Methanol/dimethyl carbonate separation using graphene oxide membrane via cationic control of molecular transport channels

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ARTICLE INFO

Keywords:
Organic-organic mixtures
Graphene oxide membrane
Pervaporation
Methanol/dimethyl carbonate
Cationic control

ABSTRACT

The separation of small molecular organic-organic mixtures by membranes show considerable potential in energy efficiency, while the performance of polymeric membranes is unattractive. Two-dimensional (2D) graphene oxide (GO) membranes having ultra-fast and selective molecular transport channels could be an ideal platform for separating the organic-organic mixtures, however, such potential is not fully explored. In this paper, towards pervaporation separation of methanol (MeOH)/dimethyl carbonate (DMC) solvents, GO membrane with tunable interlayer and stable structure was prepared by anchoring metal ions between GO sheets. The introduced cations formed cation-π interaction with the sp² region of GO, and electrostatic attraction with carboxyl, hydroxyl and epoxy groups on GO sheets. The molecular transport channels of GO membrane was optimized by optimizing the cation species (Na⁺, K⁺, Zn²⁺, Ca²⁺), cation content and GO flake sizes. The total flux of GO-Zn²⁺ membrane is 707.3 g/(m²⋅h) as well as separation factor is 61.9 for separation of 10 wt% MeOH/DMC mixtures by pervaporation at 50 °C. Meanwhile, the cationic control highly enhanced the stability of the GO membrane during continuous pervaporation process. This work reveals that GO membranes are the feasible for the application in pervaporation separation of organic-organic mixtures.

1. Introduction

The separation of small molecular organic mixtures is high energy consumption by distillation and extraction [1]. Membrane process to separate organic mixtures show considerable potential in energy efficiency (e.g., pervaporation [2-5], organic solvent nanofiltration [6,7] and reverse osmosis [8,9] etc.). The components can selectively permeate the membrane by applying a driving force on one side of the membrane [10]. It is important that precisely constructed membrane pore structure with size sieving effect and chemical environment providing preferential adsorption of organic component, which can achieve high separation efficiency toward small molecular organic-organic mixtures [11].

Over the past decades, various membrane materials have been explored to separate the small molecular organic mixtures, such as polymers [8], zeolites [12], silica [4], and carbon materials [9]. Among them, polymeric membranes based on free volumes cavities could hardly provide regular transport channels, and are prone to be swelled in organic solvents. Inorganic membranes exhibited outstanding separation efficiency and solvent tolerance, while the defined crystalline pore size sometimes is difficult to match the molecular size of variable organic mixtures. Alternatively, 2D materials, such as GO [13,14], owing to the atomic thickness and controllable interlayer channels, showed exciting performance for gas separation [15,16], water purification [17,18] and dehydration of organic solvent [19-21]. GO membranes is promising for the separation of small molecular organic mixtures [22,23].

Precisely constructing interlayer channels with molecular sieving performance and enhanced membrane stability are important for the application of GO membranes [24,25]. There are many strategies to improve the GO membranes pervaporation performance, such as surface modification [26] and intercalation [20]. Crosslinking is another powerful tool, which can precisely construct the interlayer distance of GO membranes and avoid excessive swelling of GO membranes [27,28].
Until now, most of these works regarding GO pervaporation membranes focused on dehydration of organic solvents, such as ethanol and butanol. Although organic solvent nanofiltration membranes have higher flux of solvent, these membranes are mostly used to reject dyes and drug molecules with relatively large molecular sizes \[6, 7, 29\]. However, as another important while more challenging application, the separation of small organic solvents, such as MeOH/DMC, is rarely realized \[11\]. The challenges include constructing suitable transport channels in GO membranes to effectively separate these small-sized organic molecules, and the structural stability of GO membranes in organics.

