Amine-containing polymer/zeolite Y composite membranes for CO₂/N₂ separation

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Abstract

New amine-containing polymer/zeolite Y composite membranes were successfully synthesized for CO₂/N₂ separation from flue gas. The polyvinylamine (PVAm) with a high molecular weight ($\overline{M}_w = 719,000$) was synthesized and used as the fixed-site carrier for CO₂ facilitated transport. The PVAm was incorporated with different aminoacid salts (mobile carriers), including potassium glycinate (KG), lithium glycinate (LiG) and piperazine glycinate (PG). The amine-containing polymer blend solution was coated onto a zeolite Y seed layer on top of a polyethersulfone (PES) substrate. The composite membrane with a selective amine layer thickness of more than 200 nm showed a better CO₂/N₂ separation performance compared to the membrane without the zeolite Y seed layer, which was due to the fact that the zeolite Y layer had a smaller interparticle pore size than the PES substrate, resulting in minimizing the penetration of amine-containing polymer solution into the pores underneath and thus reducing the mass transfer resistance of CO₂ molecules through the membrane. The effects of different kinds of mobile carriers and various compositions and thicknesses of the amine-containing polymer layer were investigated. The resultant amine-containing polymer/zeolite Y composite membrane exhibited a CO₂ permeance up to ~ 1100 GPU and a CO₂/N₂ mixed gas selectivity of at least 200 at the typical flue gas temperature of 57°C. This high separation performance showed a great potential for the application of carbon capture from flue gas.

Keywords: CO₂-selective membrane; Polymer/inorganic composite membrane; Polyvinylamine; Mobile carrier; Facilitated transport

1. Introduction

Carbon dioxide (CO₂) emission from the fossil fuel combustion is one of the main reasons for global warming, and therefore there is a significant need of developing technologies for CO₂ separation from flue gas. Membrane separation is an energy-efficient and cost-effective alternative [1-6] to the conventional technologies including absorption processes using amine-based solvents, adsorption processes employing solid adsorbents, and cryogenic distillation. The membrane transport performance for CO₂/N₂ separation from flue gas is mainly characterized by two parameters, the CO₂ permeance and the CO₂/N₂ selectivity [7]. The CO₂ permeance ($\frac{P_{CO_2}}{l}$) is defined as

$$\frac{P_{CO_2}}{l} = \frac{J_{CO_2}}{(p_{fCO_2} - p_{pCO_2})} \quad (1)$$

The common unit of permeance is the gas permeation unit (GPU), 1 GPU = 10⁻⁶ cm³(STP)/(s·cm²·cmHg). P is referred as the permeability, and its common unit is Barrer, 1 Barrer = 10⁻¹⁰ cm³(STP)·cm/(s·cm²·cmHg). The CO₂/N₂ selectivity can be expressed as the ratio of permeabilities of CO₂ over N₂, as shown in Eq. 2. To achieve a high CO₂ recovery (> 90%) with a high CO₂ purity (> 95%) in a membrane-based process for carbon capture from flue gas, both a high CO₂ permeance and a high CO₂/N₂ selectivity are required [8-11].

$$\alpha_{CO_2/N_2} = \frac{P_{CO_2}}{P_{N_2}} \quad (2)$$

Polymer and inorganic membranes are two major categories for CO₂ separation membranes, and they follow different transport mechanisms (Fig. 1). Solution-diffusion polymer membranes such as PolarisTM and Polyactive[®] have shown the potential to achieve high CO₂ permeances up to ~ 2000 GPU [11-15], but they have shown low CO₂/N₂ selectivities (usually below 30 at 57°C) governed by the Robeson upper bound [16,17].

Fig. 1. Schematic of CO₂/N₂ transport mechanisms through polymer and inorganic membranes.

