

Counter-ion controlled ionic sieving in graphene oxide/polyelectrolyte membrane for $\text{Li}^+/\text{Mg}^{2+}$ separation from low-quality brines

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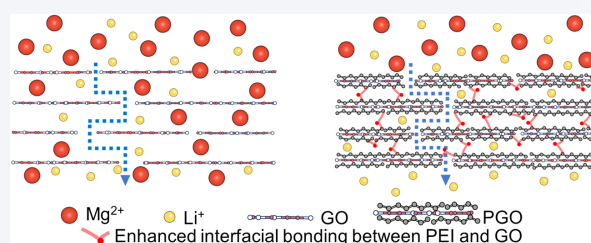
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ABSTRACT: Precise control of the interlayer spacing of graphene oxide (GO) membranes at the sub-nanometer scale offers size-exclusion-based separation of $\text{Li}^+/\text{Mg}^{2+}$, a critical step towards efficient lithium resource management and energy sustainability. While previous GO-based membranes have shown high Mg^{2+} rejections, their performance was largely limited to static diffusion settings or diluted solutions where Donnan exclusion dominates. Here, we report a GO membrane intercalated with a uniform polyelectrolyte layer. The membrane shows substantially enhanced MgCl_2 rejection over a wide concentration range, while allowing LiCl permeation under pressure-driven filtration. This enables direct lithium recovery from low-quality brines with high MgCl_2 concentrations and high $\text{Mg}^{2+}/\text{Li}^+$ ratios. Mechanistic study reveals that the adsorption of halide counter-ions onto the charged GO channel walls narrowed the interlayer spacing and enabled size-exclusion-based ionic separation. At higher ionic concentrations, a partial exchange of these adsorbed counter-ions with those in the second hydration shell of Mg^{2+} allowed moderate Mg^{2+} permeation. We further demonstrate a streamlined GO-based membrane filtration process, which rejects 99.53% Mg^{2+} from a low-quality brine, effectively upgrading it towards a high-quality lithium source, and highlighting the potential of this approach for sustainable lithium production.



KEYWORDS: two-dimensional materials, nanochannel, $\text{Li}^+/\text{Mg}^{2+}$ separation, low-quality brine, counter-ion adsorption

1 Introduction

Graphene oxide (GO) membranes, assembled by stacking of two-dimensional (2D) GO nanosheets, continue to be promising for advanced separation process [1–3], due to their precise and size-exclusion-based molecular sieving with a size cutoff at ~ 1 nm in water [2]. This cutoff, primarily determined by the swelling of interlayer spacing (d) between stacked GO nanosheets, provides selective separation [4]. However, it also limits the separation of smaller species, for example, common salt ions (K^+ : 6.6 Å, Na^+ : 7.2 Å, Li^+ : 7.6 Å, Ca^{2+} : 8.2 Å, and Mg^{2+} : 8.6 Å) cannot be effectively separated [5].

In particular, $\text{Li}^+/\text{Mg}^{2+}$ separation [6–8] holds both fundamental scientific interest due to the similar hydrated sizes that make their separation intrinsically challenging, and practical importance for

lithium resource sustainability and renewable energy technologies. Existing $\text{Li}^+/\text{Mg}^{2+}$ separation methods include precipitation [9], solvent extraction [10], sorption [11], and membrane separation [12]. While precipitation, solvent extraction, and sorption concentrate Li^+ from its brines [13], membrane separation typically concentrates Mg^{2+} by rejecting it at the feed side and allowing Li^+ permeation [14, 15]. The distinct separation mechanism of membrane technology makes it particularly suitable for lithium extraction from low-quality brines [6], which are more abundant and widely distributed than the traditional concentrated hard-rock ores and salar brines. These low-quality brines typically contain low LiCl concentration (below 1600 ppm) but a high MgCl_2 concentration (above 0.06 M, equivalent to ~ 6000 ppm for MgCl_2) [6], making Li^+ -enrichment-based approaches thermodynamically inefficient and susceptible to Mg^{2+} interference due to a high concentration (noting that the concentrations in this study represent the concentration of LiCl and MgCl_2).

Polymer-intercalated GO membrane (GOM) efficiently tailors molecular transport channels, where the intercalation of negatively charged polymers [16, 17] primarily enhances desalination performance under osmosis-driven conditions, and zwitterionic

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polymer modifications [18] are typically employed for salt/dye separation. However, the precise separation of $\text{Li}^+/\text{Mg}^{2+}$ remains largely unexplored in these systems. On the contrary, intercalating positively charged molecules into the GOM introduces surface charges and inhibits interlayer swelling. This enables $\text{Li}^+/\text{Mg}^{2+}$ separation by Donnan exclusion which is effective at low concentrations typically less than 0.01 M [18–29], and modulates d suited between Li^+ and Mg^{2+} for size-exclusion-based ionic sieving [19, 20, 30, 31]. While this strategy has been extensively studied for $\text{Li}^+/\text{Mg}^{2+}$ separation, a high $\text{Li}^+/\text{Mg}^{2+}$ selectivity realized at high ionic concentrations above 0.06 M often relies on static diffusion tests [30–33], without using pressure filtration, where the ionic selectivity becomes more sensitive to membrane defects. Conversely, a few studies [19–23] that use pressure filtration report high selectivity, but only at low ionic concentrations below 0.01 M, where the Donnan effect dominates. Moreover, existing GO-based membranes are often tested with equimolar $\text{Li}^+/\text{Mg}^{2+}$ ratio [30–33], suggesting a lack of demonstration on the GO-based membrane for practical $\text{Li}^+/\text{Mg}^{2+}$ separation from low-quality brines. Thus, despite the abundance of low-quality brines and their critical role in lithium sustainability, they are rarely studied as a recoverable lithium source in membrane-based separation, a method offering high efficiency and low environmental impact.

The absence of GO membranes for effective lithium extraction from brines with a high Mg^{2+} concentration and a high $\text{Mg}^{2+}/\text{Li}^+$ ratio possibly arises from non-uniform intercalation of external species in the GO membrane because of GO's heterogenous atomic structure and the steric hinderance of the intercalates. This non-uniform intercalation introduces misalignment defects [34–36] and ion leakage, compromising size-exclusion mechanism. This explanation is supported by the studies showing enhanced separation with uniform interlayer structures. For example, physically confined GO membrane [5] avoids intercalation-induced defects, and achieves precise ion differentiation, but it remains impractical for scale-up due to its complex fabrication process, not only involves creating horizontally aligned membrane, but also requires subsequent stacking and slicing to form vertically aligned channels. While a recent study [37] demonstrated uniform interlayer control of GO membrane using toluidine blue O (TBO) as the intercalate for stable size-exclusion-dominated salt rejections across high ionic concentrations (NaCl rejection: 81% at 0.01 M and 70% at 0.1 M). However, Li^+ and Mg^{2+} are larger than Na^+ , this size-exclusion-dominated membrane rejection suggests that such membranes are ineffective for $\text{Li}^+/\text{Mg}^{2+}$ separation.

