Enhanced CO₂ separation in membranes with anion-cation dual pathways

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Abstract

The factors contributing to the water-facilitated CO₂ capture in membranes are investigated. Since CO₂ transports through such hydrated membrane mainly in the form of bicarbonate, there is a pressing need for exploring the ionic transport mechanism. Herein, a series of composite charged membranes comprising a negatively charged polymer matrix and positively charged filler is proposed. For that, polymer brushes bearing imidazolium cations are grafted on graphene oxide and then dispersed in sulfonated poly (ether ether ketone) (SPEEK). Compared with the pristine SPEEK membranes, a significant enhancement in both CO₂ permeability and CO₂/N₂ selectivity is observed. The encouraging results are discussed considering proton conductivity and bicarbonate diffusivity. More interestingly, the membranes show simultaneously higher CO₂ permeability and CO₂/N₂ selectivity when the operating pressure or temperature are increased, supporting the occurrence of ionic transport
mechanism arising from the unique anion-cation dual pathways at the polymer-filler interface.

**Keywords:** Composite membrane; CO$_2$ capture; Graphene oxide; Imidazolium; Sulfonated poly (ether ether ketone)
1. Introduction

The increasing greenhouse gas emissions are responsible for undeniable serious environmental problems. Reducing CO₂ emissions is today a major challenge [1, 2]. Besides traditional absorption, adsorption and cryogenic separation, membrane technology is under consideration for carbon capture due to its high energy efficiency and low waste discharge [3-5]. For operation at temperatures below 250°C, polymeric materials are convenient, due to their processability in large scale and versatility of functional groups that enhances the CO₂ solubility and promotes its preferential transport [6-10], leading to more effective separations than when selectivity is driven only by size difference. However, the achievement of high permeability and high selectivity is frequently limited by the well-known trade-off effect [11]. Although many important breakthroughs have been achieved by appropriately enhancing diffusivity or solubility [12-17], other factors might enhance the performance. Facilitated transport membranes have been under consideration for decades with the expectation of overcoming the trade-off hurdle [18-24]. The presence of facilitated transport carriers allows reversible reactions so as to render the membrane reactivity-selectivity [25]. To reach high performance, an ideal balance of solubility, diffusivity and reactivity should be obtained. The diffusivity is always sacrificed when enhancing solubility or reactivity, because the required polar groups often result in high cohesive energy density and low free volume. In the past, stability has been also a detrimental issue in facilitated transport membranes. Rational design could be important for improving the state-of-the-art facilitated transport membranes.
In recent years, the dependence of facilitated CO$_2$ transport on water has been revealed [26-30]. Our group summarized the cases when water contributes to drastic enhancement of CO$_2$ separation and emphasized the concept of water-facilitated CO$_2$ capture [31]. The effects of water on CO$_2$ transport can be attributed to the following aspects:

(i) **Polymer swelling**: Hydrophilic polymers can suffer intense swelling in the presence of water, affecting the CO$_2$ permeability. This has been observed for instance for chitosan membranes [32]. Li et al. [33] studied the transfer characteristics of CO$_2$ in a series of hydrogel membranes and found that the water content in the membrane determines the permeability of CO$_2$; 

(ii) **Participation of the CO$_2$ reaction**: The participation of water in reversible reactions between CO$_2$ and the amino groups of functionalized polymers have been highlighted by different groups [22, 34] Shishatskiy et al. [30] mentioned that tertiary amines only react with CO$_2$ in the presence of water forming bicarbonate and ammonium, following the reaction

$$R_3N + H_2O + CO_2 \rightleftharpoons R_3NH^+ + HCO_3^-$$ (1)

When the membrane itself contains quaternary nitrogen groups, the reaction with CO$_2$ might involve the hydrated counter-ion [30], also forming bicarbonate, following the reaction

$$2X\cdot 4H_2O + CO_2 \rightleftharpoons HCO_3^- + HX_2\cdot 7H_2O$$ (2)

(iii) **Salting out effect**: Zhang et al. [35] revealed that a hydrated salt can greatly increase the CO$_2$/N$_2$ selectivity, due to the interruption of N$_2$ dissolution by the coordinated water. The role of water in the salting-out effect was further clarified, since the dry state membranes
had no increase of CO₂/gas selectivity, which was found highly dependent on the bound water content [36];

(iv) *Facilitated CO₂ adsorption:* González et al. [37] found that the binding of water to μ-OH groups in MOF (Metal Organic Framework) provides additional adsorption sites for CO₂ molecules, thereby increasing the CO₂ affinity and adsorption capacity.

Although the role of water as CO₂ transport facilitator is now well-known, a more detailed investigation of how the different ions facilitate the CO₂ transport needs to be done. As mentioned above, with the presence of water, bicarbonate and protons are formed by carbonic acid dissociation [30, 38]. From the view of reversible chemical reaction, rapid transfer of the product ions can promote the dissociation process. Consequently, it is envisaged that a perfect facilitated CO₂ transport membrane should be firstly well ion-conductive. In addition, *both HCO₃⁻ and proton should be efficiently transferred through the membrane.* With that in mind, membranes with mixed conductivity for protons and electrons were tested before as an alternative for CO₂ separation from other gases. The membranes were prepared from blends of sulfonated poly(ether ether ketone) (SPEEK) and polyaniline, providing high CO₂/CH₄ methane selectivity (up to 94), but with CO₂ permeability below 1 Barrer [11]. What we propose here is a different concept, having a membrane also with a SPEEK-based proton conductive path, but including a positively charged quaternary ammonium phase. The resulting membrane has both positive and negative paths for transport and can be considered a charged mosaic if bi-continuous pathways are paved. Charged mosaic membranes have been early introduced for negative osmosis and later nanofiltration [39-41], using polymer blends
or block copolymers\cite{42, 43}. It is reasonable to speculate that a membrane with “charged mosaic” structures might reveal an efficient underlying mechanism of selective CO$_2$ transport.