Facilitated transport membranes, on the other hand, can provide a high CO₂ permeance while maintaining a high CO₂/N₂ selectivity. In the facilitated transport membranes, there is a reversible reaction between CO₂ and a reactive carrier which usually contains an amino group. Fixed carriers (amine-containing polymers) and mobile carriers (amine-containing small molecules) are two major categories of carriers for CO₂ transport in facilitated transport membranes. The fixed carriers such as polyallylamine [18-22], polyethylenimine [18,23] and polyvinylamine (PVAm) [24-27] have been reported in the literature. The common mobile carriers that have been reported in the literature include ethylenediamine [27-29], aminoacid salts [30,31], and alkanolamines [32,33]. In the facilitated transport membranes, CO₂ molecules react with amine carriers first, and then the reaction products transport across the membrane, releasing the CO₂ molecules to the permeate side of the membrane. By this mechanism, the solubility of CO₂ molecules in the membrane is greatly enhanced. On the other hand, the non-reactive N₂ molecules transport through the membrane only by the solution-diffusion mechanism. Therefore,

CO₂ transport gets facilitated, and a high CO₂/N₂ selectivity can be achieved through the facilitated transport mechanism.

The gas transport in inorganic membranes such as zeolite Y (with a pore size of 7.4 Å and a Si/Al ratio of 1.5 – 3.8) follows both surface diffusion and molecular sieving mechanisms. CO₂ (with a molecular size of 3.3 Å) favorably adsorbs and diffuses along the interior zeolite surface wall, while N₂ (with a molecular size of 3.64 Å) is blocked and cannot go through the membrane. By the combination of these two mechanisms, both a high CO₂ permeance and a high CO₂/N₂ selectivity can be achieved from inorganic membranes [34-37].

In this work, an amine-containing polymer/zeolite Y composite membrane for CO₂/N₂ separation was designed. First, zeolite Y with an average particle size of around 40 nm was deposited onto the PES substrate. For the polymer layer, PVAm with a high molecular weight was synthesized and acted as the fixed carrier, while different kinds of aminoacid salts were incorporated as the mobile carriers in the coating solution. The viscous PVAm/mobile carrier coating solution was knife-coated onto the zeolite Y layer to form a thin selective layer.

2. Experimental

2.1. Materials

Glycine (98.5%), potassium hydroxide (KOH, 85%), lithium hydroxide (LiOH, 98%), piperazine (99%), n-vinylformamide (NVF, 98%), α,α' -azodiisobutyramidine dihydrochloride (AIBA, 97%) and isopropanol (IPA, 99.9%) were purchased from Sigma-Aldrich. Hydrochloric acid (HCl, Certificated ACS Plus) and ethanol (99.5%) were purchased from Fisher Scientific. Strong base anion-exchange resin (Purolite[®] A600OH) was kindly donated by Purolite Corporation (Bala Cynwyd, PA). All the chemicals were used as received without further purification.

Biomax polyethersulfone ultrafiltration flat-sheet membrane substrate with a molecular weight cut off of 300 kDa (PES300, with a pore size of ~ 72 nm and a porosity of $\sim 15\%$) was purchased from EMD Millipore (Billerica, MA). The PES300 substrate was soaked in deionized water for overnight and then in IPA for 30 min to remove the glycerol in the pores before usage.

2.2. *Synthesis of PVAm and amine-containing mobile carriers*

High-molecular-weight PVAm was synthesized following the procedure in the literature [27, 38]. First, the monomer NVF was distilled under vacuum and stored at -10 °C. Then, polymerization was carried out under nitrogen protection at 50°C for 3 h. AIBA was used as the initiator of the polymerization, and water was used as the solvent. The initial monomer concentration was 30 wt.%, and the initiator/monomer ratio was 0.5/100 (by weight). After the polymerization, 2 M HCl aqueous solution was added to carry out the acidic hydrolysis at 70°C for 5 h. The molar ratio of HCl to monomer for hydrolysis was 2:1. After hydrolysis, the polymer solution was poured into a large amount of ethanol (ethanol/polymer solution volume ratio = 4/1) for precipitation. The obtained polymer was dried in a vacuum oven at 60 °C for 48 hours and then dissolved in water to form a 3 wt.% solution. Strong base anion-exchange resin was added to the polymer solution to adjust the pH to 10, followed by vacuum filtration to remove the resin.

