POLYMER MEMBRANES FOR FLUE GAS CARBON CAPTURE AND FUEL CELL APPLICATION

DISSERTATION

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Abstract

Polymer membrane is a cost-effective and energy-efficient approach for separation and fuel cell applications. In this research, two types of polymer membranes were synthesized for different applications. The first type is CO$_2$-selective membranes for carbon capture from flue gas, and the second type is hydroxide-exchange membranes for alkaline fuel cell application.

CO$_2$ separation from flue gas streams is one of the most important solutions to greenhouse gas driven climate change. In this research, two types of CO$_2$-selective polymer membranes were synthesized: (1) ethylene oxide (EO)-based membranes and (2) amine-based membranes. The former is based on the solution-diffusion transport mechanism, while the latter is based on the facilitated transport mechanism. For the membranes containing EO groups, membranes were synthesized with polyamide-polyethyleneoxide (PA-PEO) copolymer blended with poly(ethylene glycol) dimethyl ether (PEG-DME) or polyethylene glycol (PEG). For the membranes containing amino groups, a high-molecular-weight polyamine was successfully synthesized. Selected aminoacid salts were incorporated into the polyamine solution for membrane preparation. The polyamine served as the fixed-site carrier, whereas the aminoacid salts acted as
mobile carriers. Both types of membrane have shown promising results for CO$_2$/N$_2$ separation from flue gas.

Alkaline fuel cells (AFC) has received increasing attention nowadays because they enable non-precious metals to replace the platinum as the catalyst, and they have the potential to offer fuel flexibility, reduce fuel crossover and prevent carbonate precipitation. Current research about alkaline fuel cell membranes mostly focused on quaternary ammonium-based polymer membranes. However, these membranes have shown low ionic conductivity and, poor chemical and thermal stability. Ionic liquids are organic molten electrolytes which have ideal conductivity, excellent thermal and chemical stability. In this research, ionic liquids were incorporated into polybenzimidazole (PBI) and crosslinked polyvinylalcohol (PVA) polymer matrixes to prepare hydroxide-exchange membranes (HEMs).
Dedicated to my parents, my sister Yuanqing, and to Wei
Acknowledgments

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**Fields of Study**

Major Field: Chemical Engineering
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Membrane has a wide application in both chemical industry and human life, including gas separation, seawater desalination, artificial kidney, electrodialysis, and fuel cells [1-8]. A general definition of a membrane can be a selective barrier between two phases. The membrane allows one or more species of a feed mixture to diffuse across the membrane to the permeate side while hindering the permeation of the other species. In this research, two types of polymer membranes for different applications were synthesized. The first one is gas separation membranes for CO₂ capture from flue gas, which will be discussed in Chapters 2 – 5. The second one is hydroxide-exchange membranes (HEMs) for fuel cell application, which will be discussed in Chapter 6.

1.1. CO₂-selective membranes for carbon capture from flue gas

Electricity generation through conventional coal combustion process is well-developed. However, the large amount of carbon dioxide (CO₂) emission from this conventional technology has become a main reason for greenhouse gas driven climate change. Therefore, carbon capture from flue gas has become an important solution to the
global warming problem. Conventional carbon capture technologies include absorption processes using amine-based solvents, adsorption processes employing solid adsorbents, and cryogenic distillation. However, many barriers exist when applying these technologies, including high capital cost, large footprint, numerous operational concerns, and high energy penalty for CO₂ stripping and regeneration of solvent. On the other hand, membrane separation becomes more promising because of its system compactness, energy efficiency, operational simplicity, and kinetic ability to overcome the thermodynamic limitation [9-14].

There are two main challenges for CO₂ capture from flue gas. First, there is a large amount of flue gas to be treated. For example, a 600 MW coal-fired power plant could generate flue gas at a rate of 500 m³/s [15]. Second, the flue gas contains only 12% to 14% CO₂ at one atmosphere, which means the driving force for CO₂ separation is relatively low (< 0.15 atm). To overcome these challenges, both a high CO₂ permeance and a high CO₂/N₂ selectivity are required for CO₂-selective membranes. A high CO₂ permeance can help reduce the membrane area, and further reduce capture cost. A high CO₂/N₂ selectivity can help obtaining a high CO₂ purity with low energy consumption [16,17].