Our previous work demonstrated that monovalent cations can finely construct the interlayer channels of GO membranes for ion sieving in aqueous solution \[30\]. It is expected to realize the separation of small molecular organic mixtures (<1 nm of molecular kinetic diameter) by rationally introducing cations to control the molecular transport channels of GO membranes. In this work, therefore, we introduced metal cations, to tune the molecular transport channels of GO membranes to realize efficient separation of MeOH/DMC mixtures by pervaporation. As shown in Fig. 1, we constructed two kinds of molecular interactions between cations and GO sheets \[23, 31\]. One is the electrostatic interaction, which is the interaction of the cation with carboxyl on the edges of GO sheets and hydroxy and epoxy on the planes of GO flakes. It regulates the interlayer channels of the GO membranes. Meanwhile, cations at the edge of GO sheets, especially divalent cations, can form steric hindrance. The other is the cation-π interaction, mainly occurring in the sp² area of GO sheets \[32\], which will enlarge the interlayer channel of the GO membrane. Therefore, the introduced cations not only enhance the size sieving effect of interlayer channels and silt-like pores of GO membrane, but also generate electrostatic interaction with polar MeOH molecules \[23\]. As a result, MeOH molecules were preferentially permeated through the cationic controlled GO membranes. Meanwhile, the cationic control highly enhanced the stability of the GO membrane during continuous pervaporation separation of MeOH/DMC solvents.

2. Experimental

2.1. Materials

Deionized (DI) water was homemade. Polyacrylonitrile (PAN) membrane was got from Shandong Lanjing Co., Ltd. GO dispersions (the flake sizes are 5–8, 20–30 and 40–50 μm respectively) were purchased from Hangzhou Goxi Technology Co., Ltd. NaCl, KCl, CaCl₂ and ZnCl₂ were got from Aladdin Biochemical Technology Co., Ltd.

2.2. Membrane fabrication

GO dispersions were diluted to form 5 mg/g GO suspension. The inorganic salt was formulated into an aqueous solution with a mass fraction of 0.5 wt%. Take a certain amount of GO solution in a glass bottle, then add the inorganic salt solution dropwise to the glass bottle. The mass ratio of GO to metal ions was adjusted by controlling the amount of salt solution added. Finally, DI water was added dropwise to the glass bottle to dilute the GO solution to 3 mg/g. The mixed solution was first stirred for 30 min, and then sonicated for 10 min to make it evenly mixed. The resulting solution was coated on the PAN substrate, and dried for 24 h at room temperature, and 12 h at 50 °C. The membranes fabricated by using GO, NaCl/GO, KCl/GO, CaCl₂/GO, and ZnCl₂/GO solution were named as GO, GO-Na⁺, GO-K⁺, GO-Ca²⁺ and GO-Zn²⁺ membrane, respectively.

2.3. Characterisations

The interaction of GO sheets with cations was characterized by fourier transform infrared spectra (FT-IR, Thermo, Nicolet Nexus 470 spectrometer, USA). The strength of interaction between GO sheets and cations was characterized by Zeta potential analysis (Zetasizer Nano ZS90). The surface morphologies and section thickness of the membranes were characterized by field emission scanning electron microscopy (S4800, Hitachi, Japan) and atomic force microscopy (AFM, Fig. 1. Schematic of cationic controlled GO membrane for MeOH/DMC separation.
Quartz crystal microbalance (QCM200, Stanford Research Systems, Inc.) was used to determine contact angle (CA, DropMeter A-100P, China) and the membrane's affinity for MeOH and DMC is evaluated by X-ray diffraction (XRD, Bruker D8 Advance, Germany). The membrane performance measurements were operated by pervaporation separation of 10 wt% MeOH/DMC solution at 50 °C. The membrane area is about 2.1 cm². All test results were repeated at least 3 times. Permeation total flux \( J \) and separation factor \( a \) are evaluated:

\[
J = \frac{W}{At}
\]

\[
a = \frac{Y_a/Y_b}{X_a/X_b}
\]

where \( W \) is weight of the permeate (g), \( A \) is effective area of the membrane (m²), \( t \) is the test time (h), \( X \) and \( Y \) are the weight fractions of components in the feed and permeation, respectively. The subscripts \( A \) and \( B \) refer to MeOH and DMC, respectively.

