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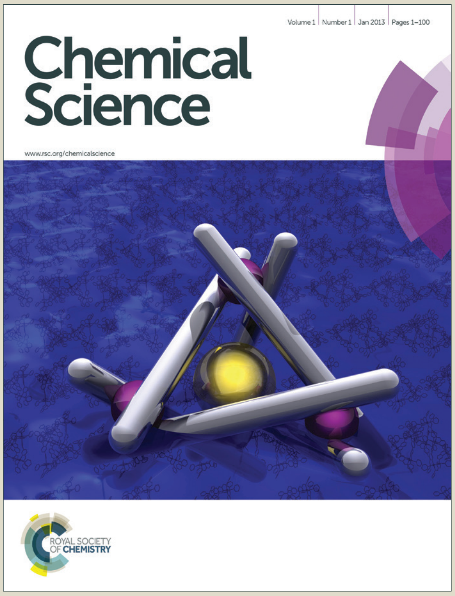

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Edge Article

Fabrication of High-performance Facilitated Transport Membranes for CO_2 Separation

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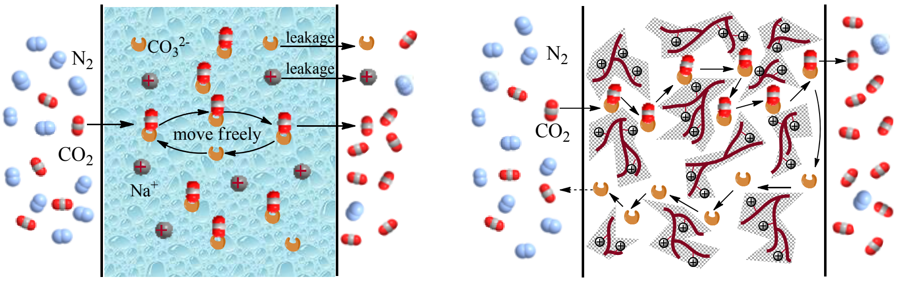
At present, liquid membrane, ion-exchange membrane and fixed carrier membrane are the three popular facilitated transport membranes for CO_2 separation. They possess their own advantage, as well as their respective deficiencies. In view of the characters of these three types of facilitated transport membrane, we report a method to combine their advantages and overcome their deficiencies. A new membrane was fabricated by establishing high-speed facilitated transport channels in the fixed carrier membrane. This membrane display excellent CO_2 separation performance and good stability. The results suggest that this is an effective way for fabricating high performance and high stability CO_2 separation membrane. Furthermore, the idea of establishing high-speed facilitated transport channels in fixed carrier membrane will be a universal route to improve the performance of gas separation membrane.

The overuse of fossil fuels has released excessive CO_2 into the atmosphere causing extreme weather, which arouses the worldwide anxiety[1-5]. It creates the urgent need for a novel material and new technology which can be used to capture CO_2 from flue gas and other sources to control greenhouse gas emission and recycle CO_2 as carbon resources[6-9]. Compared with other technologies, membrane-based CO_2 separation has the advantages of low-energy consumption, simplicity of operation, environmental friendliness and become one of the fastest developing gas separation technology[10-18]. Among various membranes, the facilitated transport membrane inspired from the biological membrane has been intensively investigated, because the CO_2 permeance and selectivity of the membrane could be simultaneously improved through the reversible reactions between CO_2 and reactive carriers (e.g. carbonate, amine group and carboxylate) in the membrane[19, 20]. The facilitated transport membrane originated from liquid membrane. In the liquid membrane, the carriers can move freely and actively transport CO_2 like a boat, which lead to the excellent performance of liquid membrane (**Scheme1 a)**. However, the poor stability of carriers in liquid membrane (carrier loss) seriously limits its application[21]. In order to prevent the loss of the carriers, the carriers are held either by electrostatic forces in ion-exchange membrane or by covalent linkage in fixed carrier membrane.