With such a transport model in mind, we designed a series of mixed matrix membranes to investigate the effect of anion-cation dual-pathways on the water-facilitated CO$_2$ capture membrane. The composite charged membrane is constituted by SPEEK matrix and dispersed imidazolium-functionalized GO, with anionic sulfonate and cationic quaternary ammonium groups, respectively (Scheme 1). Although the filler content might be not high enough to guarantee the traverse of anionic transport domains, the grafted polymer brushes, as well as the flexible GO nanosheets, are important to interconnect the filler phase \cite{44}. The imidazolium groups on GO are expected to reduce the possibility of the re-combination of proton and bicarbonate on an amine group site. Furthermore, no mobile amine carriers are present in the membrane so as to better emphasize the role of water and ions.

**Scheme 1** Schematic illustration of the CO$_2$ transport in the anion and cation pathways of the composite charged membrane.

2. Experimental
2.1. Materials and chemicals

Poly (ether ether ketone) (Victrex® PEEK, grade 381G, purity: ≥99%) was purchased from Nanjing Yuanbang Engineering Plastics Co., Ltd. Natural graphite powder (45 μm, AR) was obtained from Sigma-Aldrich. KMnO₄ (AR) was purchased from Kewei Chemical Co., Ltd. (Tianjin, China). Chlorobutane, 3-(Methacryloxy) propyltrimethoxysilane (MPS) (AR) and 1-Vinyl imidazole (VI) (AR) were supplied by Aldrich and used without further treatment. Analytical grade Acetonitrile, ethanol, dimethylformamide (DMF), hydrogen peroxide, phosphoric acid, hydrochloric acid, sulfuric acid and ammonium hydroxide were all purchased from Kewei Chemical Co., Ltd. (Tianjin, China). 2, 2-Azobisisobutyronitrile (AIBN) (AR) was purchased from Tianjin Guangfu Fine Chemical Research Institute.

2.2. Preparation of SPEEK, GO, and functionalized GO

SPEEK was obtained by direct sulfonation of PEEK, and the sulfonation degree (SD) was controlled by the reaction time. First, PEEK was dried for more than 24 h in a vacuum oven at 80 °C. Afterwards, a certain amount of PEEK (20.0 g) was slowly transferred to a three-hole flask with 142 mL sulfuric acid and stirred at room temperature for 3.5 h, then heated to 50 °C and further stirred for 10 h. The polymer solution after reaction was precipitated in deionized water. Then the precipitation was washed several times with water until neutral pH. The prepared SPEEK was dried at room temperature firstly and then transferred to vacuum oven at 60 °C. The sulfonation degree (SD) of SPEEK was 68% in this study.
GO was synthesized by an improved Hummer’s method [45], where GO flakes were oxidized by KMnO$_4$ in concentrated sulphuric acid and phosphoric acid. The imidazolium-functionalized GO nanosheet was synthesized via a two-step method (Scheme 2). Firstly, vinylimidazole-functionalized GO (VI-GO) was prepared by depositing a layer of poly (vinylimidazole) brushes onto GO via distillation–precipitation polymerization. Then the Menshutkin reaction was performed between VI-GO and chlorobutane so as to produce vinylimidazolium-functionalized GO (VIm-GO). In details, VI-GO was synthesized through following procedures: GO (5 g) was dispersed into the mixture of ethanol (200 mL), ammonium hydroxide (12.5 mL) and water (19 mL) with vigorous stirring for 24 h at 25 °C. Then, MPS (2 mL) was transferred into above solution and stirred for another 24 h. The mixture was centrifuged, decanted, and suspended in alcohol to obtain the precipitate, which was dried in a vacuum oven to obtain MPS-modified GO (MGO). Subsequently, MGO (0.3 g) was dispersed into acetonitrile (80 mL) with vigorous stirring, then VI (0.5 mL) and
AIBN (0.018 g) were added into the solution with uninterrupted sonication. The mixture was boiled to evaporate half of the acetonitrile. The remaining mixture was centrifuged, the resulting precipitation was washed with alcohol and acetonitrile, respectively, and then dried in a vacuum oven to obtain VI-GO. In order to further synthesize VIm-GO, VI-GO (0.6 g) was dispersed to round-bottomed flask with 100 mL ethanol, and then quantitative of chlorobutane (CB) was added to the above solution (QA/VI=1:1, mol/mol) and refluxed at 80 °C for 8 h. The resultant suspension was centrifuged, and then the precipitation was repeatedly rinsed with ethanol, followed by drying in a vacuum oven overnight.

2.3. Preparation of the membranes

The membranes used herein were uniformly prepared by solution molding and solvent evaporation. First, the SPEEK pure membrane was prepared as following: SPEEK (0.3 g) was dispersed into DMF (6 mL) and vigorously stirred for 12 h at room temperature, then the above mixture was poured into Teflon molds and transferred to vacuum oven at 60 °C for 12 h and followed by drying at 80 °C for 12 h. The resultant membrane is referred here as SP.

The required amount of GO, VI-GO or VIm-GO for membrane fabrication was dispersed into DMF (6 mL) by means of intermittent sonication for 6 h. Then SPEEK (0.3 g) was added into the mixture and above solution was stirred and sonicated successively (every step for 12 h). The final mixture was poured into Teflon molds and transferred to vacuum oven using the same procedure with the preparation of SP membrane. The resultant membranes are referred here as X-GO/SP, X-VI-GO/SP or X-
VI\textsubscript{m}-GO/SP, where X represents the proportion of GO, VI-GO or VI\textsubscript{m}-GO as filler.