Mobile carriers of aminoacid salts including potassium glycinate (KG), lithium glycinate (LiG) and piperazine glycinate (PG) were synthesized by the following procedure. First, glycine was dissolved in water to form a 17.5 wt.% solution and stirred for 2 h at room temperature. Then KOH, LiOH or piperazine at the stoichiometric amount as glycine, was added to react with glycine to form the aminoacid salt. The reaction took place at room temperature for 2 h. After the syntheses of both PVAm and mobile carriers, the mobile carrier solution was incorporated

into the PVAm solution with different mobile carrier/PVAm weight ratios, which formed the amine-containing coating solution. The structures of PVAm and the aminoacid salts are shown in Fig. 2.

Fixed carrier:

Mobile carriers (small aminoacid salts):

Fig. 2. Chemical structures of PVAm, KG, LiG and PG.

2.3. Membrane preparation

The amine-containing polymer/zeolite Y composite membranes were synthesized following two steps. First, zeolite Y with a particle size of around 40 nm, which was synthesized following the procedure in the literature [39], was deposited onto the PES300 substrate using a vacuum-assisted dip-coating method [40]. The zeolite Y nanoparticles were synthesized from hydrothermal treatment of silicon and aluminum sources, followed by dialysis and ultracentrifugation, with the synthesis detail reported elsewhere [41]. After the zeolite Y deposition, the amine-containing polymer layer was coated on top of the zeolite Y layer using a

knife-coating method. The coating solution was coated on the flat-sheet Millipore PES300 substrate with the 40 nm zeolite Y seed layer using a GARDCO adjustable micrometer film applicator (Paul N. Gardner Company, Pompano Beach, FL) with a controlled gap-setting. The membrane was dried in a fume hood at room temperature for overnight before testing.

2.4. Gas transport performance measurements

Gas transport performance measurements were conducted by using a permeation apparatus described in a previous paper [19]. The synthesized composite membrane was loaded into a stainless steel rectangular permeation cell inside a temperature-controlled oven (Bemco Inc. Simi Valley, CA) with an effective membrane area of 3.4 cm². A countercurrent flow configuration (with a dry feed gas flow rate of 60 cc/min and a dry sweep gas flow rate of 30 cc/min) was applied to offer the maximum driving force across the membrane. The binary gas mixture containing 20% CO₂ and 80% N₂ was used as the feed gas, while argon was used as the sweep gas. Both the feed gas and the sweep gas were humidified by passing through 100 mL water in a 500 mL stainless steel humidifier (Swagelok, Westerville, OH) filled with 60% (by volume) packing of glass Raschig rings to achieve a saturation water content of 17% at 57°C. The testing temperature was set to be 57°C, which is the typical flue gas stream temperature. The testing pressures were 1.5 psig for the feed side and 1.0 psig for the sweep side, respectively. After the water vapor was removed in respective condensers, the outlet gas compositions of both retentate and permeate streams were analyzed by using a gas chromatograph (GC) equipped with thermal conductivity detectors (TCDs) (Agilent Technologies, Palo Alto, CA). In the GC analysis, a SUPELCO Carboxen[®] 1004 micropacked GC column (Sigma-Aldrich, St. Louis, MO) was used. From the GC analysis, CO₂ permeance and CO₂/N₂ selectivity were calculated to characterize the membrane transport performance.

2.5. Characterization of PVAm and membrane properties

The weight average molecular weight of the synthesized PVAm was characterized by dynamic light scattering (DLS) using Zetasizer Nano ZS (Malvern Instruments Inc., Westborough, MA). The viscosity of the 3 wt.% polymer solution was characterized using Brookfield Digital Viscometer DV-E (Brookfield Engineering Laboratories, Inc., Middleboro, MA). The cross-section morphology of the synthesized membranes was observed by scanning electron microscope (SEM) using FEI Nova NanoSEM400 (FEI Company, Hillsboro, OR).

3. Results and discussion

3.1. PVAm synthesis

As the fixed carrier in the selective polymer layer, PVAm not only provides amino groups for CO₂/N₂ separation, but also provides the mechanical strength and film-formation ability to the membrane. Therefore, a higher molecular weight of PVAm was beneficial. First, with a higher molecular weight, the polymer matrix will be stronger, which makes the membrane more stable. Second, due to the stronger polymer matrix, it can allow more mobile carriers to be incorporated into the polymer membrane, which can further improve the transport performance. Third, a higher viscosity of the coating solution can be obtained with a higher molecular weight of PVAm, resulting in the reduction of penetration of the polymer solution into the substrate and thus lowering mass transfer resistance and increasing CO₂ permeance. Moreover, thinner membranes can be obtained from the solution with a low concentration and a high viscosity, which can lead to a higher CO₂ permeance.