In ion-exchange membrane, the carriers are held by electrostatic forces and possess favorable stability. Moreover, the carriers can still move as well as actively meet and transport CO_2, which lead to the high selectivity of the ion-exchange membrane[22] (**Scheme1 b)**. But the polymeric matrix of ion-exchange membrane is reticular, simultaneously, its charged matrix generally has strong polarity and high cohesive energy density which easily induce oriented crystallization[22-24]. All these reasons lead to the low permeability of the ion-exchange membrane. However, a high selectivity is of limited value if the gas permeability is low since a membrane with these properties will require a large surface area and high cost.

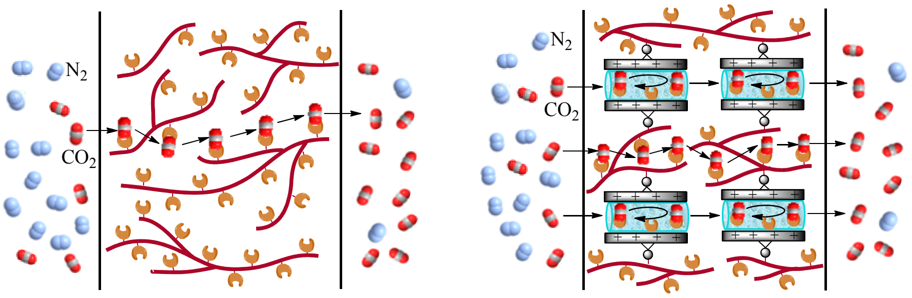
In contrast, the carriers in the fixed carrier membrane are covalently bonded in the membrane matrix and cannot move (**Scheme1 c)**. The selectivity of fixed carrier membrane is not very high, which is attributed to the fact that the carriers of fixed carrier membrane can only vibrate in a confined space and wait for the arrival of CO_2. But fixed carrier membrane is easier to get excellent permeability due to its loose flexible polymer chain[25, 26]. Simultaneously, its material is cheap, readily obtained and easy to modify by a physical or chemical method, so fixed carrier membrane is widely favorable[7, 20]. Therefore, to improve the performance of fixed carrier membrane has attracted more attention.

In view of the character of three previous facilitated transport membranes, it can be seen that the mobile carrier can actively meet CO_2 and get high selectivity, while the loose flexible polymer chain is the necessary requisite to get high permeability. Here, we report a method to combine the advantages of three previous facilitated transport membranes and overcome their deficiency. A new membrane was fabricated by establishing high-speed facilitated transport channels in the fixed carrier membrane. Firstly, fixed carrier membrane as the membrane matrix will be able to obtain good permeability for its good flexibility and loose polymer chain. Secondly, inspired by the liquid membrane and ion exchange membrane, we proposed to construct a high-speed facilitated transport channel, in which the carrier can unobstructed move and have good stability (**Scheme1 d)**. On one hand, the movable carrier in channel can meet the CO_2 actively as occured in the liquid membrane or in the ion-exchange membrane, which will significantly increase the selectivity of CO_2. On the other hand, unlike polymer network, the channel



(a) liquid membrane

(b) Ion-exchange membrane



(c) Fixed carrier membrane

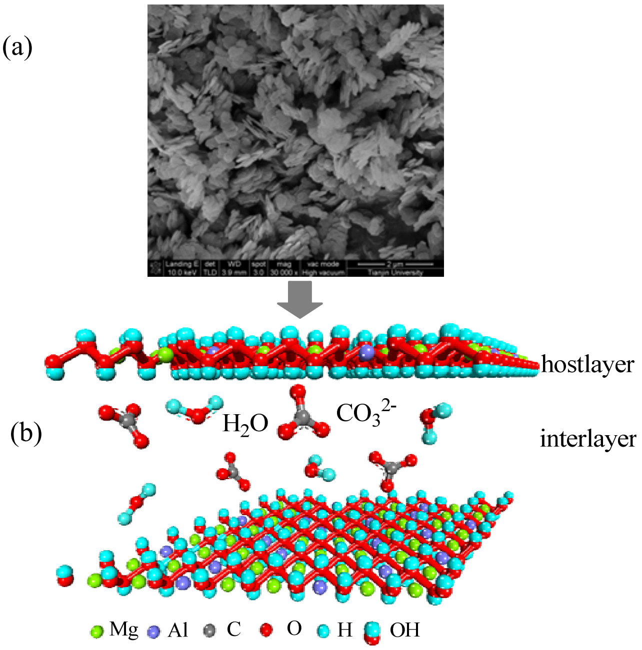
(d) High-speed facilitated transport channels in fixed carrier membrane