The activation energy of the molecular transport process was calculated by the Arrhenius equation:

\[
J_i = A_i \exp(-\frac{E_i}{RT})
\]

where \( J_i \), \( A_i \), and \( E_i \) is the permeation flux (g/(m²·h)), pre-exponential factor (g/(m²·h)), and apparent activation energy (J/mol) of MeOH and DMC, respectively. \( R = 8.314 \text{ J/mol} \cdot \text{K} \) and \( T \) is feed temperature (K), respectively.

2.4. Membrane performance measurements

The membrane performance measurements were operated by pervaporation separation of 10 wt% MeOH/DMC solution at 50 °C. The membrane area is about 2.1 cm². All test results were repeated at least 3 times. Permeation total flux \( J \) and separation factor \( a \) are evaluated:

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3. Results and discussion

3.1. Interaction of cations and GO sheets

IR spectra was used to study the interaction between GO sheets and metal cations. As shown in Fig. 2, all the membranes showed C–O, aromatic C–C, carboxy C–O, epoxy/ether C–O, alkoxy/alkoxide C–O stretches. The C–O stretch intensity of the GO-cations membranes decreased (especially Ca²⁺ and Zn²⁺) compared with pure GO membrane, while the C–O stretch intensity of the carboxyl group increased, and red shifted, indicating that the carboxylic acid coordinated with the cations (electrostatic interaction) [31]. It can be predicted that the cations will bridge GO sheets in the same plane (as shown in Fig. 1), because the carboxyl is on the edges of the GO flakes. The epoxy/ether C–O stretch intensity decreased slightly at 1222 cm⁻¹, and the C–O intensity increased at 1080 cm⁻¹. It may be because that the cations caused the ring-opening of the epoxy [34]. There is a red shift of C=C peak, indicating that cations produced a cation-π interaction with GO sheets. Furthermore, the red shift of C=O stretch at 1080 cm⁻¹ suggests that metal ions produced electrostatic interaction with –OH on the GO sheets [31]. The IR results demonstrate that the introduced metal ions formed two types of molecular interactions with GO sheets (as shown in Fig. 1). One is electrostatic interaction with the sp³ region of GO, another is cation-π interaction with the sp² region [23,32].

Different salt solutions were mixed with the GO suspension to characterize the interaction strength between the GO sheets and cations. As shown in Fig. 3a, when monovalent cations (K⁺ and Na⁺) were added to the GO suspension, the suspension did not change significantly. However, when the divalent cation solutions were mixed with the GO solution, the GO sheets immediately agglomerated. This is because the strong electrostatic interaction between GO sheets and divalent cations shields the negative charges on GO sheets [23,32]. After 18 h, obvious precipitation occurred to GO-Ca²⁺ suspension, slight aggregation occurred to GO-Zn²⁺, while the GO suspension with monovalent cations has no aggregation. We thus speculated that the interaction force between GO sheets and divalent cations is stronger than than that of monovalent cations, and Ca²⁺ is stronger than Zn²⁺.

To further study the interaction between GO sheets and cations, we analyzed the Zeta potential of the pure GO and the GO-Cation solutions. It can be seen from Fig. 3b that the Zeta potential of GO-Na⁺, GO-K⁺, GO-Zn²⁺, and GO-Ca²⁺ solution continuously increased compared with the pure GO solution. Which demonstrate that cations connected with the negative GO flakes [23]. Notably, the Zeta potential of the solution does not decrease significantly after the addition of monovalent cations. Because smaller metal cations are more prone to cation-π interactions with the benzene ring [35]. In addition, a small cation radius will give it a higher hydration energy. The cation with a small ionic radius will be surrounded by many water molecules to form a hydrated cation [36], which prevent the metal ion bonding with the sp³ region with oxygen-containing functional groups by coordination [25].

3.2. Structural and performance optimization of GO-Cation membranes

The influence of cation types on the membrane morphology was investigated. As shown in Fig. 4, all membrane surfaces are complete and defect-free, membrane thickness is about 50 nm. The wrinkles on the surface of GO-Na⁺, GO-K⁺ and GO-Zn²⁺ membranes become smaller compared to pure GO membrane. This is because that the electrostatic interaction and the cation-π interaction could assist the assembly of GO sheets. Obvious agglomeration appears on the surface of GO-Ca²⁺ membrane because of the excessive electrostatic interaction between Ca²⁺ and GO nanosheets. This is consistent with the above results (Fig. 3).