2.4. Characterization of fillers and membranes

The morphologies of GO and VI\textsubscript{m}-GO were imaged by transmission electron microscopy (TEM, FEI Talos™ F200S). The surface chemical compositions of GO, VI-GO and VI\textsubscript{m}-GO were measured by a multifunctional imaging electron spectrometer (XPS, Thermo ESCALAB 250XI, Thermo Scientific, USA). FTIR spectra were carried out at room temperature by PerkinElmer Spectrum Two in the range of 4000–500 cm\textsuperscript{-1} with the resolution of 4 cm\textsuperscript{-1}. The morphologies and element mapping of the membrane surface were evaluated by scanning electron microscope (SEM, Zeiss/Auriga FIB) equipped with energy dispersive X-ray (EDX). The glass transition temperature ($T_g$) was determined by differential scanning calorimetry (DSC). The thermogravimetric analysis (TGA, NETZSCH STA 2500) was used to test the thermal stability of membranes, and the samples were heated from room temperature to 800 °C at a heating rate of 10 °C min\textsuperscript{-1} under nitrogen atmosphere. X-ray diffractometry (XRD) was performed to characterize the nanostructure of nano particles in the range of 5–80°.

2.5. Ion Exchange Capacity (IEC) measurement

In order to clarify the composite charged structure, IEC was measured for both cation and anion. The cation exchange capacity (designated as $IEC_{H^+}$) of the membranes were measured via conventional titration technique (acid-base titration method): a dry sample ($W_{d1}$, g) was immersed in NaCl solution (2.0 M) for 24 h, and the amount of the liberated H$^+$ was determined by titrating with NaOH solution (0.01 M), using phenolphthalein as indicator. The $IEC$ value was obtained through the following
expression:

\[ IEC_{H^+} \text{ (mmol g}^{-1}\text{)} = (0.01 \times 1000 \times V_{NaOH}) / W_{d1} \]

where \( V_{NaOH} \) (L) and \( W_{d1} \) (g) were the consumed volume of NaOH solution in the titration and the weight of dry membranes, respectively.

The anion exchange capacity was measured and shown in two ways. Firstly, the capacity of OH\(^-\) exchange (designated as \( IEC_{OH^-} \)) was measured by the classical back-titration method. The dry membrane \((W_{d2}, \text{g})\) was soaked into 0.1 M NaOH solution at room temperature for 48 h to convert VIm-GO from Cl\(^-\) type to OH\(^-\) type. Then the membrane was repeatedly washed by deionized water until it approached neutrality. After that the membrane was immersed in a NaCl solution (2.0 M) for 24 h, and the amount of liberated OH\(^-\) was determined by titrating with HCl solution (0.02 M), using methyl orange as indicator. The \( IEC \) value was obtained through the following expression:

\[ IEC_{OH^-} \text{ (mmol g}^{-1}\text{)} = (0.02 \times 1000 \times V_{HCl}) / W_{d2} \]

where \( V_{HCl} \) (L) and \( W_{d2} \) (g) were the consumed volume of HCl solution in the titration and the weight of the dry membrane, respectively.

The second way of anion exchange capacity measurement is to know how much Cl\(^-\) can be exchanged for HCO\(_3^-\). The dry membrane \((W_{d3}, \text{g})\) was soaked into 0.2 M NaCl solution (30 mL) at room temperature for 24 h to convert SPEEK from H\(^+\) type to Na\(^+\) type. Secondly, the membrane was repeatedly washed by deionized water until Cl\(^-\) could not be detected. Then the membrane was immersed in NaHCO\(_3\) solution (2.0 M) for 24 h, and the amount of liberated Cl\(^-\) was determined by titrating with AgNO\(_3\)
solution (0.02 M), using potassium chromate as indicator at pH = 8.3. The $I_E C$ value measured by this method is designated as $I_E C_{\text{HCO}_3^-}$ and was calculated through the following expression:

$$I_E C_{\text{HCO}_3^-} \text{ (mmol g}^{-1}) = (0.02 \times 1000 \times V_{\text{AgNO}_3}) / W_{d3}$$

where $V_{\text{AgNO}_3}$ (L) and $W_{d3}$ (g) were the consumed volume of AgNO$_3$ solution in the titration and the weight of the dry membrane, respectively.

2.6. Gas permeation test

The test was based on the conventional constant pressure/variable volume method (the schematic diagram of apparatus is shown in Fig. S2). The mixed gas of CO$_2$/N$_2$ (10/90 vol %) was used as feed gas and helium was selected as sweep gas in all measurement. In the dry state measurement, the feed gas and sweep gas was introduced into the membrane cell directly. Before the wet state measurement, the membranes were immersed into water until their weight reached constant. The feed gas and the sweep gas were separately humidified by passing through their individual water bottles, and the droplets of liquid water in each gas were then removed by gravity in an individual tank. The flow rates of the feed gas and the sweep gas were controlled to 100 mL/min and 40 mL/min, respectively by mass flow meter. The relative humidity of feed gas and sweep gas was controlled at approximately 90% and 53%. The percolated gas was introduced into the gas chromatograph (GS-101 Ripuli) to obtain component detection. Owing to the relatively low humidify of the sweep gas, each membrane would lose partial of its absorbed water during the measurement, and the time-dependent permeability of SP and 8%-VIm-GO/SP was recorded and shown in Fig. S3.
Consequently, all measurements were conducted after the membrane had been in equilibrium with the humidified feed and sweep gas reaching the steady-state conditions (at least 6 hours).