Scheme 1. Schematic of CO_2 transport mechanisms in different membrane (a) Na_2CO_3 liquid membrane; (b) Ion-exchange membrane; (c) fixed carrier membrane; (d) high-speed facilitated transport channels grafted in fixed carrier membrane.

is unobstructed, which will be beneficial to the rapid movement of carriers. Thus the carrier can transport CO_2 quickly and the permeability of membrane will be improved. Moreover, this channel can increase the chain spacing of the polymer to enhance the permeability of membrane. We hope to build this channel into fixed carrier membrane to get a high selectivity and high permeability membrane. The hydrotalcite possessing positively charged host layer and movable carbonate ions is one of the perfect channels that meet the above conditions.

Hydrotalcite (HT), known as layered double hydroxides (LDHs), is a sort of anionic pillared layered materials with basicity, micropore structure, memory effect as well as interlayer anionic exchangeability and mobility[27, 28]. It consists of positively charged brucite-like host layers and hydrated carbonate anions cruised in the unobstructed interlayer gallery. SEM images and schematic drawing of HT are displayed in **Scheme 2**. The hydrated carbonate anions cruising in HT interlayer possess excellent CO_2 facilitated transport properties[29]. Therefore, we intend to graft HT's channels in the polymer chain of fixed carrier membrane to establish high-speed CO_2 facilitated transport channels. The schematic diagram is shown in **Scheme 1(d)**.

In this work, polyethyleinimine (PEI, molecular weight 70000, 50wt% aqueous solutions, from Aldrich) and epichlorohydrin (>99.5%, from Aldrich) have been copolymerized a polymer, named as PEIE, which contains abundant amino-group with facilitated transport property and moderate hydroxyl with graft reactivity property (structure shown in **Scheme 3(a)**). It has been used as the raw material of fixed carrier membrane. Then, layered double oxide (LDO), which derived from pre-calcined HT in air atmosphere, was added in PEIE solution to in-situ generate the well dispersed HT through the reconstruction method. Actually, in our first attempt to disperse the HT in PEIE solution directly, we failed to obtain well dispersed HT in polymer solution because the layers of HT has high superposition and electrostatic attraction. In contrast, the LDO is more loose and porous than HT (see N_2 adsorption-desorption in Supplementary Table S1). In addition, compared to HT, the layers of LDO without electrostatic attraction were easy to slide and exfoliate (**Scheme 3**). These will be conducive to the dispersion of LDO in PEIE solution and the superposition of layers will reduce, as shown in **Scheme 3**. Concurrently, the LDO adsorbed large amounts of



Scheme 2. Structure of HT (a) SEM image of HT synthesized in this paper, size: about 110nm; (b) Schematic drawing of HT.

CO_2 (see TG-MS in Supplementary Figure S1), which provides the necessary conditions for LDO to reconstruct the carbonate-type HT in PEIE solution. For the above reasons, the LDO was used as raw materials to in-situ reconstruct the well dispersed HT in the polymer solution.

After the reconstruction of HT in the PEIE solution, the 3-Aminopropyltriethoxysilane (APTES) was used as a molecular bridge to couple the PEIE and HT by reacting with hydroxyl groups of PEIE and hydroxyl groups of HT, The typical process of preparing the PEIE-HT complex is shown in **Scheme 3** and detailed experimental procedures see Supplementary.

The chemical structure of PEIE-HT complex were analyzed by FTIR-ATR, XPS, TEM, STEM-EDS and XRD (Supplementary Figure S2-S5). The result showed that PEIE has a derivative structure of PEI and contains hydrophilic amino-groups and hydroxyls. The HT can be reconstructed well in the PEIE solution, Moreover, the HT and PEIE were coupled by using APTES as the molecule bridge. The results indicated that the high-speed facilitated transport channels established by HT was immobilized in PEIE.