Achieving uniform channel surface with suitable d and minimal structural defects is crucial for size-exclusion-based $\text{Li}^+/\text{Mg}^{2+}$ separation. Our recent study [38] shows that polyamine forms a uniform 1-nm-thick adlayer on GO, creating a stable, positively charged colloid. We hypothesize that assembling this colloid into a membrane will transform the adlayer into a uniform intercalation layer, enabling size-exclusion-based ionic sieving suitable at high concentrations. Here, we demonstrate this strategy by assembling polyamine-GO membrane (PGOM) to construct a highly charged and uniform 2D nanochannel, which provides a unique platform for understanding the ionic transport and achieving ionic selectivity in the nano-confined space. This interlayer spacing was further finely controlled through crosslinking the polyamine intercalated layer enabled by *in-situ* reduction of GO nanosheets. The CO_2 generated during thermal reduction of GO strengthened the polyethyleneimine (PEI)–PEI interfaces through the formation of

carbamate/carbamic acid pairs, resulting in a structurally tighter GO membrane for enhanced ionic sieving, which enables size-exclusion-based ionic separation with enhanced Mg^{2+} rejections sustained over a wide concentration range with fast Li^+ permeation.

2 Experimental

2.1 Materials and chemicals

Polyether sulfone (PES) substrates with a nominal pore size of 200 nm were purchased from Jinteng Co., Ltd. (Tianjin, China). Deionized (DI) water was laboratory-made. The GO dispersion was purchased from Shenzhen Matterene Technology (Shenzhen, China). PEI (analytical grade, molecular weight of ~ 25k Da) was purchased from Sigma-Aldrich (Shanghai, China). Inorganic salts, including KCl, NaCl, LiCl, LiBr, LiI, MgCl_2 , MgBr_2 , MgI_2 , CaCl_2 , and CeCl_3 , were all of analytical grade and purchased from Macklin Biochemical (Shanghai, China).

2.2 Preparation of polyamine GO (PGO) nanosheets

Commercially available GO was purchased from Shenzhen Matterene Technology. Colloidal PGO dispersions were prepared by following the procedure reported previously [38]. 10 mL of 0.3 $\text{mg}\cdot\text{mL}^{-1}$ GO dispersion in ultrapure water and 20 mL of 18 $\text{mg}\cdot\text{mL}^{-1}$ solution of PEI (branched PEI, weight-average molecular weight of ~ 25k and number-average molecular weight of ~ 10k) in a 0.1 M NaCl solution (pH of ~ 2, adjusted by adding 1 M HCl solution) were mixed. The mixture was centrifuged, the sediment was collected and repeatedly washed with ultrapure water for at least 5 repeats, and the sediment was collected and re-dispersed in water for membrane preparation.

2.3 Preparation of PGOM membrane

The membrane was prepared by vacuum filtrating the diluted dispersion through a PES substrate (pore size of 200 nm, 47 mm in diameter). Then, the PGOMs were mildly crosslinked by placing the sample in an oven at temperatures of 25, 80, 120, and 150 °C for 0.5 h, respectively. For comparison, pristine GO membranes were also prepared by filtering 50 mL of 0.003 $\text{mg}\cdot\text{mL}^{-1}$ GO dispersion onto a PES substrate, and the resulting GO membranes were treated using the same procedure as PGOM.

2.4 Filtration test

Pressure-driven filtration was performed using a Sterlitech high-pressure dead-end filtration cell (HP4750X). Compressed nitrogen gas connected to the cell provided a constant transmembrane pressure of 8 bar. The effective area for permeation test was 2 cm^2 . For dead-end filtration experiments, a feed volume of 100 mL was introduced into the cell, and approximately 15 mL of permeate was collected for each test. The water permeance (J_w) was measured with ultrapure water, and the salt rejection R was determined using salt solutions. They were calculated using Eqs. (1) and (2), respectively. The $\text{Li}^+/\text{Mg}^{2+}$ selectivity ($S_{\text{Li}/\text{Mg}}$) and Li purity (η_{Li}) were calculated using Eqs. (3) and (4), respectively.

$$J_w = \frac{V}{A\Delta tP} \quad (1)$$

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \quad (2)$$

$$S_{\text{Li/Mg}} = \frac{C_{\text{Mg},f}/C_{\text{Li},f}}{C_{\text{Mg},p}/C_{\text{Li},p}} \quad (3)$$

$$\eta_{\text{Li}} = \frac{C_{\text{Li},p}}{C_{\text{Li},p} + C_{\text{Mg},p}} \quad (4)$$

where V (L) is the volume of permeated water, A (m^2) is the effective membrane area, t (h) is the testing time, and P (bar) is the applied pressure. Besides, the membrane flux ($\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$) was calculated by multiplying the permeance to applied pressure. The C_p ($C_{\text{Mg},p}$ and $C_{\text{Li},p}$) and C_f ($C_{\text{Mg},f}$ and $C_{\text{Li},f}$) ($\text{mol}\cdot\text{L}^{-1}$) are the salt concentrations in the permeate and feed solutions, respectively. For single-ion filtration test, the concentration of the solution was determined by ion conductivity meter (conductivity meter RS485, Mettler Toledo). For binary-ion filtration test, the concentration of Mg^{2+} and Li^+ were measured by inductively coupled plasma optical emission spectroscopy (ICP-OES, MDTC-EQ-M29-01). Note that the concentrations in terms of ppm represent the concentrations of MgCl_2 , LiCl , and KCl , and the $\text{Mg}^{2+}/\text{Li}^+$ ratio was calculated through dividing the mass concentration of Mg^{2+} ions to Li^+ ions.

2.5 Ion permeation measurement

Ion permeation test was conducted using a H-shaped diffusion cell. PGOM-80 was used to separate the feed and permeate chambers. The effective membrane area was 1 cm^2 . The feed side contained 20 mL of 0.1 M salt solution and the permeated side contained 20 mL of deionized water. For diffusion test under different pH, the pH of feed solution was adjusted with 0.1 M $\text{HCl}/\text{NH}_4\text{OH}$. During diffusion test, two chambers were stirred at $\sim 300\text{ rpm}$ and the concentration change was monitored to calculate the ion permeation rate (J_i) using Eq. (5). The concentration variation at permeate side was monitored by a conductivity meter (conductivity meter RS485, Mettler Toledo).

$$J_i = \frac{\Delta C \times V}{A \times \Delta t} \quad (5)$$

where ΔC ($\text{mol}\cdot\text{L}^{-1}$) is the ion concentration difference over Δt in the permeate side, V (L) is the volume of solution at permeate side, A (cm^2) is the effective membrane area, and Δt (h) is the permeation time (8 h in this work). All error bars are standard deviations obtained from at least three measurements.