Considering two components, CO₂ and N₂, in flue gas (where CO₂ is the more permeating component), the CO₂ permeance and the CO₂/N₂ selectivity of a membrane are defined as below:

\[
\text{CO}_2 \text{ permeance} = \frac{P_{\text{CO}_2}}{l} = \frac{J_{\text{CO}_2}}{(p_{f \text{CO}_2} - p_{P \text{CO}_2})} \quad (1.1)
\]

\[
\text{CO}_2/N_2 \text{ selectivity} = \alpha_{\text{CO}_2/N_2} = \frac{P_{\text{CO}_2}}{P_{N_2}} \quad (1.2)
\]
where \( \frac{P_{CO_2}}{l} \) is the CO₂ permeance, the common unit of which is the gas permeation unit (GPU), \( 1 \) GPU = \( 10^{-6} \) cm\(^3\) (STP)/(s·cm\(^2\)·cmHg). \( J_{CO_2} \) is the flux of CO₂, \( P \) is the permeability, \( l \) is the selective layer thickness of the membrane, \( p_{f_{CO_2}} \) and \( p_{p_{CO_2}} \) are the feed and permeate pressures of CO₂, respectively. \( \alpha_{CO_2/N_2} \) is the CO₂/N₂ selectivity, which is the permeability (or permeance) ratio between CO₂ and N₂. 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 [15-19].

Polymer and inorganic membranes are two major categories for CO₂ separation membranes, and they follow different transport mechanisms as shown in Figure 1.1. Most of the polymer membranes follow the solution-diffusion mechanism for gas transport. For solution-diffusion membranes, CO₂ and N₂ gas molecules dissolve in the membrane first, and then diffuse across the membrane to the permeate side. The transport performance of the solution-diffusion membrane depends on both the solubility and diffusivity of gas molecules in the membrane. Because of the polar nature of CO₂ molecules, researchers usually use copolymers which contain polyethyleneoxide (PEO) segments to provide the CO₂ affinity and improve the CO₂ solubility in the membrane. Solution-diffusion polymer membranes such as Polaris™ and Polyactive® have shown the potential to achieve high CO₂ permeances up to ~ 2000 GPU [15,20-23], but they have shown low CO₂/N₂ selectivities (usually below 30 at 57ºC) governed by the Robeson upper bound [24,25].
On the other hand, facilitated transport membranes can provide a high CO$_2$ permeance while maintaining a high CO$_2$/N$_2$ selectivity. In the facilitated transport membranes, there is a reversible reaction between CO$_2$ and a reactive carrier which usually contains an amino group. Fixed-site carriers (amine-containing polymers) and mobile carriers (amine-containing small molecules) are two major categories of carriers for CO$_2$ transport in facilitated transport membranes. The fixed-site carriers such as polyallylamine [26-30], polyethylenimine [26,31] and polyvinylamine (PVAm) [32-35] have been reported in the literature. The common mobile carriers that have been reported in the literature include ethylenediamine [35-37], aminoacid salts [38,39], and alkanolamines [40,41]. In the facilitated transport membranes, CO$_2$ molecules react with amine carriers first, and then the reaction products transport across the membrane, releasing the CO$_2$ molecules to the permeate side of the membrane. By this mechanism, the solubility of CO$_2$ molecules in the membrane is greatly enhanced. On the other hand, the non-reactive N$_2$ molecules transport through the membrane only by the solution-diffusion mechanism. Therefore, CO$_2$ transport gets facilitated, and a high CO$_2$/N$_2$ selectivity can be achieved through the facilitated transport mechanism.

Inorganic membranes for CO$_2$/N$_2$ separation are microporous and have a different transport mechanism compared to solution-diffusion membranes. The CO$_2$/N$_2$ separation from microporous inorganic membranes depends on both molecular sieving and surface diffusion. The similar kinetic diameter of CO$_2$ (3.3 Å) and N$_2$ (3.64 Å) molecules indicates that achieving a CO$_2$ rich permeate by the simple molecular sieving is not very effective. Surface diffusion, particularly in combination with the molecular sieving, then
becomes a main factor for the separation. In microporous inorganics such as zeolite Y (with a pore size of 7.4 Å and a Si/Al ratio of 1.5 – 3.8), CO$_2$ favorably adsorbs and diffuses along the surface wall, providing a high CO$_2$ permeance as well as a high CO$_2$/N$_2$ selectivity in combination with the molecular sieving. The performances of such membranes approach or cross the upper bound set by polymer membranes. Recent literatures have shown that zeolite membranes on an inorganic substrate, such as alumina, showed a CO$_2$ permeance of around 2000 – 3500 GPU and a CO$_2$/N$_2$ selectivity of around 30 – 500 at room temperature [42-45]. Although these inorganic membranes have shown higher separation performances compared to polymer membranes, it is very difficult to fabricate defect-free inorganic layers reproducibly. Besides, due to the fact that the inorganic substrates are thick, brittle, expensive and not amendable to continuous fabrication, the scale-up of inorganic membranes is complicated and costly.