Table 1 shows the comparison of the synthesized PVAm in this work and the commercially available PVAm (Lupamin[®] 9095, from BASF Corporation). It can be seen that the PVAm synthesized in this work had a much higher molecular weight than Lupamin[®]. Besides, the

viscosity of the 3 wt.% synthesized PVAm solution was significantly higher than the 3 wt.% Lupamin[®] polymer solution. Moreover, Lupamin[®] was obtained by basic hydrolysis using sodium hydroxide (NaOH), therefore the byproduct (sodium formate salt) was formed in the polymer product. The large amount of non-reactive salts can damage the stability of the membranes due to the salting-out problem. In contrast, acidic hydrolysis was used in this work, and no byproduct was formed. Overall, the high molecular weight PVAm synthesized in this work was advantageous for the membrane transport performance compared to the commercially available Lupamin[®] product.

Table 1. Comparison of the PVAm synthesized in this work and Lupamin[®] 9095.

	Lupamin [®] 9095	Synthesized PVAm
$\overline{M}_w$	340,000	719,000
Viscosity of 3 wt.% polymer solution (cp)	50	486
Hydrolysis	Basic	Acidic
Byproduct	Sodium formate salts	None

3.2. Membrane morphology via SEM

The SEM image in Fig. 3 shows the cross-section of the composite membrane synthesized in this work. As can be seen, the thin composite membrane with a thickness of ~ 100 nm was successfully synthesized. The two layers on top of the porous PES substrate were (A) selective amine layer and (B) zeolite Y layer, respectively. Zeolite Y particles were packed closely on top of the PES substrate, forming a layer of around 300 nm thick. On top of the zeolite Y layer, the dense amine layer showed a thickness of around 100 nm. Fig. 4 shows the cross-section of another composite membrane with a thicker amine layer. The thickness of the amine layer was around 350 nm.

Fig. 3. SEM image of the cross-section morphology of the composite membrane with an amine layer thickness of ~ 100 nm: (A) selective amine layer and (B) zeolite Y layer.

Fig. 4. SEM image of the cross-section morphology of the composite membrane with an amine layer thickness of ~ 350 nm: (A) selective amine layer and (B) zeolite Y layer.

3.3. Correlation between amine layer thickness and wet coating thickness

Fig. 5 shows the linear correlation between the amine layer thickness and the wet coating thickness. The dry amine layer thicknesses shown in Fig. 5 were measured by SEM. The empirical equation for the relationship between the wet coating thickness and the amine layer thickness was then obtained:

$$l \times \rho_{dry} = 0.5 \times c \times \rho_{solution} \times l_{wet} \quad (3)$$

where l (μm) is the dry amine-containing polymer layer thickness, ρ_{dry} (g/cm^3) is the density of the dry amine-containing polymer layer, $\rho_{solution}$ (g/cm^3) is the density of the coating solution, c

(by weight) is the total solid concentration of the amine coating solution, and l_{wet} (μm) is the wet coating thickness or the gap-setting of the coating knife.

Fig. 5. Correlation between the dry amine layer thickness and the wet coating thickness.

3.4. Influence of the zeolite Y layer on membrane separation performance

To study the effect of the zeolite Y layer on the composite membrane separation performance, membranes with only amine-containing polymer layer on top of the bare PES substrate without the zeolite Y layer were also prepared. Fig. 6 shows the comparison of the CO_2 permeances of the membranes with and without the zeolite Y layer. It was observed that when the amine-containing polymer layer thickness was more than 200 nm, a higher CO_2 permeance was obtained with the zeolite Y layer. This can be explained by the fact that the zeolite Y layer had a smaller interparticle pore size (~ 10 nm) compared to the bare PES substrate (~ 72 nm), which could reduce the penetration of the amine solution into the pores underneath, resulting in less

