRD patterns were measured by a MiniFlex 600-C (Rigaku, Tokyo, Japan) with Cu-Ka radiation. X-ray photoelectron spectroscopic (XPS) spectra were obtained by a XSAM800 XPS spectrometer (Kratos, Manchester, UK). The permeability of cations on the permeate side was measured by atomic absorption spectrometer (AAS) on a contrAA 800 AAS (analytikjena, Jena, Germany). Br⁻ permeability was measured by ion chromatography (IC) on a CIC-D160 IC (SHINE, Qingdao, China). The zeta potential of the GO membrane was measured using a SurPASS 3 electrokinetic solid surface analyzer (Anton Paar, Graz, Austria).

Ion permeability measurement: The ion diffusion experiments were conducted in a custombuilt permeation setup. In the diffusion environment without K⁺, the feed side contained a 0.1 mol/L NaCl solution, while the permeate side was filled with DI water. The conductivity of the permeate side was measured at regular time intervals using a conductivity meter, allowing for the determination of Na⁺ concentration, corresponding to the AAS results. In the diffusion environment with K⁺ on the both sides, the feed side consisted of a mixed ion solution of 0.25 mol/L KCl and 0.1 mol/L NaCl, while the permeate side contained a 0.25 mol/L KCl solution. After a certain diffusion period, the solution from the permeate side was collected for AAS testing to analyze the Na⁺ permeability. The formula for calculating ionic permeability is provided by Equation 1:

$$J = \frac{\Delta C \times V}{At} \tag{1}$$

where *J* is the ion permeation rate (mol h⁻¹ m⁻²); ΔC is the concentration change of salts after diffusing for a certain interval (mol L⁻¹); *V* is the volume of the solution on the permeate side; *A* is the valid membrane area of permeation (m²); *t* is the time for ionic diffusion (h).

Experiments on Na⁺ diffusion cycles: A cycling experiment was conducted to evaluate Na⁺ transport across the GO membrane under conditions with and without K⁺ on both sides of the diffusion device. As shown in Fig. 2b, in the "no" condition, the feed side contained 0.1 mol/L NaCl, while the permeate side was filled with DI water. In the "with" condition, the feed side consisted of a mixture of 0.25 mol/L KCl and 0.1 mol/L NaCl, while the permeate side contained 0.25 mol/L KCl. Each diffusion step lasted 24 hours, after which the permeate solution was collected and analyzed for Na⁺ concentration using AAS. After each diffusion step, before switching to the next condition, the remaining solutions were removed, and the system was rinsed with deionized water until the conductivity of the rinse solution dropped below 2 μ S/cm. The alternate solution was then introduced to initiate the next cycle, while the GO membrane remained unchanged throughout the experiment.

Supporting Information

Code	Feed side	Permeate side
NaCl/H ₂ O	0.1 mol/L NaCl	DI water
NaCl+KCl/H ₂ O	0.1 mol/L NaCl+0.25 mol/L KCl	DI water
NaCl/KCl	0.1 mol/L NaCl	0.1 mol/L KCl
NaCl+KCl/KCl	0.1 mol/L NaCl+0.25 mol/L KCl	0.25 mol/L KCl

Table S1 Detailed Na⁺ diffusion conditions through the GO membrane as shown in Fig. 2c.

Code	Feed side	Permeate side
NaBr/H ₂ O	0.1 mol/L NaBr	DI water
NaBr+KCl/H ₂ O	0.1 mol/L NaBr+0.25 mol/L KCl	DI water
NaBr/KCl	0.1 mol/L NaBr	0.1 mol/L KCl
NaBr+KCl/KCl	0.1 mol/L NaBr+0.25 mol/L KCl	0.25 mol/L KCl

Table S2 Detailed Na⁺ and Br⁻ diffusion conditions through the GO membrane as shown in Fig. 2d.



Fig. S1 Zeta potential of the GO membrane.

The zeta potential was measured using a SurPASS 3 electrokinetic solid surface analyzer (Anton Paar, Graz, Austria). The measurements were conducted in a 0.001 mol/L ionic buffer solution at pH \sim 5.6, with the temperature maintained at 25 °C. To ensure the accuracy and consistency of the zeta potential measurements, nine measurements were performed at different locations on the GO membrane. The GO membrane exhibited an average zeta potential of -25.7 mV, indicating its negative surface charge.



Fig. S2 FT-IR spectra of the GO membrane.