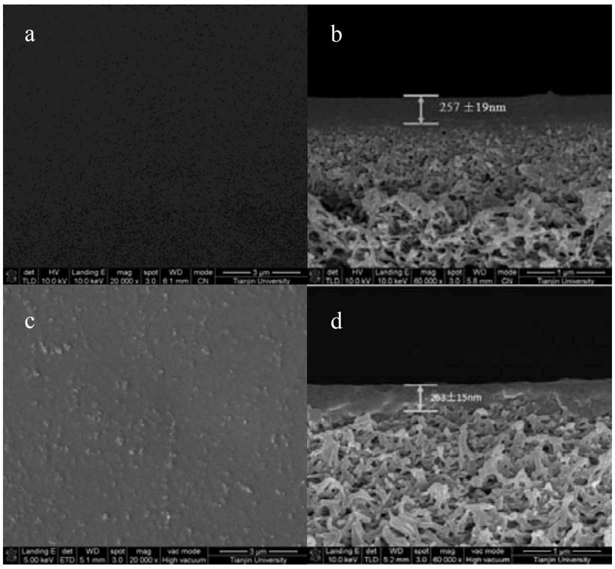
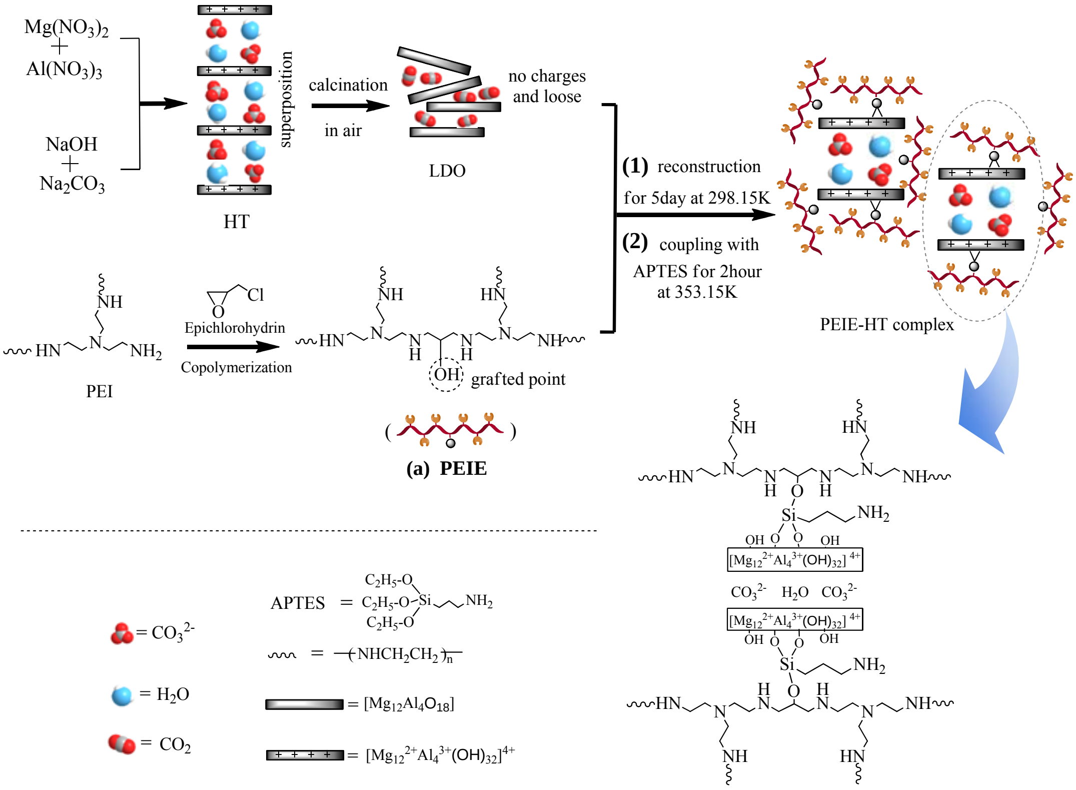


Figure 1. SEM images of PEIE-HT and PEIE membrane with 50μm wet coating thickness. (a) (b) surface morphology and cross-section morphology of PEIE membrane; (c) (d) surface morphology and cross-section morphology of PEIE-HT membrane; the thickness is average value of three membrane.