The permeability coefficient can be calculated by the following equation:

$$ P_i = \frac{Q_l}{\Delta P_i A} $$

where $P_i$ (Barrer, 1 Barrer = $10^{-10}$ cm$^3$ (STP) cm cm$^{-2}$ s$^{-1}$ cmHg$^{-1}$) is the permeability coefficient of gas “i” (cm$^3$/s), $Q_l$ is the volumetric permeation flow rate of gas “i” at standard temperature and pressure (STP), $l$ is the membrane thickness (cm), $\Delta P_i$ is the transmembrane partial pressure difference of gas “i” (cm Hg), and $A$ is the effective membrane area (15.9 cm$^2$). The mixed-gas CO$_2$/N$_2$ selectivity was calculated through dividing CO$_2$ permeability by N$_2$ permeability.

2.7. Water state analysis of membranes

The water state of the membrane has a great influence on the gas permeability. The following method was used to calculate total water, free water and bound water of membranes. Each membrane after completed gas permeation test was weighted to obtain the humidified weight ($m_1$, mg), then membranes were transferred into a vacuum oven for 6 h at 100 °C and reweighted ($m_2$, mg). After heating at 150 °C for another 6 h, the membranes were weighted to obtain their dried weight ($m_0$, mg). Then the content of total water ($W_t$, %), free water ($W_f$, %) and bound water ($W_b$, %) were calculated by the following way:

$$ W_t = \frac{(m_1 - m_0)}{m_0} \times 100\% $$
\[ W_f = \frac{(m_1 - m_2)}{m_0} \times 100\% \]
\[ W_b = \frac{(m_2 - m_0)}{m_0} \times 100\% \]

2.8. Ion and proton Conductivity of the Membranes

Bicarbonate permeability was measured with a diffusion cell (Fig. S1), which was similar to a methanol penetration test [46]. 0.2 mol L\(^{-1}\) sodium bicarbonate solution (100 mL) was added to the A side, and deionized water (100 mL) was placed on the other side. Then the membrane to be tested was placed between A and B. The average concentration of bicarbonate in the B-side solution over time was calculated by acid-base titration, and the bicarbonate permeability (\(P\), cm\(^2\) s\(^{-1}\)) was determined by the following equation:

\[ P = S \frac{V_B l}{A C_{A0}} \]

where \(S\) was the slope of the line of concentration versus time, \(V_B\) is the volume of deionized water in the B side; \(C_{A0}\) is the concentration of sodium bicarbonate solution; \(A\) and \(l\) are the membrane area and thickness, respectively.

The ion conductivity of the four membranes was measured in a conductivity cell by the AC impedance method using a Princeton (ParStat MC 1000) potentiostat. The samples were immersed in deionized water for 24 h before testing. Each temperature tested needs to be stable at least 30 minutes to obtain equilibrium data. The ion conductivity (S cm\(^{-1}\)) is calculated by \(\sigma = l/R\), where \(l\) (cm) refers to the membrane thickness, \(A\) (cm\(^2\)) is the membrane cross-sectional area, and \(R\) (\(\Omega\)) refers to the membrane resistance.

3. Results and discussion
3.1. Characterization of fillers

![TEM image of (a) GO and (b) VIm-GO](image1)

![XRD and FTIR spectra of GO, VI-GO and VIm-GO](image2)

![XPS spectra of VI-GO and VIm-GO](image3)

![N 1s spectra of VI-GO and VIm-GO](image4)

**Fig. 1.** TEM image of (a) GO and (b) VIm-GO; (c) XRD and (d) FTIR and (e) XPS spectra of GO, VI-GO and VIm-GO; (f) N 1s spectra of VI-GO and VIm-GO.

The morphologies as well as physical and chemical structures of the nanosheets were obtained and shown in **Fig. 1.** The typical sheet-like structure with wrinkles can be observed on the surface of GO (**Fig. 1a**). Compared to GO, although a slight change occurs on the surface of VIm-GO, the layered structure is well maintained (**Fig. 1b**). According to the XRD patterns (**Fig. 1c**), the typical diffraction peak of GO is found to become much weaker for both VI-GO and VIm-GO, since GO is diluted by the polymer, but the peak was observed at the same position, confirming that at least a partially ordered orderly packing of nanosheets driven by π-π interaction. The peak corresponds to an interlayer spacing of ~0.9 nm. As shown in **Fig. 1d**, the appearance of the FTIR bands assigned to the stretching vibration of C=N and the heteroaromatic ring of vinylimidazole indicates that imidazole groups have been introduced on the GO surface.
The grafting is also supported by the XPS data. The N1s peaks of VI-GO and VIm-GO appear in Fig. 1e, and the specific content of the elements is listed in the Table S1. The content of N1s on the surface of VI-GO and VIm-GO is calculated to be 10.26% and 9.61%, respectively. The latter possesses less N1s content because the butyl-bearing quaternization agent increases its C1s content (from 68.16% to 70.4%). To estimate the degree of the quaternization reaction, the N1s peak of VI-GO and VIm-GO was deconvoluted into two peaks (Fig. 1f), and the percentage of N=C and N–C is shown in Table 1. The increment of N–C composition from 27.51% to 35.49% clearly shows the occurrence of quaternization reaction on imidazole rings. It can be further calculated that the quaternization reaction actually brings about a 28.6% increase in the number of N–C and an 11.3% decrease in that of N=C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Element (atom %)</th>
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<tbody>
<tr>
<td></td>
<td>N–C</td>
<td>N=C</td>
</tr>
<tr>
<td>VI-GO</td>
<td>27.51</td>
<td>72.49</td>
</tr>
<tr>
<td>VIm-GO</td>
<td>35.49</td>
<td>64.51</td>
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</table>