In this research, EO- and amine-containing polymer membranes were synthesized and studied. EO-containing polymer membranes based on the solution-diffusion mechanism were synthesized on top of zeolite layer to form composite membranes, which will be discussed in Chapter 2. Amine-containing polymer membranes based on the facilitated transport mechanism were also synthesized on top of zeolite layers, which will be discussed in Chapter 3. To reduce the cost of the membrane, high-molecular-weight polyamine membranes were synthesized on bare polymer substrates instead of inorganic layers, which will be discussed in Chapter 4. In Chapter 5, pilot-scale flat-sheet membrane and module testing of aforementioned membranes will be discussed.
1.2. Hydroxide-exchange membranes for fuel cell application

Fuel cells have a great potential to reduce the world’s dependence on petroleum for energy use. A fuel cell is an electrochemical cell that converts chemical energy from a fuel into electric power. Electricity is generated from the reaction between a fuel (such as hydrogen, methanol, and ethanol) at the anode and an oxidizing agent (such as oxygen) at the cathode. It is very clean and has a higher efficiency compared to conventional batteries. Fuel cells have several types, including proton-exchange membrane (PEM) fuel cells, alkaline fuel cells, direct methanol fuel cells, and so on.

Among all the types of fuel cells, the most widely used one is a PEM fuel cell. PEM has reasonable power and energy density in fuel cell applications such as vehicle propulsion, portable electronics, and auxiliary power applications. Figure 1.2(a) shows a typical structure of a PEM fuel cell. The PEM in the cell acts as the electrolyte which separates the anode and the cathode, and transfers protons from the anode to the cathode during the process. In the overall process, hydrogen from the anode and oxygen from the cathode react electrochemically and convert into water and heat. PEM fuel cell has a high efficiency but has a high cost because it uses the noble metal Pt as the catalyst.

There has been an increasing interest in developing hydroxide-exchange membranes (HEMs) for fuel cell applications because it enables non-precious metals as catalysts, such as silver or iron phthalocyanines for the cathode and nickel for the anode. Figure 1.2(b) shows a typical structure of a HEM fuel cell. The HEM separates the fuel...
(hydrogen) and oxygen, and transfers hydroxyl ions from the cathode to the anode. The whole fuel cell works in an alkaline environment.

Up to date, the most commonly used HEMs are quaternary ammonium-based polymers [46-49]. However, these polymer membranes appeared to be unstable in alkaline environment, especially at high temperature. Besides, currently available quaternary ammonium-based HEMs were found to have low hydroxyl ion conductivity. To overcome these limitations, ionic liquids were incorporated to stable polymer matrixes including polybenzimidazole (PBI) and crosslinked polyvinylalcohol (PVA) to form HEMs in this research, which will be discussed in Chapter 6.
Figure 1.1. Schematic of CO$_2$/N$_2$ transport mechanisms through polymer and inorganic membranes.
Figure 1.2. Schematic of (a) PEM fuel cell and (b) HEM fuel cell.
Nomenclature

\( J \)  
gas flux

\( J_{CO_2} \)  
flux of CO₂

\( l \)  
membrane thickness

\( P_{CO_2} \)  
permeability of CO₂

\( P_{N_2} \)  
permeability of N₂

\( p \)  
pressure

\( p_f \)  
pressure on the feed side of the membrane

\( p_p \)  
pressure on the permeate side of the membrane

\( p_{f_{CO_2}} \)  
CO₂ partial pressure on the feed side of the membrane

\( p_{p_{CO_2}} \)  
CO₂ partial pressure on the permeate side of the membrane

Greek letters

\( \alpha \)  
selectivity

\( \alpha_{CO_2/N_2} \)  
selectivity of CO₂ over N₂
Chapter 2 : EO-Containing Polymer/Inorganic Composite Membranes for CO₂ Separation from Flue Gas