2.6 Characterizations

X-ray diffraction (XRD) spectra were collected on a Bruker D8 Advance X-ray diffractometer with $\text{Cu K}\beta$ radiation. Fourier

transform infrared (FTIR) spectra were recorded on a Bruker TENSOR 37 FTIR spectrometer. The thicknesses of PGO nanosheets and PGOM were measured by Atomic force microscopy (AFM) (Bruker Dimension Icon, tapping mode). Differential scanning calorimetry (DSC) was conducted using NETZSCH 3500 Sirius. The conductivity of the solution in the permeate side of single-ion filtration test was measured with a conductivity meter (conductivity meter RS485, Mettler Toledo). Cation concentrations in binary-ion filtration test were measured using ICP-OES (Optima 7300 DV). X-ray photoelectron spectroscopy (XPS) spectra were recorded using a Kratos AXIS SUPRA+ instrument. Zeta potential of the membrane surface was analyzed by the potentiometric analyzer (SurPASS, Anton Paar Co., Austria). The surface morphology of the membrane was characterized using a scanning electron microscopy (SEM, ZEISS Sigma300).

3 Results and discussion

3.1 Microstructure of PGOM

The membrane preparation involves the following steps. First, GO nanosheets were chemisorbed with PEI, a polyamine electrolyte, to form hybrid 2D nanosheets (PGO) (Section 2), in which a GO nanosheet is sandwiched between two uniform 1-nm-thin PEI layers, resulting in a uniform thickness of PGO nanosheet of $\sim 3\text{ nm}$ verified by AFM measurement (Fig. S1 in the Electronic Supplementary Material (ESM)). The obtained PGO nanosheet exhibits a positive charge with a high charge density [38] and forms a stable aqueous colloid. Next, the PGO nanosheets were assembled into a laminar membrane on a PES substrate using vacuum filtration. Finally, the resulting membrane was treated at various mild temperatures (T) in an ambient environment for 0.5 h, yielding the PGOM- T (Fig. 1). As shown in Fig. S2 in the ESM, both the SEM images and the photograph of PGOM show a complete, uniform, and defect-free membrane structure, similar to those of many previously reported GO-based membranes [20, 22].

The PGOM was characterized using AFM and XRD. Typically, the used PGOM has an optimized thickness of $\sim 45\text{ nm}$ (Fig. 2(a)). At this thickness, membrane performance tests were conducted on its PES support, similar to many previous reports [24, 25]. Further reduction in membrane thickness results in a loss of membrane selectivity (Fig. S4 in the ESM). As each PGO nanosheet is $\sim 3\text{ nm}$ thick (Figs. S1(a) and S1(e) in the ESM), a thickness of 45 nm indicates that the PGOM consists of only ~ 15 layers of nanosheets, which is good for a high membrane permeance due to a small

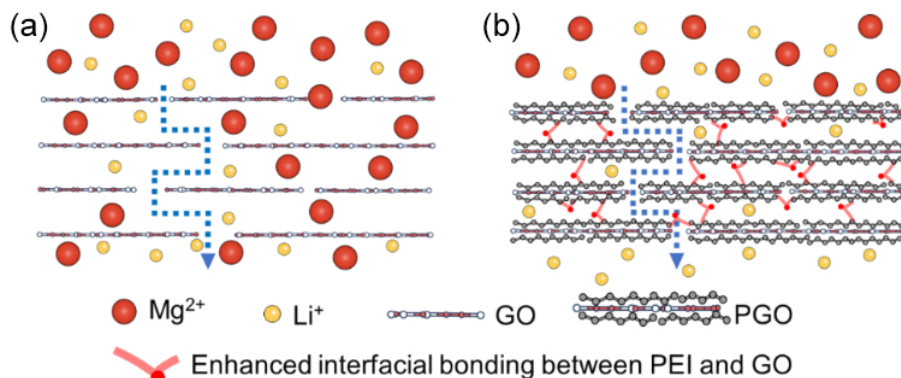


Figure 1 Schematic of (a) GOM and (b) PGOM and their ionic sieving properties.