The PEIE membrane and PEIE-HT membrane were prepared by coating the PEIE solution and PEIE-HT complex solution on porous polysulfone ultrafiltration membrane (average cut-off molecular weight of 6,000, from Vontron Technology Co., Ltd. (China)) by a coating applicator, followed by drying at 303.15K and 40% relative humidity in an artificial climate chamber (Climacell 222R, Germany) for at least 12 hour. The surface and cross-section of membranes with 50 μm wet coating thickness were characterized by SEM, as shown in **Figure 1**. The thickness of the active layer for PEIE membrane and PEIE-HT membrane is about 257±19 nm and about 263±15 nm, respectively (the thickness is average value of three membranes). Generally, the small size of particle is beneficial to dispersion in the polymer, on the contrary, the large particles would induce defects of the membrane. In this work the size of HT is about 110nm, which is less than all thickness of the membranes. It ensures that HT can effectively embedded into the membrane. As shown in Figure 1,



(b) chemical structure of PEIE-HT complex

Scheme 3. Reaction pathways to formation of the PEIE-HT complex the HT showed excellent adhesion with the PEIE and interfacial voids were absent. Moreover, the HT was well dispersed in the membrane.

Gas permeation studies were conducted by a homemade apparatus using CO_2/N_2 gas mixture (15/85 by volume) at 298.15K. The feed gas (CO_2/N_2 mixed gas) flow and the sweep gas (H_2) flow is 16 $cm^3(STP)/s^{-1}$ and 0.5 $cm^3(STP)/s^{-1}$, respectively. Before contacting the membrane, the feed gas and the sweep gas were both saturated with water. Since water is the necessary condition for reversible reaction between CO_2 and carriers in the membrane[26, 29], the water absorption of membrane materials were investigated in the feed gas. The results show that the water absorption of the PEIE is approximately 108 ± 5%. The water absorption of PEIE-HT is about 175 ± 5%. Obviously, the water absorption of the complex is greatly improved because the PEIE-HT complex contains the HT channels, which are larger than molecular gap of polymer, resulting in an increase of water condensation. Simultaneously, this is a good evidence of the presence of HT channels.