2.1. Summary

In this chapter, EO-containing polymer/zeolite Y composite membrane with three layers on top of the polyethersulfone (PES) substrate was designed and successfully synthesized for CO₂ capture from flue gas. The three layers were the zeolite Y inorganic layer, selective Pebax® layer, and polydimethylsiloxane (PDMS) cover layer, respectively, from bottom to top. Zeolite Y with a particle size of about 40 nm was synthesized and deposited onto the PES substrate. On top of the zeolite Y layer, a selective polymer layer was deposited with the blend solution of Pebax® and ethylene oxide (EO)-containing small molecules. A PDMS cover layer was applied on top of the Pebax® layer for defect abatement. The composite membrane showed a better CO₂/N₂ separation performance compared to the membrane without the zeolite Y layer, which was due to two reasons. First, the hydrophilic zeolite Y layer improved the adhesion between the Pebax® polymer layer and the substrate, which allowed for the preparation of much thinner and defect-free membranes. Second, the zeolite Y layer had a smaller
interparticle pore size than the PES substrate and thus minimized the penetration of polymer solution into the pores, which reduced the mass transfer resistance of CO$_2$ molecules through the membrane. The effects of different Pebax® blend compositions and various coating conditions on the membrane separation performance were also investigated. The resulting Pebax®/zeolite Y composite membrane exhibited a CO$_2$ permeance up to 940 GPU and a CO$_2$/N$_2$ mixed gas selectivity of 30 at 57°C, indicating promising potential for CO$_2$ capture from flue gas.

2.2. Introduction

Polymer membranes and inorganic membranes are two major categories of CO$_2$ separation membranes. Gas transport through most of the polymer membranes follows the solution-diffusion mechanism, which is based on both the solubility of gases in the membrane and the diffusivity of gases through the membrane. Most of the recent work on the polymeric solution-diffusion membranes has focused on copolymers which generally have a hard (glassy) polymer segment such as polyamide (PA) or polyester and a soft (rubbery) polymer segment such as polyethyleneoxide (PEO) [18]. The hard segment provides the mechanical strength to the membrane, while the soft segment interacts with CO$_2$ molecules for enhanced transport. Solution-diffusion polymer membranes usually suffer from a trade-off between permeability and selectivity, which can be represented by the Robeson upper bound for the membrane performance [24-25]. Recent work has shown that solution-diffusion polymer membranes such as the Polaris™
membrane from Membrane Technology and Research, Inc. (USA) and the ultra-thin Polyactive® membrane from GKSS Research Centre Geesthacht GmbH (Germany) have the potential to achieve high CO₂ permeances (1000 – 2000 GPU) [15,20-23], but the selectivity was limited by the Robeson upper bound, which was usually below 30 at 57°C (flue gas temperature).

Pebax® 1657 copolymer contains 60 wt.% PEO and 40 wt.% polyamide 6 (PA6), the structure of which is shown in Figure 2.1. In this copolymer structure, PEO acts as the soft segment and provides the CO₂-philic property, while PA serves as the hard segment and provides the film-forming ability and mechanical strength to the membrane. Yave et al. reported that Pebax® 1657 had a CO₂ permeability of around 175 Barrers and a CO₂/N₂ selectivity of 32 at 50°C [22]. Although researchers did a lot of work on Pebax® membranes, they usually reported CO₂ permeabilities for thick membranes (more than 2 µm) [50-59], while very few reported high CO₂ permeances for thin membranes (< 2 µm). Car et al. reported that a Pebax®/PEG blend composite membrane of less than 2 µm showed a CO₂ permeability of 122 Barrers at 30°C [60]. Liu et al. reported a CO₂ permeance of around 350 GPU and a CO₂/N₂ selectivity of 35 for a thin Pebax® 2533 membrane with a thickness of 0.7 µm at 25°C [61,62].