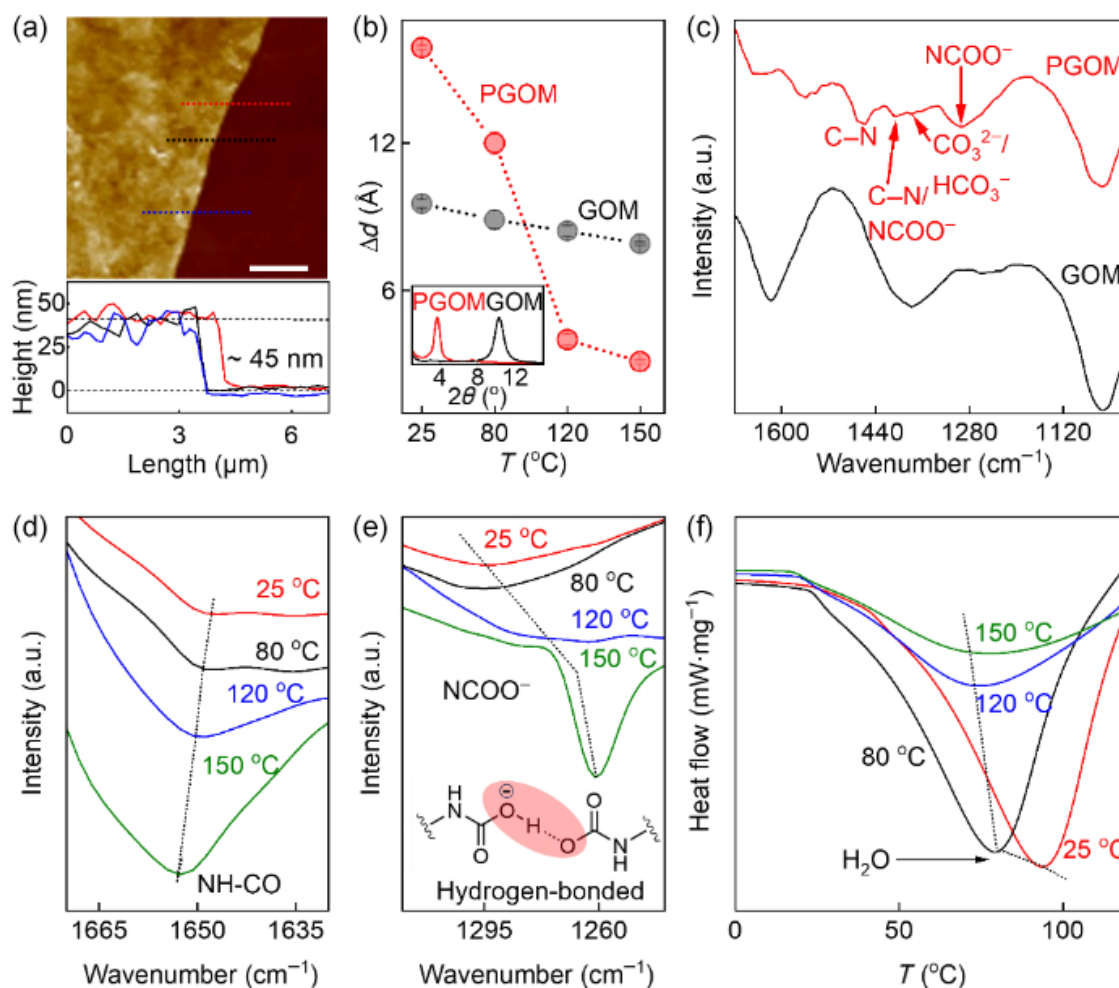


Figure 2 Structure of PGOM. (a) AFM image of PGOM-80 and the height profiles along the dashed lines. Scale bar is 4 μm . (b) The Δd of PGOM (red) and GOM (black) as a function of T . Inset: XRD patterns of dry PGOM-25 (red) and GOM-25 (black). (c) FTIR spectra of the GOM-25 and PGOM-25. ((d) and (e)) The detailed FTIR spectra of PGOM- T at regions around (d) 1650 and (e) 1265–1307 cm^{-1} . Inset: schematic illustration of PEI-PEI crosslinking. (f) DSC analysis of PGOM- T .

thickness. The XRD pattern of PGOM (inset in Fig. 2(b)) shows a single diffraction peak distinct from GOM, such structural periodicity further confirms the formation of uniformly aligned and two-dimensional channel. Besides, the XRD analysis (Fig. S3(a) in the ESM) reveals that T , ranging from ~ 25 to 150 $^{\circ}\text{C}$, notably changed the swelling behavior of the PGOM- T . To quantify this, we followed the previously reported method [5] and defined effective interlayer gallery width $\Delta d = d_{\text{wet}} - t$, where d_{wet} is the interlayer distance of water-soaked PGOM, and t is PGO nanosheet thickness (Fig. S1 in the ESM). The error bars for Δd at different T presented in Fig. 2(b) denoted the standard deviations, and they were obtained from at least three independent measurements across different batches, validating the reproducibility and reliability for the effective control of Δd . At $T = 25$ $^{\circ}\text{C}$, Δd is 1.6 nm, but decreases to 1.19, 0.38, and 0.30 nm at 80, 120, and 150 $^{\circ}\text{C}$, respectively (Fig. 2(b)). In contrast, the pristine GO membrane shows only a marginal Δd reduction (< 0.2 nm) over the same temperature range, suggesting that the sharply decreased Δd in PGOM- T cannot be attributed to structural changes of GO nanosheets by mild thermal reduction.

Rather, the substantial Δd reduction arises from interfaces within the PGO composite, where PEI is confined between GO nanosheets, forming GO-PEI and PEI-PEI interfaces. FTIR

spectroscopy reveals that the band at 1650 cm^{-1} , attributed to amide groups [33, 38] formed by the reaction between carboxyl groups of GO and amine groups of PEI [39, 40], intensifies with increasing T (Figs. 2(c) and 2(d)), suggesting an enhanced covalent bonding at the GO-PEI interface. XPS further corroborates this chemical evolution of PGOM (Fig. S7 in the ESM). Upon PEI modification, the C/O ratio increases from 2.79 for pristine GOM to 3.31 for PGOM, which is attributed to the *in-situ* thermal reduction of oxygen-containing functional groups. In the C 1s spectrum of PGOM, a new peak emerging at ~ 285.3 eV corresponds to C-N bond [19, 20]. This covalent bonding is further confirmed by the N 1s spectrum, which shows the characteristic peaks for N-C=O (~ 399.3 eV) and HN-C=O (~ 398.5 eV) [32]. Simultaneously, a band at 1265 – 1307 cm^{-1} , absent in pristine GOM but present in PGOM (Fig. 2(c), and Figs. S5 and S6 in the ESM), increases in intensity and redshifts with T (Fig. 2(e)). This band, previously [41, 42] assigned to NCOO $^{-}$ skeletal vibrations from CO $_2$ chemisorption by PEI, could be the sign of the formation of mixed carbamate/carbamic acid pairs through hydrogen bonding and ion-pairing [43] (inset in Fig. 2(e)), indicating PEI-PEI crosslinking. To explain the source of CO $_2$, we recall that thermal treatment of GO triggers partial decomposition of carboxylic acids and releases CO $_2$ [44–46], promoting PEI chain crosslinking and also in good

agreement with a higher level of crosslinking at a high T as GO reduction becomes stronger. This crosslinking eliminates the hydration of amine group, retarding the swelling behaviour, explaining the decreased Δd at a high T . DSC further supports this [47], and water desorption temperature decreases from 93 °C in PGOM-25 to ~ 70 °C in PGOM-150 (Fig. 2(f)), indicating weaker water-PGOM interactions consistent with increased PEI crosslinking. In addition, the membrane surface potential analysis also supports the PEI crosslinking with increased T (Fig. S8 in the ESM). While pristine GOM shows a negatively charged surface, PGOM-25 has a positive surface zeta potential of 49.03 mV, which decreases to 34.17 and 16.17 mV for PGOM-80 and PGOM-120, respectively, suggesting that a higher degree of PEI crosslinking at elevated T decreases the availability of free amine groups, leading to a lower positive surface charge. Together, the synergistic strengthening of GO-PEI (amide formation) and PEI-PEI (CO_2 -mediated crosslinking) interfaces (Fig. 1(b)) finely tunes interlayer spacing, promising for size-exclusion-based ionic sieving.