3.2. Characterization of membranes

Two types of functionalized GO and the pristine GO nanosheets were incorporated into the SPEEK (abbreviated as “SP” in membrane samples) matrix to prepare composite membranes. The FTIR spectra of membranes show that the nanosheets and the polymer are physically blended (Fig. S4). Fig. 2a shows that the SPEEK control membrane exhibits dense, defect-free and smooth cross section. A rough cross section is showed in the 8%-GO/SP membrane, evidencing layers of GO with poor adhesion
or compatibility with the matrix. In contrast, the dispersion and adhesion of fillers in 8%-VI-GO/SP (Fig. 2c) and 8%-VIm-GO/SP (Fig. 2d) with the matrix is improved, as well as their interfacial compatibility. Especially, the cross-section image of VIm-GO/SP reveals a honeycomb-like heterogeneous structure, which is typically seen in glassy polymer-based composite membranes[47], especially when there is high content of filler or strong interactions between polymer matrix and the fillers [48, 49]. EDX mapping patterns on the cross section of 8%-VIm-GO/SP (Fig. S5) reveal the local segregation of nitrogen to some degree (Fig. 3a), despite its relatively homogeneous distribution. Fig. 3b further shows that the majority of nitrogen patterns are not overlapped by those of sulfur. The nitrogen partial segregation reflects the

**Fig. 2.** Cross-section images of (a) SP, (b) 8%-GO/SP, (c) 8%-VI-GO/SP, (d) 8%-VIm-GO/SP. The scale bars in all images are 2 μm.
Fig. 3. EDX mapping patterns of nitrogen (green dots) on the cross section of 8%-VIm-GO/SP with the background of (a) membrane morphology image and (b) sulfur mapping patterns (red dots), respectively. The scale bars represent 2 μm.

The position of imidazolium separated from sulfonate groups in the composite charged mosaic membrane.

More evidence about the strong interactions between VIm-GO and SPEEK can be found in Fig. 4. In Fig. 4a, both the SPEEK control membrane and the composite membranes show a broad crystallization peak at 2-theta = 9-23°. With the introduction of GO, VI-GO and VIm-GO, the crystallization peak intensity is generally weakened, indicating that the filler disturb the packing of the polymer chains in crystallites. In particular, 8%-VIm-GO/SP shows the weakest crystallization peak, correlating with the strongest interfacial interactions. The appearance of

Fig. 4. (a) XRD patterns and (b) DSC curves of membranes.
endothermic peaks in the DSC reflects the relaxation process of polymer backbones upon heating (Fig. 4b). Although this phase transition differs from glass transition, it can more or less reflect the change of glass transition temperature, $T_g$, and herein the peak temperature value is called “transition temperature”. The measured transition temperature for SP was 178°C, right in the range of the $T_g$ value previously reported for SP by other groups [50]. Because the chain mobility is restrained in tight contact with the fillers, both transition temperature and $T_g$ increase. The increase can be correlated with the strength of the interaction with the filler, in the following order SP<GO/SP<VI-GO/SP<Vim-GO/SP. Furthermore, VIm-GO/SP exhibits the remarkably higher Young's modulus—as well as the relatively lower maximum elongation—than the other samples (Fig. S6). The TGA curve of 8%-VIm-GO/SP shows slower decline at around 400 °C than other membranes, indicating that the strong interface interactions might affect even the thermal stability of the membrane (Fig. S7).

3.3. Ion exchange capacity of membranes

There are three kinds of $IEC$ in this study. $IEC_{H^+}$ is available for each type of membrane owing to the SPEEK matrix. The $IEC_{H^+}$ of SPEEK (1.89 mmol g$^{-1}$) is consistent with the literature where the sulfonation degree is comparable [51, 52]. As shown in Table 2, the incorporation of GO reduces $IEC_{H^+}$ from 1.89 to 1.73 mmol g$^{-1}$, which can be explained by the intrinsically low ion exchange capacity of GO. By comparison, the membrane doped with VI-GO shows lower $IEC_{H^+}$, consistent with the fact that the sulfonate groups form acid-base pairs with basic groups [53]. The incorporation of VIm-GO results in the largest decrease of $IEC_{H^+}$, suggesting the
possibility of partial salt formation between sulfonate groups and imidazolium groups.

On the other hand, the anion exchange capacities of the membranes were examined. Detectable $IEC_{OH^-}$ ($0.312 \text{ mmol g}^{-1}$) and $IEC_{HCO_3^-}$ ($0.294 \text{ mmol g}^{-1}$) values could only be measured for VIm-GO/SP membranes. This indicates that the expected composite charged structures with VIm-GO and SPEEK paths is present in this membrane. Given that such level of $IEC_{OH^-}$ is rather high compared with those anion exchange membranes based upon poly (vinyl alcohol), a polymer matrix with no charged groups [54, 55], this fact also indicates that the majority of imidazolium groups on VIm-GO do not form salts with the sulfonate groups of SPEEK. $IEC_{HCO_3^-}$ is slightly lower than $IEC_{OH^-}$, because $HCO_3^-$ as a hydrolysable anion cannot replace $Cl^-$ as efficiently as $OH^-$. Nevertheless, the $IEC_{HCO_3^-}$ values confirm that the membrane has rather good capacity of $HCO_3^-$ exchange and transfer.

### Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>SP</th>
<th>8%-GO/SP</th>
<th>8%-VI-GO/SP</th>
<th>8%-VIm-GO/SP</th>
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<tbody>
<tr>
<td>$IEC_{H^+}$</td>
<td>1.89</td>
<td>1.73</td>
<td>1.64</td>
<td>1.55</td>
</tr>
<tr>
<td>$IEC_{OH^-}$</td>
<td>N.A.</td>
<td>N.A.</td>
<td>N.A.</td>
<td>0.312</td>
</tr>
<tr>
<td>$IEC_{HCO_3^-}$</td>
<td>N.A.</td>
<td>N.A.</td>
<td>N.A.</td>
<td>0.294</td>
</tr>
</tbody>
</table>

**3.4. Gas transport properties of the membranes**

The gas separation performance was tested under both dry and humidified conditions. In the dry-state test, all membranes show rather poor $CO_2$ permeability and $CO_2/N_2$ selectivity (Fig. S8), in line with the previous finding that a polymeric membrane with abundant polar groups is not suitable for dry-state $CO_2$ separation. [33] However, the
separation performance of all membranes becomes much better after humidification.