In this Chapter, a Pebax®/zeolite Y composite membrane with three layers was synthesized for CO₂/N₂ separation, the structure of which is shown in Figure 2.2. Zeolite Y with a particle size of about 40 nm was synthesized and successfully deposited onto the PES substrate. A thin Pebax® layer was then coated on top of the zeolite Y layer. The inorganic zeolite Y layer not only improved the adhesion between the polymer layer and
the substrate, but also had a smaller pore size than the PES substrate, which could improve the CO₂ permeance by reducing the penetration of the polymer solution into the pores underneath. A PDMS cover layer was coated on top to cover any possible defects of the thin Pebax® layer. The resultant composite membrane had a Pebax® layer thickness of less than 500 nm, showing a high CO₂ permeance (~940 GPU) while maintaining a good CO₂/N₂ selectivity (~30) at 57°C.

2.3. Experimental

2.3.1. Materials

Poly(ethylene glycol) with an average molecular weight of 200 (PEG200), poly(ethylene glycol) dimethyl ether with an average molecular weight of 500 (PEG-DME500), heptane (99%) and isopropanol (IPA, 99.9%) were purchased from Sigma-Aldrich. Ethanol (99.5%) was purchased from Fisher Scientific. Pebax® 1657 was kindly donated by Arkema Inc. (King of Prussia, PA). PDMS with a trade name of Dehesive® 944 and its corresponding crosslinker (Wacker® Crosslinker V24) and catalyst (Wacker® Catalyst OL) were kindly provided by Wacker Silicones, Inc. (Adrian, MI). All the chemicals were used as received without further purification. Nano zeolite Y with a 40 nm average diameter was provided by Dr. Prabir Dutta’s group in the Chemistry Department. The zeolite Y was synthesized in their group using a method reported in the literature [63,64].
Biomax PES ultrafiltration membrane substrate with a molecular weight cut-off of 300 kDa (PES300, flat sheet substrate with a ~ 100 µm PES layer on top of a ~ 200 µm non-woven fabric) was purchased from EMD Millipore (Billerica, MA). The average pore size of the PES substrate was around 72 nm and the porosity was around 15%. 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.

2.3.2. Membrane preparation

The polymer/zeolite Y (ZY) composite membrane was synthesized by following three steps to form the structure with three layers (Figure 2.3). Zeolite Y was first deposited onto the PES300 substrate using a vacuum-assisted dip deposition method [65,66]. Basically, the zeolite Y dispersion in water was dip deposited onto the PES substrate with the help of a vacuum applied on the backside of the PES substrate. The substrate with the zeolite Y layer was then kept in a humidity chamber with a relative humidity of ~ 60% to prevent the zeolite Y layer from forming cracks before the coating of the Pebax® layer.

The Pebax® layer was prepared with a Pebax® blend solution consisting of ethylene oxide (EO)-containing small molecules using a spin-coating method. Pebax® 1657 was first dissolved in a 70/30 (weight ratio) ethanol/water mixture solvent to form a 3 wt.% solution with stirring under reflux at 80°C for overnight. Then, PEG200 or PEG-DME500 at a predetermined amount was incorporated into the solution. The weight ratio of Pebax®/PEG200 was 50/50, and the weight ratio of Pebax®/PEG-DME500 was 25/75.
After that, an additional amount of 70/30 ethanol/water solvent was added to form a solution with a total solid concentration of 2 wt.%. The solution was stirred at room temperature for 1 hour. Finally, the solution was spin-coated onto the zeolite Y layer on top of the PES substrate using a WS-650 spin-coater (Laurell Technologies, North Wales, PA). The spinning speed for coating the Pebax® layer was kept at 3000 rpm for 1 minute.

After the coating of the Pebax® layer, the membrane was placed in a hood at ambient temperature for around 6 hours to allow all the solvent to evaporate. Then, a PDMS cover layer was coated on top to cover any defects of the selective Pebax® layer. The PDMS solution with a concentration of 1.5 wt.% (in heptane solvent, PDMS/crosslinker/catalyst weight ratio of 100/1/0.5) was spin-coated on top of the selective layer. The spinning speed for PDMS coating was kept at 6000 rpm for 1 minute. After the coating, the membrane was kept in a hood for 2 h and then kept in an oven at 100°C for 0.5 h to evaporate the solvent and to complete the crosslinking of PDMS.