3.2 Ion sieving over a wide concentration range

We firstly evaluated ion permeability through PGOM- T using pressure-driven filtration at concentrations of 50 and 1000 ppm. As shown in Fig. 3(a), at 50 ppm (0.0006, 0.001, and 0.0005 M for K^+ , Li^+ , and Mg^{2+} , respectively), the PGOM-25 rejects 80%, 88.1%, and 90.5% of K^+ , Li^+ , and Mg^{2+} , respectively. Besides, the PGOM shows an insensitivity of ionic selectivity to the increased T (decreased Δd), suggesting a Donnan-effect-dominated ionic sieving at low ionic concentration, consistent with the previous reports on positively charged membranes [22]. At 1000 ppm (0.013, 0.02, and 0.01 M for K^+ , Li^+ , and Mg^{2+} , respectively), where the Donnan effect weakens due to the substantially reduced Debye length, PGOM-25 shows significantly decreased rejections to K^+ (10.2%), Li^+ (9.3%), and Mg^{2+} (30%), resulted from the contribution loss from Donnan exclusion and absence of size-sieving with large Δd .

In contrast, PGOM-80 maintains a rejection of 95.3% for Mg^{2+} , but a decreased rejection for K^+ (50.4%) and Li^+ (48.1%), suggesting that a size-exclusion-based mechanism starts to dominate the ionic sieving with Δd smaller than 0.85 nm (hydrated diameter of Mg^{2+}). PGOM-120 achieves more than 82% rejections for all three ions, consistent with the measured small Δd (Fig. 2(b)). Moreover, as expected, high selectivity leads to decreased permeance. For example, PGOM-80 shows a water permeance of $2.3 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ (Fig. S9 in the ESM), with a stable long-term performance for MgCl_2 sieving measured at 8 bar for more than 100 h (Fig. S11 and Table S3 in the ESM), but PGOM-120 shows only a water permeance of $0.7 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$. Considering a balance between ionic selectivity and permeance and a significant rejection difference between Mg^{2+} and Li^+ , we focused on PGOM-80 and studied its use for $\text{Li}^+/\text{Mg}^{2+}$ separation under realistic conditions.

We compared the energy barriers for various ions diffusing through PGOM-80 at different temperatures using Arrhenius equation, $\exp(-E/k_B T)$ (Fig. 3(b)). It is found that Ca^{2+} ($53.76 \text{ kJ}\cdot\text{mol}^{-1}$) and Mg^{2+} ($58.99 \text{ kJ}\cdot\text{mol}^{-1}$) ions experience higher energy barriers, compared to monovalent ions (K^+ : $48.08 \text{ kJ}\cdot\text{mol}^{-1}$, Na^+ : $36.59 \text{ kJ}\cdot\text{mol}^{-1}$, and Li^+ : $25.1 \text{ kJ}\cdot\text{mol}^{-1}$). The largest energy barrier difference between Li^+ and Mg^{2+} further supports the selectivity of PGOM-80 for $\text{Li}^+/\text{Mg}^{2+}$ separation.

Since a high Mg^{2+} rejection maintained at a higher concentration above 0.06 M is essential for $\text{Li}^+/\text{Mg}^{2+}$ separation from low-quality brines [6], we measured the Mg^{2+} rejections at MgCl_2

concentrations of 1000, 5000, and 10,000 ppm (0.01, 0.05, and 0.1 M, respectively) (Fig. 3(c)). Compared to the pristine GOM-80, which shows rejections of only ~ 20% to Mg^{2+} across these concentration ranges (Fig. S10 in the ESM), the PGOM-80 sustains a high Mg^{2+} rejection larger than 75.2% at 0.1 M, similar to previously reported TBO-GO membrane for NaCl rejection at similar high ionic concentration (70% to 0.1 M NaCl) [37]. We also prepared two other types of GO-PEI composite membranes following previous reports by dip-coating PEI on the GO membrane surface [48] and by assembling a mixture of PEI solution and GO suspension [49]. Both membranes show significantly lower Mg^{2+} rejections, especially at the high concentration of 10,000 ppm (Mg^{2+} rejection less than 30%) (Fig. S12 in the ESM), manifesting the advantages of the positively charged uniform 2D nanochannel for enhanced MgCl_2 rejection at high concentrations (Section S2.1 in the ESM). Furthermore, we compared the PGOM-80 with previously reported 2D material-based membranes including GO [18–29], MXene [50], layered double hydroxide [51], and montmorillonite membranes [52], as they all share similar 2D nanochannel. These previously reported 2D membranes either largely focus on the Mg^{2+} rejection at low concentrations (Fig. 3(d) and Table S1 in the ESM), or achieve high selectivity under static diffusion tests (Table S2 in the ESM). In contrast, PGOM-80 maintains high Mg^{2+} rejections across a wide concentration range under pressure-driven filtration, exhibiting a permeance comparable to most state-of-the-art 2D material-based membranes recently reported for $\text{Li}^+/\text{Mg}^{2+}$ separation (Table S1 in the ESM). This performance provides unambiguous evidence for its use in lithium extraction from low quality brines.

To examine lithium extraction from low-quality brines, we measured the membrane's selectivity to $\text{Li}^+/\text{Mg}^{2+}$ using a series of mixtures with fixed low LiCl concentration (250 ppm) and increased MgCl_2 concentrations from 1000, 5000, 10,000, and 20,000 ppm, respectively. Notably, 250 ppm LiCl and 10,000 ppm MgCl_2 are similar to the concentration of some low-quality salt-lakes (for example, East Taijinar Lake, China [53]). We observe sustained Mg^{2+} rejection (> 75.16%) at high concentration (0.1 M) (Fig. 3(e)), similar to the rejection obtained from the single-ion filtration test, while the Li^+ rejection becomes negative due to the synergistic effect of co-ion competition [54, 55] and charge-balance [14, 56]. During this process, Li^+ experiences lower transport resistance than Mg^{2+} , which, combined with the facile permeation of Cl^- , leads to a significant Li^+ enrichment in the permeate side. After filtration, the $\text{Mg}^{2+}/\text{Li}^+$ ratio decreases from 66, 34, and 6.4 in the feed side to 15, 4.5, and 0.49 in the permeate side, respectively (Fig. S13(b) in the ESM), and the corresponding selectivity was estimated to range from 5.2 to 11.6, which is higher than that of many commercial membranes (Fig. S13(c) and Table S4 in the ESM), especially at high salinity. In stark contrast, the pristine GO membranes show neglectable changes in the $\text{Mg}^{2+}/\text{Li}^+$ ratio after filtration (from 66, 34, and 6.4 in the feed side to 65, 33.2, and 5.8 in the permeate side, respectively). In addition, the observed $\text{Li}^+/\text{Mg}^{2+}$ separation in PGOM-80 is stable. For a continuous pressurized filtration process (more than 100 h at 8 bar), the membrane shows only a decrease of ~ 6% in water flux while maintaining a Mg^{2+} rejection of ~ 72.1% (10,000 ppm MgCl_2 and $\text{Mg}^{2+}/\text{Li}^+$ ratio of 66) (Fig. S14 and Table S3 in the ESM).