Fig. 5 shows the effects of the filler type and content of humidified membranes in mixed gas measurements. The incorporation of pristine GO up to 6% causes only minor changes in the CO₂ permeability. Only with 8% GO, a measurable increase could be seen. At this loading GO nanosheets might be percolated enough to

Fig. 5. Mixed gas CO₂ permeability (columns) and CO₂/N₂ (10 vol% CO₂) selectivity (symbols with eye-guiding lines) under humidification (Temperature: 25 °C; Feed gas: 2 bar at 90 % R.H; Sweep gas: 0 bar at 53% R.H.). Herein the pressure refers to Gauge pressure (the same below).

Fig. 6. Effect of feed pressure on (a) CO₂ permeability and (b) CO₂/N₂ selectivity (Temperature: 25 °C; Feed gas: 90 % R.H; Sweep gas: 53% R.H.)

pave broad pathways along the interface for gas transport. The simultaneous increase
of CO$_2$ permeability and CO$_2$/N$_2$ selectivity for GO/SP membranes in our work indicates that the transport mechanism of the humidified membranes is not purely solution-diffusion, although no mobile basic carriers are added to enable facilitated transport. Shen et al. previously demonstrated that even in membranes based on PEBAX, a non-ionic polyether copolymer known for high CO$_2$ permeability, the introduction of very limited amount of GO nanosheets ($\leq 0.1$wt%) forming hydrogen bonds with the polymer can offer additional paths with a significant transport enhancement in the dry state [56].

For VI-GO/SP and VIm-GO/SP membranes, both CO$_2$ permeability and CO$_2$/N$_2$ selectivity become much higher than those for GO/SP. The matrix polymer, SPEEK, is not a conventional facilitated transport membrane material. In the case of VI-GO/SP the imidazole with tertiary amine groups could act as a reactive carrier for CO$_2$ in contact with water, following reaction (1). Fig. 6a shows a pressure-independence for the CO$_2$ permeability of VI-GO/SP and VIm-GO/SP membranes, which is not characteristic of facilitated transport. However, this does not exclude the possibility of having the solubility and diffusivity components of the permeability counterbalancing their contribution, as reported before for membranes PEBAX with quaternary ammonium functionalization [30]. In the case of the VIm-GO/SP, as for the reported PEBAX membrane, quaternary ammonium membranes might facilitate the CO$_2$ transport. More specifically, water is even more necessary for this system, since the hydrated counter-ions should be those playing the most important role in the transport, following reaction (2). Fig. 7 quantifies the amount of water in the membranes. The
permeability and selectivity of membranes can be correlated with their water uptake and bound water content, respectively (Fig. S9). The VIm-GO/SP membranes are clearly those with the highest amounts of water, followed by VI-GO/SP membranes. However, the dependence of the CO$_2$ permeability on the water content is not as simple as the correlation reported for other membranes before [18-23, 57, 58]. In Fig. 8, the CO$_2$ permeability was correlated with
the water content measured in two different ways: (1) total percentage of water absorbed by the membrane before the experiment and (2) percentage of water remaining absorbed in the membrane after concluding the experiment. Each group of data can be linearly correlated, but the slope for the former group is significantly larger than the latter one. This is a strong evidence that water is very important in the CO₂ transport for this class of membrane. The total absorbed water includes a large amount of free water molecules. The remaining water at the end of the experiment has a much larger percentage of bound water. Its exact proportion of free and bound water is seen in Fig. 7. Therefore, the free water molecules have a much higher effect on the CO₂ permeability. As mentioned above, in membranes with quaternary ammonium groups, the facilitated transport of CO₂ happens through the reaction between the counter ions and water (reaction (2)), in this case Cl⁻. The reaction is in this case the main source of HCO₃⁻. The free water in the membrane seems to act as a fast vehicle for the HCO₃⁻ transport, leading to the high slope of the CO₂ permeability vs (bound) water content line. The bound water might still react and influence the CO₂ transport, but due to the much lower mobility the effect is less pronounced.