The gas separation results of PEIE-HT membrane and PEIE membrane are presented in **Figure 2**. The unit of gas permeance in this paper is GPU (1 GPU $=1\times10^{-6}$ $cm^3(STP)$ cm^{-2} $s^{-1}cmHg^{-1}$). Generally, when the downstream component's partial pressure of membrane is negligible compared to the upstream component's partial pressure of membrane, the separation selectivity (α) is approximately equivalent to the ratio of the CO_2 permeance to the N_2 permeance. In this work, the H_2 is used as the sweep gas, the downstream component's partial pressure is very small and can be negligible. Thus, the separation selectivity (α) is defined as the ratio of the CO_2 permeance to the N_2 permeance in this work[26, 30]. All error bars present the standard errors of performances obtained from triplicate experiments. As shown in **Figure 2**, the CO_2 permselectivity decreases with increasing feed pressure, which indicates that both of the membranes show the typical characteristic of facilitated transport[31]. Compared with the PEIE membrane, both the CO_2 permeance and the CO_2/N_2 selectivity of PEIE-HT membrane were enhanced significantly. The CO_2 permeance of PEIE-HT membrane can reach 5693 GPU and the CO_2/N_2 selectivity can reach 268 at 0.11 MPa, which are 6.7 times and 3.8 times of the CO_2 permeance and the CO_2/N_2 selectivity of the PEIE membrane, respectively. Though the performance declines at the high pressure due to the carrier approaching saturation[22, 25, 26], the CO_2 permeance and CO_2/N_2 selectivity of PEIE-HT membrane still reach 450 GPU and 29 at 1.5 MPa, which are 1.7 times and 1.5 times of those of the PEIE membrane, respectively. The results indicate that the unobstructed facilitated transport channels, which contain movable carriers, can supply a highly efficient passageway to transport CO_2 in the PEIE-HT membrane. Therefore, both the CO_2 permeance and the CO_2/N_2 selectivity of membrane can be obviously improved. It also illustrates that this is an efficient approach to obtain a high performance CO_2 separation membranes by establishing high-speed CO_2 facilitated transport channels in the fixed carrier membranes. It is worth mentioning that the more of the HT does not mean the better performance of PEIE-HT membrane. Since the excessive HT would inevitably lead to the agglomeration of HT itself in the membrane, which would make the performance (especially the selectivity) of the membrane decrease (see Supplementary Figure S6). In this work, when the loading of LDO (precursor of HT) is 1.0wt%, the PEIE-HT membranes possess relative high permeability and selectivity, which is the suitable dosage. The performance of PEIE-HT membrane was compared with the state of the art membranes with high performance reported in the literature[7, 16, 25, 26, 32-39]. As shown in **Figure 3**, the novel membrane prepared in this work shows higher CO_2 permeance and CO_2/N_2 selectivity than most of common polymeric membranes and fixed carrier membrane membranes.

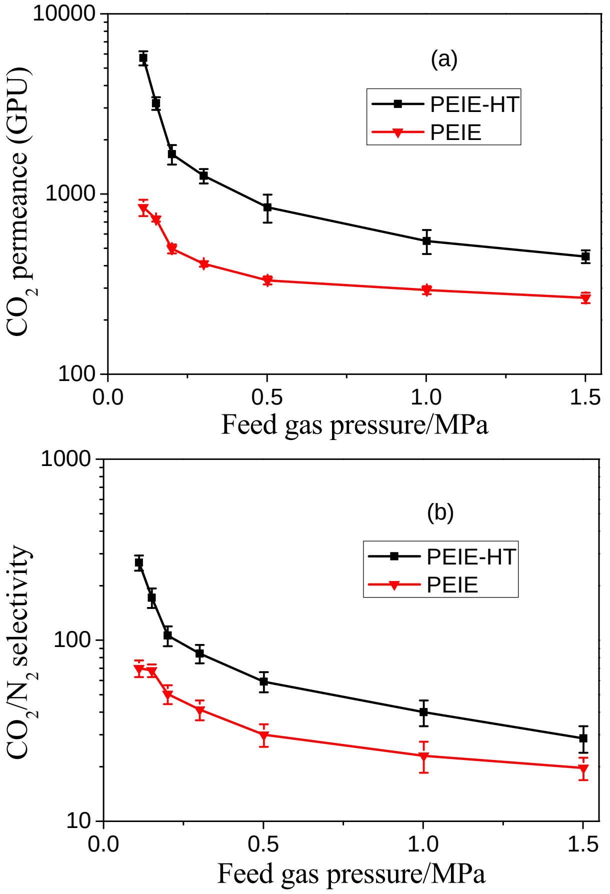


Figure 2. The CO_2/N_2 separation performance of PEIE-HT membrane and PEIE membrane (a) CO_2 permeance; (b) CO_2/N_2 selectivity. Wet coating thickness: 50μm; Feed gas: 15vol% CO_2 and 85vol% N_2. 298.15K.