2.3.3. Gas transport performance measurements

Gas transport performance measurements were conducted by using a gas permeation apparatus described in a previous paper [27]. The synthesized composite membrane with an effective membrane area of 3.4 cm² was loaded into a small rectangular permeation cell. A countercurrent flow configuration was applied to offer the maximum driving force across the membrane. A binary gas mixture containing 20% CO₂ and 80% N₂ on dry basis was used as the feed gas. The flow rate of the dry feed gas was 60 cc/min, and
the pressure on the feed side was kept at 1.5 psig. The flow rate of the argon sweep gas was 30 cc/min, and the sweep pressure was kept at 1.2 psig. The cell was loaded inside a temperature-controlled oven (Bemco Inc. Simi Valley, CA) and the testing temperature was kept at 57°C, which was the average flue gas temperature. After leaving the gas permeation cell, the gas compositions of both retentate and permeate gas streams were analyzed by a gas chromatograph (GC) equipped with thermal conductivity detectors (TCDs) (Agilent Technologies, Palo Alto, CA). The GC column used was the SUPELCO Carboxen® 1004 micropacked type (Sigma-Aldrich, St. Louis, MO). The test was conducted under the dry condition, and no water was introduced to the system. Based on the transport measurement, CO₂ permeance and CO₂/N₂ selectivity were calculated to characterize the membrane transport performance.

The effect of water vapor on the membrane transport performance was also investigated. For the test with the existence of water, all the other testing conditions were the same, except that 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 the saturation water content of 17% at 57°C.

2.3.4. Characterization of membrane properties

The surface hydrophilicity of the bare PES300 substrate and the zeolite Y/PES300 support was evaluated by contact angle measurements using the sessile drop technique
with deionized water as the reference liquid. About 1 µL deionized water droplet was deposited onto the leveled membrane surface to measure the contact angle of each sample.

The cross-section and surface morphology of the synthesized membranes were observed by scanning electron microscope (SEM) using FEI Nova NanoSEM400 (FEI Company, Hillsboro, OR).

2.4. Results and discussion

2.4.1. Membrane morphology via SEM

The SEM image in Figure 2.4 shows the cross-section of the composite membrane synthesized in this work. As can be seen, the composite membrane with three layers was successfully synthesized. The three layers on top of the porous PES substrate were the nano zeolite Y layer, selective Pebax® layer and PDMS cover layer, from bottom to top. Zeolite Y particles were observed to be packed closely on top of the PES substrate, forming a much smaller pore size compared to the porous PES substrate. The thickness of the zeolite Y layer was around 300 nm. On top of the zeolite Y layer, the dense Pebax® layer showed a thickness of around 400 nm. The top-most layer of the composite membrane was the PDMS cover layer, which showed a thickness of around 100 nm. Such a composite membrane showed a CO₂ permeance of 940 GPU and a CO₂/N₂ selectivity of 30 at 57°C from the transport performance measurement.
2.4.2. Effect of Pebax® blend composition on membrane separation performance

To improve the performance of Pebax® membranes, Yave et al. incorporated different 
EO-containing small molecules including PEG200 and PEG-DME500 into the Pebax® 
solution [22,50,60]. With up to 50 wt.% of PEG200 or PEG-DME500 in the 
composition, a much higher permeability was obtained compared to the pure Pebax® 
membrane. The CO₂ permeability for a 50/50 ratio of Pebax®/PEG-DME500 membrane 
was reported to be around 850 Barrers, with a CO₂/N₂ selectivity of 30 at 50°C.

In this work, both PEG200 and PEG-DME500 were used as the EO-containing small 
molecules for blending into the Pebax® solution. It was found that higher CO₂ 
permeance could be obtained with increasing the amount of EO-containing small 
molecules in the membrane composition. However, when the PEG200 or PEG-DME500 
content was too high, there was a significant reduction on the CO₂/N₂ selectivity of the 
membrane. This could be caused by the fact that the polymer blend matrix was not stable 
with such a high content of small molecules. The maximum content of EO-containing 
small molecules in the blend solution was found to be 50 wt.% for PEG200 and 75 wt.% 
for PEG-DME500. Beyond these two values, the membranes showed a poor selectivity 
even with a PDMS cover layer due to the weak polymer blend matrix. It could be clearly 
shown in Table 2.1 that by incorporating PEG200 or PEG-DME500, the CO₂ permeance 
was much higher compared to the pure Pebax® membrane. This could be explained by 
two reasons. First, PEG200 or PEG-DME500 introduced more polar EO groups, which 
could enhance the solubility of CO₂ molecules into the membrane. Second, small
molecules introduced more free volume and improved the flexibility of the polymer chains, which further enhanced the diffusivity of CO$_2$ molecules through the membrane. Based on the solution-diffusion mechanism, higher CO$_2$ permeance could be obtained with both larger solubility and diffusivity.