The pressure-dependent CO₂ separation performance reveals some other possibilities (Fig. 6b). All the three composite membranes, GO/SP, VI-GO/SP and VIm-GO/SP, show almost constant CO₂ permeability and an unusual increment of CO₂/N₂ selectivity when elevating the operating pressure, which is seldomly reported in the previous water-swollen membranes, but as mentioned above has been seen in membranes with quaternary ammonium functionalization [30]. Such selectivity increment is not obvious
for GO/SP but remarkable for both VI-GO/SP and VIm-GO/SP (especially for VIm-GO/SP), indicating that the functionalities on GO play pivotal roles, more than manipulating the water content. As such, it is reasonable to speculate that the CO₂ transport can be facilitated by a highly efficient ion transport, once some water is available. The composite charged structure of VIm-GO/SP permits the rapid transport of both anions and cations, promoting the CO₂ hydration and dissociation, and finally the transport as a whole. Although VI-GO does not bear a net positive charge, HCO₃⁻ can be also formed via reaction (1) and transferred by the aid of the protonated imidazoles, while the sulfonate groups of SP still provides plenty of proton exchange sites. We hypothesize that the anion-cation (HCO₃⁻-proton) dual pathway enables fast and selective CO₂ transport. To verify the role of the anion-cation dual pathways of the membranes, we measured both the bicarbonate diffusivity and the proton conductivity. The variation of the permeate-side bicarbonate concentration over time was recorded in Fig. S10, and the diffusivity was calculated and listed in Table 3, based on the early-stage part of the curve (almost straight) representative of the stage of pseudo-steady state diffusion (see Supporting Information). The measured bicarbonate diffusivity in 8%-GO/SP, 8%-VI-GO/SP and 8%-VIm-GO/SP membranes are 3.1, 5.3 and 11-times higher than in SP, respectively. The enhancement for 8%-GO/SP or 8%-VI-GO/SP might arise from the disruption of polymer chain packing and the decrease of $IEC_{H^+}$, while that for 8%-VIm-GO/SP can be further attributed to the incorporation of cationic domains. By comparison, the calculated enhancement ratio of the CO₂ permeability for the three membranes, compared to SP are 1.9, 2.3 and 3.5-times higher, respectively.
Consequently, the accelerated CO$_2$ transport is in close relationship with that of bicarbonate. The CO$_2$ transport through the membranes might follow a more complex mechanism, and the bicarbonate transport is only one of the major factors. Meanwhile, the ion conductivity was measured at 25 to 65 °C and reported in Fig. 9. Considering the transfer of H$^+$ is known much faster than Cl$^-$, and the content of H$^+$ is much higher than Cl$^-$ in the composite membranes with 8% loading, herein the ion conductivity data can be analysed as proton conductivity. The enhancement of proton conductivity at elevated temperature has been reported for SPEEK-based membranes [52]. The calculated enhancement ratios for the proton conductivity at 25°C of the three membranes, compared to SP, are 1.3, 1.4 and 1.6-times, respectively, illustrating the synchronous increase of proton conductivity and bicarbonate permeability. Such synergetic permeation of both cation and anion guarantees no accumulation of each one at any site of the membrane, which can further promote the dissociation of the carbonic acid. Fig. 8 also shows that the proton conductivity increases rapidly with temperature, which provides another clue to elucidate the role of the ion transport. Following this clue, we measured the CO$_2$ separation performance of the four typical membranes at different temperatures. The results are shown in Fig. 10. Both CO$_2$

| Table 3. Diffusivity of bicarbonate through the membranes. |
|-------------------------------|----------------|----------------|----------------|----------------|
| Sample                      | SP            | 8%-GO/SP      | 8%-VI-GO/SP    | 8%-VIm-GO/SP   |
| Diffusivity (10$^{-7}$ cm$^2$ s$^{-1}$) | 0.235         | 0.724         | 1.235          | 2.595          |
| Normalized by the SP value  | 1             | 3.1           | 5.3            | 11             |
permeability and CO$_2$/N$_2$ selectivity increase with temperature. It is well known that increasing temperature results in high permeability, but such increase of gas permeability reported in the literature usually is accompanied by a decrease of selectivity in rubbery polymers, since the polymer chains become softer. In this study, the characterization has been done far below T$_g$, and the polymer is in a glassy state. Furthermore, the GO nanosheets even decrease the polymer chains mobility and consequently increase transition temperature (Fig. 4b). The increase of CO$_2$/N$_2$ selectivity with temperature clearly indicates that the separation is not dominated by diffusivity selectivity. An analogous increase of CO$_2$/N$_2$ selectivity with temperature was recently reported for piperazine brushes intercalated in GO hollow fibers. [59] In that case, piperazine is confined between GO layers, also restricting its mobility. Piperazine is a secondary amine and can facilitate the CO$_2$ transport by reacting and forming carbamate without the presence of water. In our system, the tertiary amine imidazole and the quaternary ammonium groups in water promote the conversion of CO$_2$ to bicarbonate ions. Even the negatively charged groups in GO could lead to

Fig. 9. Temperature-dependent ion conductivity of membranes at 100 RH%.
bicarbonate formation. The transport of CO₂ facilitated by these groups becomes more efficient at elevated temperature. According to Fig. 10b, a slight increment of selectivity with temperature is observed for all membranes, including the pristine SP. These facts indicate that the enhancement of proton transport (shown in Fig. 9) contributes to facilitated CO₂ transport. Such enhancement is particularly high for VIm-GO/SP, and this can be due to the co-existence of permanent cations and anions that pave dual pathways for protons and bicarbonate ions.

Despite the findings above, we must point out that there is another type of ion-conducting mechanism for water-facilitated CO₂ transport membranes. That is, CO₂ can directly react with hydroxide ion and produce bicarbonate: CO₂ + OH⁻ ⇌ HCO₃⁻. In this way, proton conducting is not necessary and two types of anions transport in the opposite directions. This route covers the most cases of water-facilitated transport membranes because of the high content of alkaline groups, typically amino groups [38]. The reaction (2) mentioned in Introduction is also an example of this route when the counter-ion X⁻ is OH⁻ [60]. To support this
idea, we investigated the effect of VIm-GO on quaternized chitosan (QCS) membrane (See experiment details in Supporting Information). Table S2 shows that addition of 8% VIm-GO in QCS increases the CO₂ permeability and CO₂/N₂ selectivity by 51.9% and 51.5%, respectively. In this case the membrane is a real anion exchange membrane, and the contribution of proton transport discussed above is impossible. More importantly, after treatment by NaOH solution, both QCS membrane and VIm-GO/QCS membrane show remarkably enhanced CO₂ permeability and CO₂/N₂ selectivity, compared to the untreated ones. This phenomenon further demonstrates that the ion transport mechanism in water-facilitated transport membrane strongly depends on the alkalinity of membranes.