The structure and separation performance of GO and GO-Cation membranes were studied. It can be seen from Fig. 5a that the pure GO membrane exhibited permeation flux of 1201.5 g/(m²·h) and MeOH/DMC separation factor of 10.2. The MeOH/DMC separation performance of GO-Na⁺ and GO-K⁺ membranes were close to the GO membrane. By contrast, the separation factor of GO-Zn²⁺ and GO-Ca²⁺ membranes were significantly enhanced to 61.9 and 24.6 respectively, correspondingly with the decrease of permeation flux. The variation of separation performance might be related to the change of interlayer structures of GO membrane.

The GO and GO-Cation membranes interlayer structure was studied by XRD. Interlayer height (h) of membranes could be obtained from XRD
Patterns. The method calculating the interlayer height of GO membrane can be found in our previous work [20]. It can be seen from Fig. 5b that the interlayer height of GO membrane is 3.6 Å, while those of GO-Na\(^+\) and GO-K\(^+\) membranes are both about 4.0 Å. The enlarged interlayer distance of the GO membrane after cationic control is consistent with our previous work [30]. The cations and GO sheets intercalation can enlarge the GO membrane interlayer spacing. On the other hand, cations especially divalent cations have strong electrostatic attraction with the
GO sheets (Fig. 3) that could reduce the interlayer spacing. The above two factors governed the change of interlayer height in the GO membrane with cationic control, and the size could be dependent on the hydrated ionic diameter and strength of the attraction force. The almost two factors governed the change of interlayer height in the GO membrane with cationic control, and the size could be dependent on the GO sheets (Fig. 3) that could reduce the interlayer spacing. The above S. Liu et al.

unchanged interlayer height in the GO-Zn membrane with cationic control, and the size could be dependent on the GO sheets (Fig. 3) that could reduce the interlayer spacing. The above

Besides of interlayer channels, GO membrane also has slit-like pores between the edge of GO sheets. The cation introduced electrostatic effect could bridge the GO sheets on the same plane [31], and large ionic radius will also hinder the molecular transport (Fig. 1). This effect reduced the flux of the GO membrane, whereas enhanced the size sieving performance and thus separation factor of the GO membrane. Moreover, the divalent cations could interact with the polar MeOH molecules electrostatically [23], which can also enhance the selective permeation of the GO-Zn\(^{2+}\) (Ca\(^{2+}\)) membrane to MeOH. The stronger electrostatic attraction of GO-Ca\(^{2+}\) than GO-Zn\(^{2+}\) (Fig. 3) generated narrower interlayer transport channels, and large ionic radius will also hinder the molecular transport (Fig. 1), leading to the lower flux of GO-Ca\(^{2+}\) than GO-Zn\(^{2+}\) membrane. Such stronger electrostatic attraction also caused agglomeration of GO sheets (Fig. 4e), which reduced the separation factor of the GO-Ca\(^{2+}\) membrane. Notably, GO-Zn\(^{2+}\) membrane exhibited fast and selective permeation of MeOH over DMC, although the interlayer spacing of is smaller than the molecular kinetic diameter of MeOH (3.8 Å). This can be explained by the following reasons: MeOH molecules are not spherical, and the interlayer size of the GO membrane is not uniform, as well as the swelling of GO membrane. Overall, the introduction of divalent cations in GO membrane is beneficial to improve the MeOH/DMC separation performance of GO membrane, and Zn\(^{2+}\) is the optimal cation studied in this work.