Next, we used a streamlined separation process containing three-stage successive nanofiltration to demonstrate its application for lithium extraction from the simulated low-quality brines, which

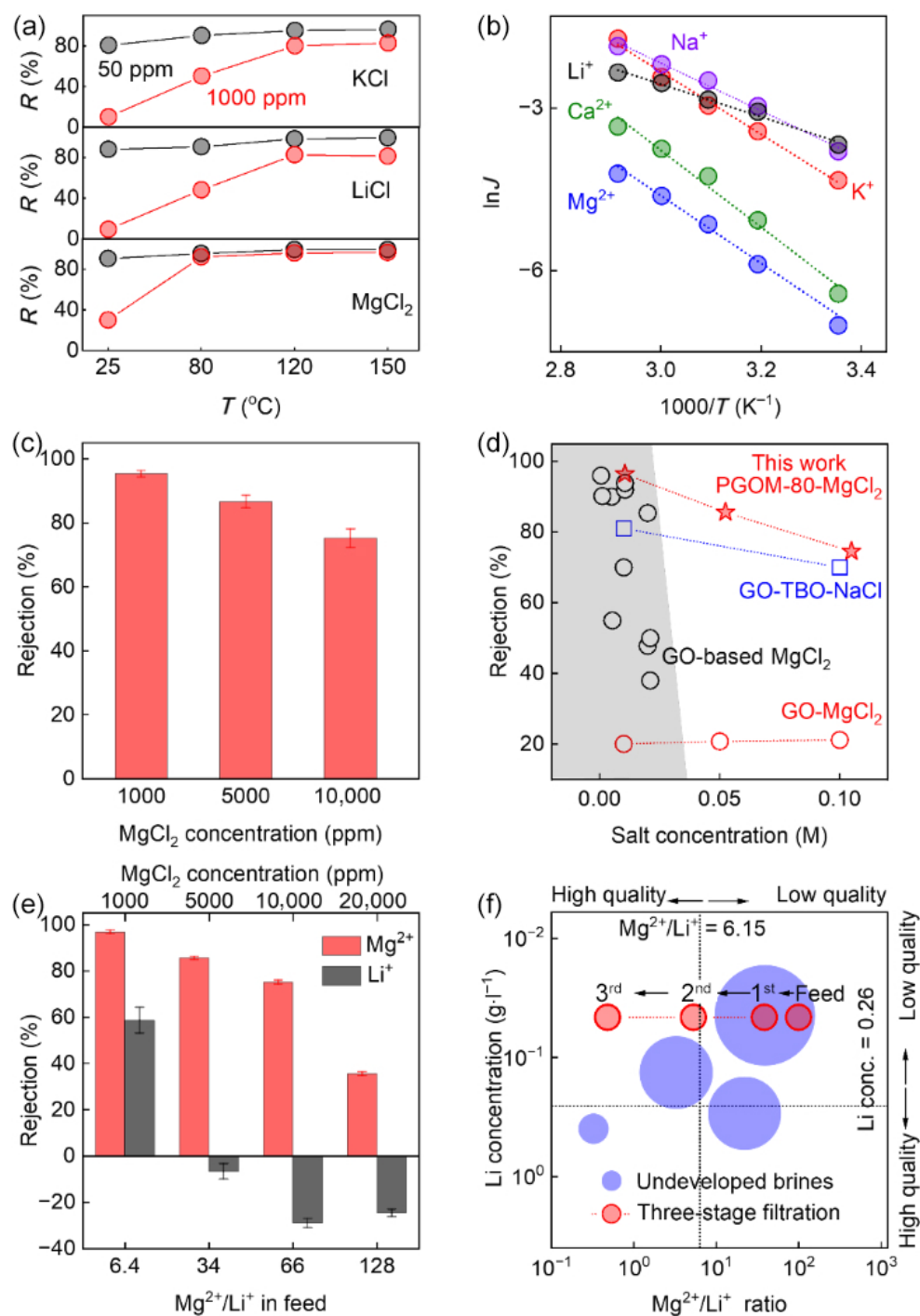


Figure 3 Ion sieving through the atomic-scale nanochannels. (a) PGOM's rejections to ions as a function of T . (b) Arrhenius plots of temperature against ion permeation rates through PGOM-80. (c) PGOM-80's rejections to $MgCl_2$ with different salt concentrations. (d) Comparison of salt rejection to feed concentrations with other 2D materials-based membranes. (e) PGOM-80's rejections to Mg^{2+} and Li^+ in mixed-ion systems. (f) The Mg^{2+}/Li^+ ratios during the three-stage nanofiltration and the distribution of undeveloped salt lakes with respect to Mg^{2+}/Li^+ ratio and Li^+ concentration, highlighted as blue circles.

contains 16,250 ppm $MgCl_2$ and $LiCl$ with a Mg^{2+}/Li^+ ratio of 100, similar to the composition of brine water in East Taijinar Lake [53]. As a result, the Mg^{2+}/Li^+ ratio in the feed solution decreases from 100 to 38.32, 5.29, and 0.48 after the 1st, 2nd, and 3rd filtration steps, respectively (Fig. 3(f)), while most of the undeveloped brines are characterized with low lithium concentrations, high Mg/Li ratios, or both, as highlighted as blue circles. The larger the circle, the greater the number of salt lakes within the corresponding ranges of lithium

concentration and Mg/Li ratio. Notably, after the 2nd filtration step, the Mg^{2+}/Li^+ ratio has fallen within the needed Mg^{2+}/Li^+ range for high quality brines, thus the permeate can be further processed either using a 3rd filtration step, as shown in Fig. 3(f), which achieved an Mg^{2+} rejection of 99.53% and a lithium purity of 79.3%, outperforming many commercial membranes (Table S5 in the ESM) or the use of commercial solar evaporation–precipitation process which enriches lithium from the brine with high Li^+/Mg^{2+}

ratios, enabling efficient and industrial-compatible lithium extraction. We note that in practical brine systems, co-existing ions may influence interfacial ion transport behaviour in membrane processes, which warrants further investigation in future studies. Practical implementation is therefore expected to rely on multi-stage process integration, in which the membrane developed in this work serves as a targeted $\text{Li}^+/\text{Mg}^{2+}$ separation unit within an overall lithium recovery process.