mass transfer resistance in the membrane. On the other hand, when the amine-containing polymer layer thickness was less than 200 nm, the effect was not obvious. With an amine-containing polymer layer thickness of 100 nm, the CO₂ permeance of the membrane without the zeolite Y layer was even higher than that with the zeolite Y layer. One possible explanation was that the zeolite Y layer provided certain mass transfer resistance to the composite membrane, especially with the presence of water vapor. Even though this resistance could be less compared to the resistance from the amine-containing polymer layer, the effect of this resistance became more pronounced when the amine-containing polymer layer was thinner. All the membranes shown in Fig. 6 exhibited a CO₂/N₂ selectivity in the range of 150 – 220. No obvious effect of the zeolite Y layer on the CO₂/N₂ selectivity was observed from this study.

Fig. 6. Influence of the zeolite Y layer on membrane transport performance (membrane solid composition: 65/35 PG/PVAm).

3.5. Effects of mobile carrier amount on membrane separation performance

For the facilitated transport mechanism, the CO₂ transport of the fixed carrier is limited by the mobility of the CO₂-carrier complex. Therefore, the incorporation of mobile carriers becomes necessary to help enhance the CO₂ transport. Fig. 7 shows the comparison of the composite membrane separation performance with and without mobile carriers in the amine coating solution. Both of the membranes had a thickness of around 100 nm. Both CO₂ permeance and CO₂/N₂ selectivity were observed to be lower without the mobile carriers in the membrane composition, which proved that the mobile carriers played a big role on improving the transport performance.

Fig. 7. Comparison of the composite membrane separation performances with and without mobile carriers.

In this work, different amounts of mobile carriers (KG, LiG or PG) were incorporated into the PVAm solution to form the coating solution. From Fig. 8 to Fig. 10, it can be concluded that with any kind of the mobile carriers, a higher mobile carrier amount resulted in a higher CO₂ permeance, while the CO₂/N₂ selectivity was maintained at a high level (170 – 210). This trend was observed within the range of 50 wt.% to 65 wt.% mobile carrier amount in the solid content of the amine-containing polymer layer. When the mobile carrier amount was more than 65 wt.%, the membrane exhibited instability. As can be seen from Fig. 11, with 70 wt.% PG in the solid content of the amine-containing polymer layer, both the CO₂ permeance and the CO₂/N₂ selectivity showed a decreasing trend after the 6-h test. Besides, the CO₂/N₂ selectivity was lower compared to that of the membrane with 65 wt.% PG. The reason was that the polymer matrix was not strong enough to hold large amount of mobile carriers. There might also be carrier leakage into the pores of the substrate, which caused the instability of the membrane performance. For comparison, the membrane with 65 wt.% of the mobile carrier in the total solid content of the amine-containing polymer layer did not show any sign of performance dropping over 24 h, which will be discussed in Section 3.8.

Fig. 8. Transport performances of membranes with different **KG** amounts in the total solid composition.

Fig. 9. Transport performances of membranes with different LiG amounts in the total solid composition.

Fig. 10. Transport performances of membranes with different PG amounts in the total solid composition.

Fig. 11. Membrane stability with 70 wt.% PG in the total solid composition of the amine layer.

3.6. Influence of different mobile carriers on membrane separation performance

As mentioned, there were three kinds of mobile carriers (KG, LiG and PG) which were incorporated into the PVAm solution. The effect of different mobile carriers on the membrane separation performance was studied. As can be seen from Fig. 8 – 10, with different amounts of mobile carrier (50 wt.% – 65 wt.%), the composite membrane with PG as the mobile carrier showed the highest CO₂ permeance compared to those with LiG or KG. This can be explained by the fact that each PG molecule has two amino groups, while each LiG or KG molecule has only one amino group. The extra amino group enhanced the CO₂ facilitated transport in the membrane, resulting in a higher CO₂ permeance. The composite membrane with LiG as the

mobile carrier showed a higher CO₂ permeance than that with KG as the mobile carrier. This can be explained by two reasons. First, LiG has a lower molecular weight than KG, which means that there are more moles of carrier with the same weight ratio of the mobile carriers in the amine-containing polymer layer. Second, since LiG is a smaller molecule than KG, the diffusivities of both LiG mobile carrier and the CO₂-carrier complex are higher. Due to these two reasons, a higher CO₂ permeance was obtained from the composite membrane with LiG as the mobile carrier than that with KG as the mobile carrier.