In order to investigate the stability of the PEIE-HT membrane, it was tested continuously for 200 hours by using CO_2/N_2 mixed gas (15/85 by volume). Many studies show that the optimal feed pressure for flue gas CO_2 capture ranges from 0.1 to 0.3MPa[25, 36]. Therefore, stability tests were carried out at 0.2Mpa firstly. As shown in **Figure 4**, the performance of PEIE-HT membrane tested with humidified CO_2/N_2 mixed gas is quite stable. Both CO_2 permeance and CO_2/N_2 selectivity of the membrane tested with dry CO_2/N_2 mixed gas decrease due to lack of water and absence of reversible reaction of CO_2, H_2O and the carrier. However, the performance recovers well in humidified gas because of the restoration of reversible reaction. It suggests that the carrier (dry components) would not be lost with the loss of water, in other words, the carriers in this membrane is stable. In order to fully investigate the stability of PEIE-HT membrane, the

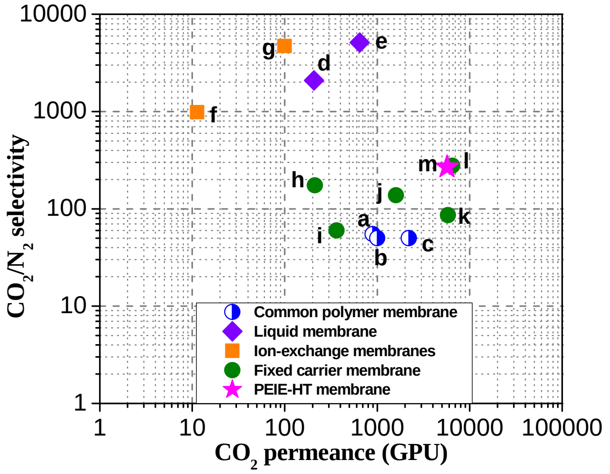


Figure 3. Performance comparison of various membranes. Detailed data list in Supplementary Table S2.

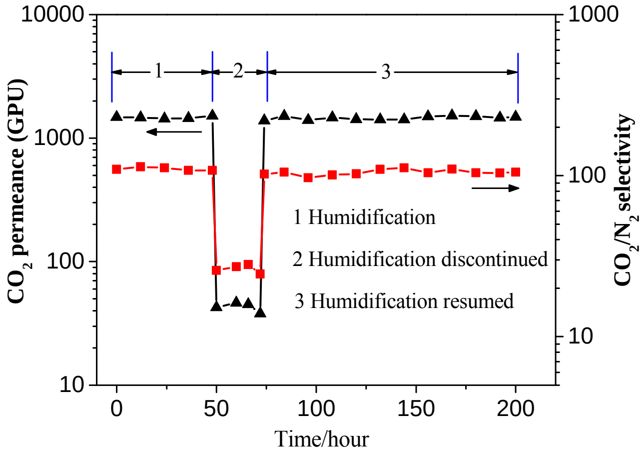


Figure 4. Separation performance stability of PEIE-HT membrane. Wet coating thickness: 50μm; Feed gas: 15vol% CO_2 and 85vol% N_2, 0.2MPa. 298.15K.

performance stability of the PEIE-HT membrane was also investigated at low pressure--0.11Mpa and at high pressure--1.5Mpa, respectively (Supplementary Figure S9). The results show that the PEIE-HT membrane also has good stability at 0.11 Mpa and 1.5 Mpa. It indicate that stability of the carriers in PEIE-HT membrane will not be affected by pressure.

Generally, the membranes used to purify air in confined spaces, e.g. space station and submarines, are usually operated at room temperature. While the membranes used to capture CO_2 from flue gas are usually operated at 323.15K. But the occasional temperature fluctuation may impact on the performance of membrane. Hence, the effect of temperature on the performance of the membranes was investigated in our work (see Supplementary Figure S10). The results show that the membrane performance does not change obviously at temperatures below 373.15K, while the membrane performance decreases obviously at temperatures beyond 373.15K. The reason is that the moisture in the membrane is almost entirely vaporized at temperatures beyond 373.15K, and the facilitated transport reaction of CO_2 is restricted. However, the membrane performance recovers again when temperature decrease. It indicates that the membrane can be applied to capture CO_2 from flue gas, even with the occasional temperature fluctuations.