We then further optimized the fabrication conditions including Zn\(^{2+}\) content and GO flake size for GO-Zn\(^{2+}\) membranes. As shown in Fig. 6, when a small amount of Zn\(^{2+}\) was introduced into GO, the surface of the GO-Zn\(^{2+}\) becomes smooth and flat (Fig. 6b and c), indicating a more regular stacking of GO sheets [38]. However, as show in Fig. 6d, when the Zn\(^{2+}\) content reaches 1.00 wt%, agglomeration appears on the GO-Zn\(^{2+}\) membrane surface. This is because excessive Zn\(^{2+}\) will weaken the negative charge of GO suspension, affecting the uniform dispersion of GO nanosheets (Fig. 2) and subsequent stacking of GO nanosheets. All GO-Zn\(^{2+}\) membrane surfaces looked defect-free, and the membrane thickness is ~50 nm.

We further analyzed AFM images of GO-Zn\(^{2+}\) membrane with different mass fraction of Zn\(^{2+}\). As shown in Fig. 7, GO and GO-Zn\(^{2+}\) membranes show different undulating states. The \(R_a\) and \(R_q\) of pure GO membrane are 17.9 nm and 13.9 nm, respectively. When a small amount of Zn\(^{2+}\) was introduced to the GO membrane, the \(R_a\) and \(R_q\) decreased slightly. Instead, when the Zn\(^{2+}\) content increases to 1.00 wt%, \(R_a\) and \(R_q\) of the GO-Zn\(^{2+}\) membrane increased to 21.2 nm and 16.7 nm. These results are consistent with the SEM characterization.

The rate of selective permeation of components in membrane is determined by the size sieving property and the sorption ability of the membrane material [39]. As a control sample, GO-Zn\(^{2+}\) membrane was reduced at 80 °C for 4 h. As shown in Fig. 8a, the d-spacing of GO-Zn\(^{2+}\) membranes before and after reduction was almost unchanged, because Zn\(^{2+}\) between layers can support the GO sheets. To study the affinity of GO-Zn\(^{2+}\) membrane toward MeOH and DMC, we employed QCM and CA test to characterize the sorption ability and surface affinity of the GO-Zn\(^{2+}\) membrane. It can be seen from Fig. 8b that the adsorption amount of MeOH on the GO-Zn\(^{2+}\) membrane increased rapidly, while the increase rate of DMC was relatively slow, and the DMC sorption capacity is much smaller than MeOH, with operating time increasing. As shown in the inset of Fig. 8b, although both MeOH and DMC can instantly wet the GO-Zn\(^{2+}\) membrane due to the high surface energy of the organics, the CA of MeOH is much smaller than that of DMC. The good affinity of GO-Zn\(^{2+}\) membrane toward MeOH probably because the oxygen-containing functional groups on the GO sheets and Zn\(^{2+}\) can generate electrostatic interaction with polar MeOH [23]. Compared with GO-Zn\(^{2+}\) membrane, the adsorption of MeOH on the R-GO-Zn\(^{2+}\) membrane decreased significantly and the adsorption of DMC increased slightly, which is due to the removal of oxygen-containing functional groups on the GO sheet.

![Fig. 6](image_url)

**Fig. 6.** Surface SEM images of (a) pure GO and GO-Zn\(^{2+}\) membranes: (b) Zn\(^{2+}\) 0.67 wt%, (c) Zn\(^{2+}\) 0.80 wt% membrane, inset is cross-section image, (d) Zn\(^{2+}\) 1.00 wt %. (GO flake size: 3–5 μm).
As shown in Fig. 8c, compared with GO-Zn\textsuperscript{2+} membrane, the flux and separation factor of R-GO-Zn\textsuperscript{2+} membrane decreased from 707.3 to 529.6 g/(m\textsuperscript{2}\cdot h) and from 61.9 to 24.5, respectively. This result suggests that the preferential sorption toward MeOH over DMC of GO-Zn\textsuperscript{2+} membrane is beneficial to pervaporation separation of MeOH/DMC. Furthermore, the separation factor of R-GO-Zn\textsuperscript{2+} membrane is more than 2-fold compared to pure GO membrane, again confirming the key role of regulation of Zn\textsuperscript{2+} on GO membrane channels to enhance the size-sieving property.