3.7. Influence of amine-layer thickness on membrane performance

A thinner selective layer can lead to a higher CO₂ permeance due to the fact that the permeance is inversely proportional to the selective layer thickness. In this work, amine layers with different thicknesses were coated on top of the zeolite Y layer using different gap-settings of the coating knife. Fig. 12 shows the trend of increasing CO₂ permeance with decreasing selective layer thickness, which is similar to the results reported in the literature [42]. All the membranes shown in Fig. 12 were prepared with the 65/35 PG/PVAm composition for the amine-containing polymer layer. The highest CO₂ permeance (with a good CO₂/N₂ selectivity) was around 1100 GPU, which was obtained from the composite membrane with an amine-containing polymer layer thickness of 100 nm.

Fig. 12. Membrane transport performances with different amine layer thicknesses (membrane solid composition: 65/35 PG/PVAm).

Lower CO₂/N₂ selectivity was obtained from the membranes with an amine-containing polymer layer thickness of less than 100 nm. From Fig. 13, it can be clearly seen that although the CO₂ permeance kept increasing with thinner amine layers, there was a significant decline of the CO₂/N₂ selectivity with decreasing thickness. The low selectivity might be due to the reason that there were defects formed in the ultra-thin amine-containing polymer layer. Therefore, a minimum of 100 nm thickness was required in this work to obtain a good CO₂/N₂ selectivity.

3.8. Stability of amine-containing polymer/zeolite Y composite membrane

Fig. 13 showed the 24 h stability test of the amine-containing polymer/zeolite Y composite membrane. The membrane showed an average CO₂ permeance of 1100 GPU and a CO₂/N₂

selectivity of 210. It can be seen that the membrane performance was stable within 24 h. No sign of performance degradation was observed for either CO₂ permeance or CO₂/N₂ selectivity. The membrane stability in the presence of SO₂ and O₂ will be studied in the future.

Fig. 13. Membrane transport performances during 24 h stability test at 57°C (membrane solid composition: 65/35 PG/PVAm).

4. Conclusions

New amine-containing polymer/zeolite Y composite membranes were successfully synthesized. PVAm with a higher molecular weight compared to the commercial PVAm (Lupamin®) was synthesized and was beneficial for the improvement of the membrane transport performance. A higher mobile carrier amount and a lower thickness of the amine-containing

polymer layer were found to be effective to improve the membrane separation performance. PG was found to provide a better separation performance as the mobile carrier over KG and LiG. The zeolite Y layer had a smaller interparticle pore size compared to the bare PES substrate, resulting in reduction of penetration of the coating solution into the PES pores and improving the CO₂ permeance by minimizing the mass transfer resistance. However, this effect only applied for membranes with an amine-containing polymer layer thickness of ≥ 200 nm. When the membrane was thinner, this effect was opposite and the membrane without the zeolite Y layer had a higher CO₂ permeance, due to the fact that the zeolite Y layer itself would also provide certain mass transfer resistance to the composite membrane. The resulting composite membrane showed a CO₂ permeance of around 1100 GPU and a CO₂/N₂ selectivity of more than 200. This high separation performance indicates that our membrane has a great potential for the application of carbon capture from flue gas [43].

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Nomenclature

c	concentration of amine coating solution
J	gas flux
J_{CO_2}	flux of CO ₂
l	amine layer thickness
l_{wet}	amine layer wet coating thickness
$\overline{M}_w$	weight average molecular weight
P_{CO_2}	permeability of CO ₂
P_{N_2}	permeability of N ₂
p	pressure
p_f	pressure on the feed side of the membrane
p_p	pressure on the permeate side of the membrane
p_{fCO_2}	CO ₂ partial pressure on the feed side of the membrane
p_{pCO_2}	CO ₂ partial pressure on the permeate side of the membrane

Greek letters

α	selectivity
α_{CO_2/N_2}	selectivity of CO ₂ over N ₂
ρ_{dry}	density of the dry amine-containing polymer layer
$\rho_{solution}$	density of coating solution

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