Another comparison could be made between PEG200 and PEG-DME500. From Table 2.1 (Samples 2 and 3), it could be seen that with the same amount (50 wt.%) of small molecules, the membrane with PEG200 showed a higher CO$_2$/N$_2$ selectivity, while the membrane with PEG-DME500 showed a higher CO$_2$ permeance. This could be explained by the different structures of PEG200 and PEG-DME500. It can be seen from Figure 2.1 that the PEG-DME500 molecule has two methyl end groups, which could introduce more free volume compared to PEG200 and further improve the CO$_2$ permeance. On the other hand, there were more EO groups in the Pebax$^\text{®}$/PEG200 blend due to the lower molecular weight of PEG200, which provided more affinity to CO$_2$ molecules, resulting in a higher CO$_2$/N$_2$ selectivity.

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

The key to prepare a selective Pebax$^\text{®}$ layer with a high CO$_2$ permeance is to make it as thin as possible, due to the fact that the permeance is inversely proportional to the selective layer thickness. However, if the membrane is too thin, there will be defects in the selective layer, which could dramatically reduce the CO$_2$/N$_2$ selectivity. In this study, the zeolite Y layer played a big role to allow for the preparation of much thinner
membranes due to its good adhesion with the Pebax® layer. Table 2.2 (Samples 2, 5, 4 and 6) and Figure 2.5 show the comparison of the membrane separation performance with and without the zeolite Y layer. It could be seen that for thin (~ 400 nm) Pebax® layers, membranes without the zeolite Y layer showed a much lower CO₂/N₂ selectivity, indicating that there were defects in the membrane which could not be covered even with a PDMS cover layer. However, with the help of the zeolite Y layer, the membrane showed a relatively good CO₂/N₂ selectivity. This could be due to the fact that the zeolite Y layer was more hydrophilic than the PES substrate, which improved the adhesion with the Pebax® layer. This could be further proved by the contact angle measurement of the bare PES substrate and the zeolite Y/PES substrate. The contact angle of a water droplet on bare PES substrate was measured to be around 30°, while with a zeolite Y layer, it reduced to only 3°. The much lower contact angle indicated a higher hydrophilicity with the help of the zeolite Y layer, which could further improve the adhesion between the Pebax® layer and the substrate.

Thicker and defect-free composite membranes were also prepared to compare the transport performances with and without the zeolite Y layer. Table 2.2 (Samples 7 to 10) and Figure 2.6 show that the composite membranes with the zeolite Y layer exhibited a higher CO₂ permeance compared to the membranes without the zeolite Y layer. This could be explained by the fact that the zeolite Y layer had a smaller interparticle pore size than the PES substrate, which reduced the penetration of the Pebax® solution into the pores underneath. Therefore, the mass transfer resistance was further reduced, leading to a higher CO₂ permeance. Figure 2.7 shows the surface morphology of the bare PES
substrate (a) and the zeolite Y layer/PES substrate (b). According to the image analysis, 
the average pore size of the porous PES substrate was 72 nm, while the zeolite Y layer 
had an interparticle pore size of only around 10 nm. The smaller pore size was the key to 
reduce the penetration, therefore a higher CO$_2$ permeance was observed from the 
membranes with the zeolite Y layer.

2.4.4. Influence of PDMS cover layer on membrane performance

Even though the zeolite Y layer can improve the adhesion between the Pebax$^\text{®}$ layer 
and the substrate, there will still be some defects existing on the Pebax$^\text{®}$ layer if it is too 
thin. To prevent the pin-hole defects in the thin polymer layer, a PDMS cover layer was 
applied on top of the composite membrane. PDMS is a low-cost polymer with good 
flexibility, non-toxicity and good resistance to heat or moisture. Besides, it is among the 
most gas permeable materials available for use as the caulking layer [67]. According to 
literature, PDMS has a CO$_2$ permeability of 3800 Barrers at 35°C [68]. All of these 
advantages make PDMS a good choice to develop a protective coating layer on top of 
membranes. In this work, the PDMS solution was spin-coated on top of the selective 
Pebax$^\text{®}$ layer to make a thin layer with a thickness of around 100 nm.