The influence of Zn\textsuperscript{2+} content on the membrane performance was investigated. As shown in Fig. 9a, when Zn\textsuperscript{2+} was introduced into the GO membrane, the permeation flux was first decreased and then slightly increased, while the MeOH/DMC separation factor first significantly increased and then obviously dropped. The GO-Zn\textsuperscript{2+} membrane shows the best performance when the Zn\textsuperscript{2+} content is 0.8 wt\%: flux of 707.3 g/(m\textsuperscript{2}\cdot h) and separation factor of 61.9. As discussed above, introducing Zn\textsuperscript{2+} could regulated the interlayer channels and slit-like pores, and meanwhile interact with the polar MeOH molecules electrostatically. Therefore, the separation factor was enhanced and the flux was declined. Nevertheless, the excessive amount of Zn\textsuperscript{2+} (1.00 wt\%) would cause agglomeration of GO sheets to generate non-selective defects in the GO membrane, resulting in the reduction of separation factor.

The size of GO flakes directly affected the pervaporation performance of GO-Zn\textsuperscript{2+} membranes. It can be seen from Fig. 10a that the total flux of GO-Zn\textsuperscript{2+} membrane decreases rapidly, as the GO flake size increases. When the GO flake size was increased to 40–50 μm, the permeate flux decreased to 385.2 g/(m\textsuperscript{2}\cdot h), while the separation factor increased slightly to 69.4. As Geim et al. demonstrated [40], the effective transport length of GO membranes is L \times h/d, here L, h and d represents the size of the GO flakes, the GO laminates thickness and the...
Fig. 9. (a) Separation performance and (b) XRD of pure GO, and GO-Zn$^{2+}$ membranes. (GO flake size: 3–5 μm, feed temperature 50 °C.)

Fig. 10. (a) Pervaporation performance of GO-Zn$^{2+}$ membranes prepared with different GO flake sizes. (b) Possible molecular transport pathways. (Zn$^{2+}$ content: 0.80 wt%, feed temperature 50 °C.)

Fig. 11. (a) Pervaporation performance of GO-Zn$^{2+}$ membrane at different temperatures. (b) Arrhenius curves for MeOH and DMC. (GO flake size: 5–8 μm, Zn$^{2+}$ content: 0.80 wt%).
d-spacing. It can be seen from Fig. 10b as the thickness and d-spacing of the GO-Zn\textsuperscript{2+} laminates are fixed, the effective transport length of GO-Zn\textsuperscript{2+} laminates is proportional to GO flake size. Thus, small GO flake would have more molecular transport channels [41], thereby achieving higher permeance flux. On the other hand, membrane assembled by larger GO flakes tends to generate fewer defects and thus higher separation factor. In this work, the separation factor of GO-Zn\textsuperscript{2+} membrane increases only slightly with the increase of the GO flake size. Thus, we chose GO flakes with size of 5–8 μm for further investigation.

### 3.3. Separation performance of GO-Zn\textsuperscript{2+} membrane

We studied the influence of feed temperature on the pervaporation process of GO-Zn\textsuperscript{2+} membranes. As shown in Fig. 11a, the increase of operating temperature directly leads to the increase of the driving force, so the permeation flux will gradually increase. And high temperature will cause the GO-Zn\textsuperscript{2+} membrane to swell slightly. The solvent-swelled GO-Zn\textsuperscript{2+} membrane caused the separation factor slightly decreasing from 72.1 to 56.3. Nevertheless, the GO-Zn\textsuperscript{2+} membrane still exhibited outstanding separation performance with total flux of 765.8 g/(m\textsuperscript{2} h) and separation factor of 56.3, when the operating temperature increases to 60 °C. It is helpful to elucidate the relationship between operating temperature and membrane performance by calculating the activation energy of permeation of components in GO-Zn\textsuperscript{2+} membranes. As Fig. 11b show that the activation energies of MeOH and DMC are 7.32 and 15.96 kJ/mol, respectively. Both values are positive, so both MeOH and DMC permeation rates increase with increasing operating temperature [26]. However, the activation energy value of DMC is larger, so high temperature will increase the penetration rate of DMC more, which is another reason for the decrease in separation factor of GO-Zn\textsuperscript{2+} membrane.