3.3 The separation mechanism

The positively charged 2D nanochannels in PGOM-80 not only enable lithium extraction from low-quality brines, which is not achieved in 2D material-based membranes previously, but also provide a new platform for mechanistic studies of ionic transport in the nano-confinement with positively charged surfaces. The Δd (1.19 nm) observed in PGOM-80 is larger than the hydration size of Mg^{2+} , but the membrane shows a size-exclusion-dominated ionic sieving to Mg^{2+} . To understand this seemingly counterintuitive phenomenon, we first consider the role of counter-ion adsorption. The charged channel surfaces attract counter-ions (ions with opposite charge), which in our case are Cl^- . Unlike static adsorption, Cl^- adsorption layer is dynamic, as the ions diffuse directionally from the feed side to the permeate side driven by the concentration gradient. This dynamic behavior makes XRD ineffective in capturing Δd shrinkage caused by such Cl^- adsorption. To further verify Cl^- adsorption on the channel surfaces, we performed XPS analysis on MgCl_2 -immersed PGOM-80. The results reveal an atomic ratio of Cl/Mg^{2+} of ~ 3 (Fig. S15 in the ESM), deviating significantly from the stoichiometric ratio of MgCl_2 , thus suggest Cl^- adsorption at the channel surface. Given that Cl^- has an ionic diameter of 0.36 nm, its adsorption on the channel surface should narrow the effective interlayer gallery width, allowing the size-exclusion-based ionic sieving.

To quantify this effect, we conducted molecular dynamics (MD) simulations using two simplified nitrogenated graphene (GN) sheets with positive charge to construct the channel (Section S4.1 in the ESM). The results show that Cl^- ions readily adsorb on the charged surface due to the electrostatic attraction, forming a counter-ion layer that dynamically moves through the channel, which is independent of ionic concentration (Fig. 4(a) and Fig. S16 in the ESM). The interlayer distance measured between the $\text{Cl}-\text{Cl}$ resulting in Δd of 9 Å (Fig. 4(b)), similar to the hydrated size of Mg^{2+} ions, but significantly larger than the hydrated size of Li^+ ion, quantitatively explaining the size-exclusion-based rejection of Mg^{2+} while permeation of Li^+ .

To further validate the counter-ion adsorption enabled ionic sieving property in PGOM-80, we tested Mg^{2+} permeation rates though the PGOM-80 with suppressed counter-ion adsorption by increasing pH and replacing Cl^- with larger counter-ion of Br^- and I^- . At pH of ~ 10 , amine group of PGOM deprotonates, the surface zeta potential measurements show that the membrane surface becomes negatively charged (Fig. S17(b) in the ESM), which suppresses the Cl^- ion adsorption due to the weakened electrostatic attraction. As a result, Mg^{2+} permeation rate increased nearly 10-fold compared to that at pH of ~ 4 and 7 where the membrane potential is positive (Fig. S17(a) and Table S6 in the ESM), and this also aligns with the PGOM-80's rejections to Mg^{2+} at various pH measured by pressure-driven nanofiltration (Fig. 4(e)). Specifically, MgCl_2 rejections decreased to $\sim 76\%$ and $\sim 50\%$ under pH of 10 at the concentrations of 1000 and 10,000 ppm, respectively. Since XRD analysis (Fig. S17(c) in the ESM) showed no significant

change in Δd (~ 1.2 nm) at pH of ~ 4 , 7, and 10, Donnan repulsion under such high concentrations becomes less effective, confirming that the increase in Mg^{2+} permeation (decrease in MgCl_2 rejection) stems from the suppressed Cl^- adsorption induced weak counter-ion narrowing effect. Conversely, through replacing Cl^- with larger counter-ions, such as Br^- or I^- (using MgBr_2 and MgI_2 for diffusion test) (Figs. 4(f) and 4(g), and Table S7 in the ESM), we found that the Mg^{2+} diffusion rate decreases from ~ 0.0015 to $0.0006 \text{ mol}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$ for MgBr_2 and to $0.0003 \text{ mol}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$ for MgI_2 . Note that these halide-ions are still smaller than Mg^{2+} , hence their contribution to the size-exclusion-based Mg^{2+} rejection is neglectable. Together, these results confirm that counter-ion adsorption reduces the effective interlayer gallery width, enabling high Mg^{2+} rejection.

While counter-ion adsorption explains $\text{Li}^+/\text{Mg}^{2+}$ selectivity at high ionic strengths (where Donnan effect diminishes), it also contributes to the mild decrease in Mg^{2+} rejection at high Mg^{2+} concentrations ($\sim 10,000$ ppm). A similar trend at high concentrations has been reported for NaCl rejection in TBO-GO membranes [37], but the underlying mechanism had remained unclear.

The observed mild rejection decreasing at higher Mg^{2+} concentration clearly indicates that ion sieving is not purely governed by geometric constraints. In contrast to diluted solutions, the ion hydration behavior at high Mg^{2+} concentrations should consider the interplay between the Mg^{2+} hydration structure and its ionic pairing effects with Cl^- [57]. This is attributed to the relatively soft second hydration shell of Mg^{2+} , due to weakened hydrogen bonding between water molecules at second hydration shell and Mg^{2+} ions [58]. Concurrently, ionic pairing ($\text{Mg}^{2+}-\text{Cl}^-$) in the solution becomes more significant at high ionic concentrations due to reduced interionic distances compared to dilute solutions [59]. This competition between hydration ($\text{Mg}^{2+}-\text{H}_2\text{O}$) and pairing ($\text{Mg}^{2+}-\text{Cl}^-$) allows Cl^- ions to disrupt and penetrate the softened second hydration shell of Mg^{2+} , displacing water molecules and forming a hybrid hydration structure of Mg^{2+} incorporating both water and Cl^- at high concentrations, as confirmed both experimentally and theoretically in previous reports [58, 60–63], and is also in good agreement with our MD simulation results (Fig. 4(c)).

Subsequently, our simulations of Mg^{2+} ion transport with this Cl^- -hybridized hydration shell (Fig. S18 in the ESM) reveal a counter-ion exchange mechanism, as illustrated in Fig. 4(d). Specifically, as Mg^{2+} approaches the channel entrance, adsorbed Cl^- ions on the channel surface begin to pair with the hydrated Mg^{2+} , replacing Cl^- in Mg^{2+} hydration shell. This effectively reduces the apparent size of the hydrated Mg^{2+} , facilitating Mg^{2+} permeation through the nanochannel. Together, counter-ion adsorption not only narrows the membrane's effective interlayer gallery width, but also contributes to mild permeation of ions with altered hydration structure under high concentrations through this counter-ion exchange mechanism.