The infrared absorption spectrum (800-4000 cm⁻¹) of the GO membrane shows distinct peaks at 1080 cm⁻¹, 1224 cm⁻¹, 1416 cm⁻¹, 1621 cm⁻¹, 1731 cm⁻¹, and 3030 cm⁻¹, corresponding to C-O, C-O-C, C-OH, C=C, C=O, and O-H vibrational modes, respectively^{1, 2}. The peaks at 1080 cm⁻¹ and 1224 cm⁻¹ indicate a high content of oxygen-containing groups, including C-O and epoxy structures. The 1416 cm⁻¹ peak confirms the presence of hydroxyl groups, while the 1621 cm⁻¹ peak suggests that some graphene conjugation remains intact despite oxidation. The 1731 cm⁻¹ peak reflects a higher oxidation degree at the membrane edges, attributed to carboxyl or ester groups. The broad absorption at 3030 cm⁻¹ corresponds to O-H stretching from hydroxyl groups and adsorbed water. These results demonstrate that the GO membrane is rich in oxygen functional groups, enhancing hydrophilicity and providing active sites for ion transport.



Fig. S3 XRD spetra of the GO membrane after Na⁺ diffusion under different KCl concentration. The NaCl concentration was maintained at 0.1 mol/L on the feed side, while the KCl concentration was identical on both sides and systematically varied from 0 to 1 mol/L.



Fig. S4 Na^+ permeability through the GO membrane under different thicknesses in diffusion environments without and with K^+ on the both sides.



Fig. S5 Na⁺ permeability through the GO membrane under different GO nanosheet lateral sizes in diffusion environments without and with K^+ on the both sides.



Fig. S6 Na⁺ permeability through the GO membrane with different HI reduction times in diffusion environments without and with K^+ on both sides.



Fig. S7 (a-c) Diffusion performance of $Li^+/K^+/Cs^+$ across the GO membrane under different monovalent ion environments regulated by the Debye length. (d) Variation in Mg²⁺ permeability with increasing LiCl concentration.

The diffusion behavior of Li⁺/K⁺/Cs⁺/Mg²⁺ across GO membranes under different ionic environments was systematically investigated. Taking Figure S7 (a) as an example, the diffusion of Li⁺ was analyzed. When the feed side contained a 0.1 mol/L LiCl solution and the permeate side was DI water, the Li⁺ permeation rate was slow. However, when both sides contained 0.25 mol/L NaCl, KCl, or CsCl, the Li⁺ diffusion rate increased significantly by approximately tenfold, further confirming that the reduction of the Debye length induced by ionic strength enhances ion diffusion.

Additionally, the transport behavior of the multivalent ion Mg^{2+} in GO membrane channels was explored. The initial $MgCl_2$ concentration on the feed side was maintained at 0.1 mol/L, while the LiCl concentration on both sides was varied at 0, 0.01, 0.05, 0.1, and 0.25 mol/L. By adjusting the LiCl concentration, it was observed that the Mg^{2+} permeation rate increased with higher LiCl concentrations, further validating the universality of the dynamic Debye length regulation mechanism in ion transport. The specific diffusion conditions for different ionic environments are detailed in Table S3 :

Code	Feed side	Permeate side
LiCl/H ₂ O	0.1 mol/L LiCl	DI water
NaCl+LiCl/NaCl	0.25 mol/L NaCl+0.1 mol/L LiCl	0.25 mol/L NaCl
KCl+LiCl/KCl	0.25 mol/L KCl+0.1 mol/L LiCl	0.25 mol/L KCl
CsCl+LiCl/CsCl	0.25 mol/L CsCl+0.1 mol/L LiCl	0.25 mol/L CsCl
KCl/H ₂ O	0.1 mol/L KCl	DI water
LiCl+KCl/LiCl	0.25 mol/L LiCl+0.1 mol/L KCl	0.25 mol/L LiCl
NaCl+KCl/NaCl	0.25 mol/L NaCl+0.1 mol/L KCl	0.25 mol/L NaCl
CsCl+KCl/CsCl	0.25 mol/L CsCl+0.1 mol/L KCl	0.25 mol/L CsCl
CsCl/H ₂ O	0.1 mol/L CsCl	DI water
LiCl+CsCl/LiCl	0.25 mol/L LiCl+0.1 mol/L CsCl	0.25 mol/L LiCl
NaCl+CsCl/NaCl	0.25 mol/L NaCl+0.1 mol/L CsCl	0.25 mol/L NaCl
KCl+CsCl/KCl	0.25 mol/L KCl+0.1 mol/L CsCl	0.25 mol/L KCl

Table S3 Detailed $Li^+/K^+/Cs^+$ diffusion conditions under different ionic environments through the GO membrane as shown in Fig. S7 (a-c).



Fig. S8 Na⁺ permeability through the MoS_2 membrane in diffusion environments without and with K⁺ on the both sides.

References

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