The stability of GO and GO-Zn\textsuperscript{2+} membranes in solvent was investigated. Since GO nanosheets contain carboxyl, hydroxyl and epoxy groups, the GO membrane is easy to be swelled in polar solvents [42]. Crosslinking will enhance the stability of GO membrane structure [25, 43]. We immersed GO and GO-Zn\textsuperscript{2+} membranes in the feed solution (10 wt% MeOH/DMC mixtures) to characterize the stability of GO-Zn\textsuperscript{2+} membrane. As shown in Fig. 12a, after immersion for 12 h, both membranes maintained an intact structure, probably because the 10 wt% MeOH/DMC solution is not as destructive to the GO membrane as water. However, the GO membrane was gradually destroyed by sonication. After 30 min of sonication, the GO membrane completely peeled off the substrate and dispersed in the solution, while GO-Zn\textsuperscript{2+} membrane still maintained a complete structure. This suggests that the cationic control highly enhanced the stability of the GO membrane structural. Furthermore, the operational stability of GO and GO-Zn\textsuperscript{2+} membranes during continuous pervaporation separation of MeOH/DMC mixtures was investigated. It can be seen from Fig. 12b that over 120 h operation the flux and separation factor of the GO-Zn\textsuperscript{2+} membrane stabilized at ~700 g/(m\textsuperscript{2} h) and 58 respectively. In comparison, separation performance of GO membrane was sharply after 10 h: the flux increased from 1120.3 to 1300.4 g/(m\textsuperscript{2} h), and the separation factor decreased from 10.3 to 5.4.

The GO-Zn\textsuperscript{2+} membrane separation performance for MeOH/DMC was compared with state-of-the-arts polymeric and GO-based membranes in literature. It can be seen from Table 1 that compared with PVA [44], GO [39] and PEEK-WC [45] membranes, GO-Zn\textsuperscript{2+} membrane showed higher flux owing to the ultra-thin membrane thickness and regular molecular transport channels. The diboric acid cross-linked GOF/PVA membrane obtained high separation factor whereas low flux due to the dense membrane structure [28]. STA-modified CS membranes exhibit ultra-high separation performance [46,47], because the

### Table 1

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<th>Membranes</th>
<th>MeOH concentration (wt%)</th>
<th>Temperature (°C)</th>
<th>Total flux (g/(m\textsuperscript{2} h))</th>
<th>Separation factor</th>
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Fig. 12. (a) Photos of GO-Zn\textsuperscript{2+} and GO membranes after different treat method in 10 wt% MeOH/DMC solution. (b) Continuous pervaporation performance of the GO and GO-Zn\textsuperscript{2+} membrane (GO flake size: 5–8 μm, Zn\textsuperscript{2+} content: 0.80 wt%, feed temperature 50 °C).
amorphous region of the CS may be enhanced with introducing STA. Generally, GO-Zn(II) membranes show well-balanced flux and separation factor compared with those of state-of-the-arts polymeric and GO-based membranes. Although Zn(II) effectively improves the separation factor of GO membrane, it narrows the interlayer spacing of the GO membrane, thereby reducing the flux of the GO membrane. In future work, the interlayer channel should be further expanded, or using a smaller GO flake to obtain more and short transport channels.

4. Conclusions

In this work, divalent cationic (Zn(II)) controlled GO membrane was designed and fabricated for pervaporation separation of MeOH/DMC mixtures. The carefully designed electrostatic interaction and cation–π interaction between GO sheets and cations, not only regularized the molecular transport channels, but also enhanced the structural stability of the GO membrane. For 10 wt% MeOH/DMC mixtures at 50 °C, the optimal GO-Zn(II) membrane exhibited total flux of 707.3 g/(m² h) and separation factor of 61.9, and maintains excellent separation performance over 120 h continuous operation. Besides of the outstanding membrane performance, this work demonstrates the great potential of GO-based membranes toward pervaporation separation of small molecular organic-organic mixtures.

CRediT authorship contribution statement


Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work was financially supported by the National Key Science Research Program (2020YFC1807202), the National Natural Science Foundation of China (21922805, 22038006, 21776125).

References