4 Conclusions

We experimentally controlled the interlayer gallery width of GO membranes through the uniform addition of a layer of polyelectrolyte (polyamine) and its *in-situ* crosslinking by a mild thermal treatment. The formed uniform and swell-restrained 2D nanochannel provides enhanced size-exclusion-based Mg^{2+}

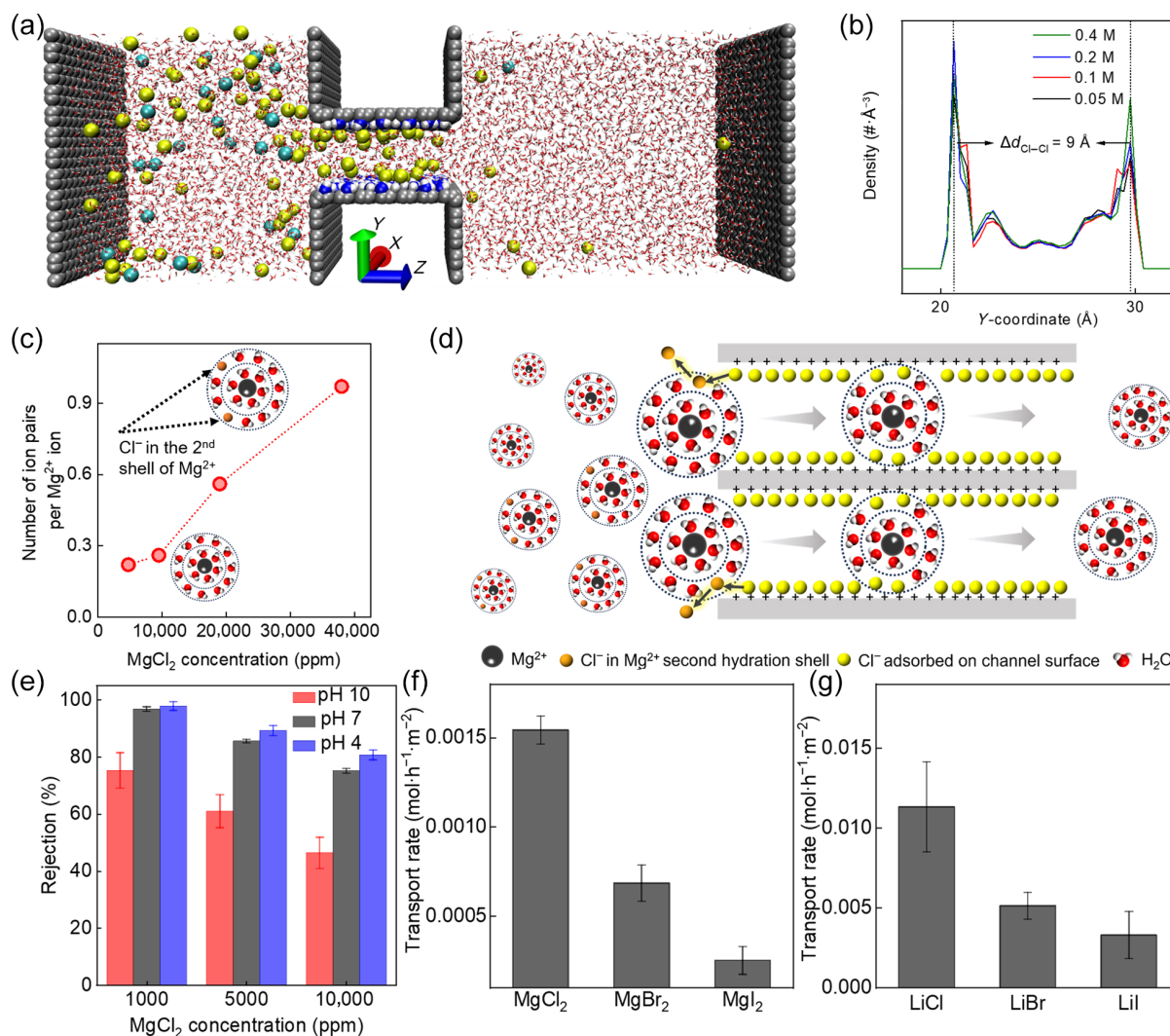


Figure 4 Ion separation mechanisms for PGOM. (a) The snapshot of the system after non-equilibrium MD simulation with initial MgCl_2 concentration of 0.4 M. (b) Number density profiles for the counter-ion (Cl^-) in the nanochannels along the Y-axis as a function of the MgCl_2 concentration. (c) The number of ion pairs per Mg^{2+} at different concentrations. (d) Schematic illustration of counter-ion exchange mechanism. (e) PGOM-80's rejections to MgCl_2 with different salt concentrations under different pH. (f) Mg^{2+} and (g) Li^+ ion permeation rates with different counter-ions.

rejections over a wide range of concentrations with a high Li^+ permeation rate. This allows the efficient lithium extraction from low-quality brines. The adsorption of counter-ions on the 2D charged channel surface is found to dominate the ionic selectivity by narrowing the effective interlayer gallery width and allowing mild Mg^{2+} permeation at high concentrations through a counter-ion exchange mechanism. The intercalation of polyelectrolyte in the GO membrane and its subsequent crosslinking provides a new route for assembly of GO-based membrane with well controlled interlayer space, and the demonstrated capability for $\text{Li}^+/\text{Mg}^{2+}$ separation from low-quality brines. We envisage that, combining with future development on scale-up preparation of large-area PGOM using the existing large-area fabrication methods for GO-based membranes including rod-coating [64] and blade coating [65], our work provides a solution to address current challenge in lithium resource sustainability. Notably, the crucial role of counter-ion adsorption in controlling the membrane's ionic sieving property, which was long overlooked, offers insights on nanoscale ionic transport through highly charged surfaces, and invites further exploration. Finally, despite the membrane permeance being

comparable to previously reported values, it could be further improved by introducing in-plane sub-nanometer pores to enhance lithium extraction efficiency.

Electronic Supplementary Material: Supplementary material (characterization, additional data, and simulation methods) is available in the online version of this article at <https://doi.org/10.26599/NR.2026.94908964>.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

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Declaration of competing interest

All the contributing authors report no conflict of interests in this work.

Author contribution statement

Y. S. conceived the idea and supervised the project. X. Y. G. performed the experiments and data analyses. X. Y. G., D. X. X., Y. X. L., and H. L. J. carried out structural characterizations. M. F. H. conducted MD simulations with the supervision of K. Y. X. Y. G., Z. C., and Y. S. wrote the manuscript. All the authors have approved the final manuscript.

Use of AI statement

None.

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