4. Conclusions

In summary, a picture of water-facilitated CO₂ transport was elucidated by a composite charged membrane comprising of a negatively charged polymer matrix and a positively charged filler, which pave anion-cation dual pathways for the two products of carbonic acid dissociation: bicarbonate and proton. Besides the previously reported role of water, we propose that the rapid transfer of bicarbonate and proton is also crucial to enable an efficient transfer of CO₂ when there are no alkaline groups to promote capture proton. The unique contribution from ion transport mechanism is supported by a pressure-dependent and temperature-dependent separation performance. In particular, the membrane shows no evidence of carrier saturation effect, a sticky problem for the conventional facilitated transport membranes relying on basic carrier groups.
Based on these findings and those already known among the community, we can tentatively conclude that there are three key factors that determine the efficiency of facilitated CO$_2$ transport: basic carrier, water and permanently charged groups (for rapid ion transport). We hope our findings can provide in-depth insights into the chemistries associated with facilitated transport and open a new avenue to design high performance CO$_2$ separation membranes following the “charged mosaic” model.

**Acknowledgments**

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Supporting Information

Elucidating the ion transport-fortified CO₂ separation in well-designed composite charged mosaic membranes with anion-cation dual pathways

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Fig. S1. The device of anion transport rate. A: 0.2M sodium bicarbonate, B: deionized water.
Fig. S2. Schematic diagram of the gas permeation apparatus.
Fig. S3. Time-dependent CO$_2$ permeability of membranes arising from water release.
As shown in Fig. S4, the three characteristic bands of the -SO$_3$H group are shown around 1216, 1076 and 1020 cm$^{-1}$. The characteristic bands of imidazole and imidazolium are not observed due to the relatively low content in membrane.
Fig. S5. EDX mapping images of all elements on the cross section of 8% VIm-GO/SP.
Fig. S6. Stress-strain curves of membranes.
Fig. 7. TGA curves of membranes.
Fig. S8. CO₂ Permeability and selectivity of membranes (25°C, without humidification).
Fig. S9. Correlations between (a) water uptake and CO$_2$ permeability and (b) bound water and CO$_2$/N$_2$ selectivity, respectively. (Temperature: 25 °C; Feed gas: 2 bar at 90 % R.H; Sweep gas: 0 bar at 53% R.H.)
Fig. S10. Time-dependent bicarbonate transfer rate of membranes.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Element (atom%)</th>
<th></th>
<th></th>
<th></th>
<th></th>
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<tbody>
<tr>
<td></td>
<td>C₁S</td>
<td>O₁S</td>
<td>N₁S</td>
<td></td>
<td></td>
</tr>
<tr>
<td>GO</td>
<td>67.66 ± 1.32</td>
<td>32.34 ± 0.76</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>VI-GO</td>
<td>68.16 ± 1.40</td>
<td>21.58 ± 0.51</td>
<td>10.26 ± 0.37</td>
<td></td>
<td></td>
</tr>
<tr>
<td>VIm-GO</td>
<td>70.40 ± 1.46</td>
<td>19.98 ± 0.45</td>
<td>9.61 ± 0.35</td>
<td></td>
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</tr>
</tbody>
</table>

Compared to GO, the content of N₁s change to 10.26% in VI-GO, which proves that the imidazole groups are successfully grafted to GO surface. The carbon content was changed from 67.66% of GO to 70.40% of VIm-GO due to butyl treatment. At the same time, compared with VI-GO, no obvious change is observed for nitrogen content, which proves that the quaternization reaction has not obvious influence on nitrogen content.
**Table S2** The gas permeation and water uptake results of quaternized chitosan and its composite membranes

<table>
<thead>
<tr>
<th>Membrane</th>
<th>( P_{CO_2} ) (Barrer)</th>
<th>( P_{CO_2}/P_{N_2} )</th>
<th>Water uptake (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>QCS</td>
<td>260</td>
<td>28.3</td>
<td>82.6</td>
</tr>
<tr>
<td>QCS (NaOH treated)</td>
<td>311</td>
<td>37.1</td>
<td>89.0</td>
</tr>
<tr>
<td>8%-VIm-GO/QCS</td>
<td>395</td>
<td>42.9</td>
<td>60.6</td>
</tr>
<tr>
<td>8%-VIm-GO/QCS (NaOH treated)</td>
<td>533</td>
<td>54.9</td>
<td>68.9</td>
</tr>
</tbody>
</table>

**Synthesis of QCS:** Quaternized chitosan (QCS) was synthesized via a modified procedure based on the literature [1]. Chitosan (6.0 g) with degree of deacetylation of 92% was dispersed in 42wt% aqueous methanol solution to obtain a 1wt% suspension. Iodomethane (16.0 g) was then added and the solution was mechanically stirred at 50 °C for 4.5 h. Next, another batch of iodomethane (16.0 g) was added, together with 0.3 g sodium hydroxide, and the reaction was allowed to proceed for another 4 h. Then NaCl (10.0 g) was added to enable ion exchange. The resulting product was precipitated in large amount of acetone, and washed repeatedly by tetrahydrofuran before drying in a vacuum oven.

**Preparation of QCS-based membranes:** The membranes were prepared from a 4wt% solution of QCS dissolved in deionized water at 80 °C with constant stirring. A certain amount of VIm-GO was firstly dispersed in deionized water and then added into the solution. The solution was cooled down and the crosslinking reaction was performed by adding the given amount of 0.25 wt% glutaraldehyde (GA) solution. The weight ratio of GA to QCS was controlled at 1.5wt% and the mixture was stirred for 1h. With bubbles removed, the homogenous solution was cast onto a clean glass plate and air-dried. Partial membranes were subjected to alkaline treatment in a 1 M sodium hydroxide solution before gas separation measurement, and others were rinsed in...
deionized water for reference.