When the membrane is used to capture CO_2 from flue gas, the raw gas may contain some impurity gas. Thus, the membrane was tested in simulated flue gas (14.5vol%CO_2, 6.5vol%O_2, 40ppmSO_2, 70ppm NO_2, 10ppmCO, balanced by N_2) [40]. When the impurity gas presents, the CO_2 permeance and CO_2/N_2 selectivity decrease by about 28% and 20%, respectively, (Supplementary Figure S11). However, the permselectivity is stable in simulated flue gas, and the performance recovers well when the impurity gases are removed. It indicates the effects of impurity gases on CO_2 transport are reversible. Moreover, the membranes were characterized by ATR-FTIR and XPS before and after being tested in simulated flue gas. As shown in Supplementary Figure S12, there were no apparent changes observed in the ATR-FTIR spectrograms of the membrane before and after being tested in simulated flue gas. Meanwhile, the elemental analysis from XPS shows that the valence state of element in the membrane has not change, and the changes of elemental composition of the membrane are not obvious (Supplementary Table S3 (a) and (b)). The results show that the membrane structure is unchanged, that is to say, the oxidative degradation of carriers does not occur. Thus, the reversible decrease of membrane performance is attributed to the competitive physical solution and competitive reaction caused by the impurity gas. Most CO_2 molecules transport through the membrane via reversible reaction with carriers, therefore, the decrease of membrane performance is mainly attributed to the competitive reaction caused by SO_2 and NO_2.[25, 41] The results suggest that the membrane possess favorable stability and could be potentially used to capture CO_2 from flue gas or purify air in confined spaces, e.g. space station and submarines.

In addition, the HT can be used to establish similar high-speed CO_2 facilitated transport channels in polyvinylamine (PVAm) -- another fixed carrier membrane material, the CO_2 permeance and CO_2/N_2 selectivity of PVAm-HT membrane can reach 3187 GPU and 296 at 0.11 MPa, which are 7.7 times and 4.3 times of those of the PVAm membrane, respectively (Supplementary Figure S7, detailed information is spelled out in another preparing article). Besides, we have found that the structure of high-speed CO_2 facilitated transport channels can be also achieved by hydrotalcite-like compounds (HTLcs), such as ZnAl-CO_3^{2-}-HTLcs and NiAl-CO_3^{2-}-HTLcs. Similar to the HT, the HTLcs could significantly improve the CO_2 separation performance of fixed carrier membranes (Supplementary Figure S8). Furthermore, it can be speculated that some other pillared layered materials containing some carriers in its interlayer can be used to establish high-speed facilitated transport channels in fixed carrier membrane for corresponding system separation. For example, the montmorillonite intercalated by Ag^+, Fe^{2+}, Cu^+ could probably be used to improve the separation performance of fixed carrier membranes for alkene, NO and CO separation, respectively. The HT channels in the membrane can significantly improve the transport efficiency of CO_2, but in our current work, the efficiency of HT channels may not reach the maximum, due to the random arrangement of HT layer in the membrane. The HT channels may be perpendicular, oblique, or paralleled to the membrane surface. Apparently, the perpendicular layers possess the maximum efficiency, oblique layers secondly and the paralleled layers could only increase the chain spacing of the polymer, like the nonporous particle. In order to maximize efficiency of channels, uniform orientation of HT would be expected and adding external electric field or in-situ directional growth technology might be the choice for our future work.[42, 43]

Conclusions

In conclusion, we propose a method to fabricate high-performance membrane by designing high-speed CO_2 facilitated transport channels in fixed carrier membrane. In this paper, the high-speed facilitated transport channels has been established in the fixed carrier membrane by using HT. The membrane displays excellent CO_2 permselectivity and good stability. The CO_2 permeance can reach 5693 GPU with the CO_2/N_2 selectivity of 268 at the feed pressure of 0.11 MPa. Furthermore, the idea of establishing high-speed facilitated transport channels in fixed carrier membrane will be a universal route to improve the performance of gas separation membrane, and it will get enormous application prospect for these membranes.

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Notes and references

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† Electronic Supplementary Information (ESI) available: details of experimental procedures, characterization techniques and characterization data, performance comparison of membrane, stability of the PEIE-HT membrane in simulated flue gas. See DOI: 10.1039/b000000x/

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