Figure 2.8 shows the transport performance of composite membranes with and 
without the PDMS cover layer. All the membrane preparation conditions for the Pebax$^\text{®}$ 
layer were the same (2 wt.% solution and 3000 rpm spinning speed). It could be clearly 
seen that without the PDMS layer, the CO$_2$/N$_2$ selectivities of the membranes were
dramatically lower, which indicated that there were defects existing in the selective Pebax® layer. After the PDMS cover layer was applied, pin-hole defects were covered, which helped maintaining a good CO₂/N₂ selectivity of the composite membrane.

2.4.5. Effects of Pebax® layer coating conditions on membrane separation performance

In this study, different membrane preparation conditions for the Pebax® layer including the spinning speed and the Pebax® blend solution concentration were investigated. These two factors played a big role on controlling the thickness of the selective Pebax® layer. Basically, a higher spinning speed or lower casting solution concentration will lead to a thinner selective layer, which provides a higher CO₂ permeance. However, if the membrane is too thin, the membrane will leak due to defects, which will lead to a very low CO₂/N₂ selectivity.

From Figure 2.9, it could be seen that the composite membrane with a Pebax®/PEG-DME500 layer showed a higher CO₂ permeance with a higher spinning speed. However, when the spinning speed was higher than 3000 rpm, there was an obvious decline on the CO₂/N₂ selectivity. This meant that the membrane was too thin and no longer defect-free. Even with a PDMS cover layer, those defects could not be covered completely. The composite membrane with a Pebax®/PEG200 layer showed a similar trend (Figure 2.10).

Similarly, it was indicated from Figure 2.11 and Figure 2.12 for Pebax®/PEG-DME500 25/75 and Pebax®/PEG200 50/50 membranes, respectively, the CO₂ permeance
increased with a lower total solid concentration of the casting solution due to a thinner membrane thickness. However, when the solution concentration was below 2 wt.%, the CO$_2$/N$_2$ selectivity decreased dramatically, indicating that there were too many defects in the selective Pebax$^\text{®}$ layer which could not be covered by the PDMS layer.

2.4.6. Effect of water vapor on membrane separation performance

Researchers have done some investigation regarding the water vapor effect on the Pebax membrane separation performance. Lokhandwala and Baker [69] showed that the CO$_2$ flux was reduced by 40 – 45 % in the presence of water vapor for natural gas treatment. However, an encouraging study done by Reijerkerk [70] showed that the CO$_2$ permeability only dropped by 5 – 10 % at 50°C with a H$_2$O/CO$_2$/N$_2$ ternary mixed gas compared to the dry CO$_2$/N$_2$ binary mixed gas. This indicates that at the low feed pressures (and thus low partial pressures of CO$_2$) in flue gas, the CO$_2$ transport performance would not be affected too much by water.

In this work, effect of water vapor on membrane separation performance was also investigated. Table 2.3 shows the comparison of membrane performance with and without water vapor. The same piece of membrane was tested under both dry and wet conditions. It was indicated that with 17 % water vapor, the CO$_2$ permeance dropped by only 5 %. This is different from the behavior generally observed for PEO-containing polymers at high CO$_2$ partial pressures such as for the natural gas. Since the Pebax
membrane in this work was mainly for CO$_2$ separation from flue gas, which was operated at a low CO$_2$ partial pressure, the CO$_2$ transport was not reduced a lot by water vapor.

2.4.7. Stability of Pebax®/zeolite Y composite membrane

Figure 2.13 shows the 24 h stability test of the Pebax®/zeolite Y composite membrane with an average CO$_2$ permeance of 940 GPU and a CO$_2$/N$_2$ selectivity of 30. It could be seen that the membrane performance was stable within 24 h. No sign of dropping was observed for either CO$_2$ permeance or CO$_2$/N$_2$ selectivity. Regarding the fact that there is no component in the composite membrane which is sensitive to SO$_2$, it can be deducted that the Pebax®/zeolite Y composite membrane would be suitable for the application of CO$_2$ separation and capture from flue gas [71].

2.4.8. Synthesis of other alternative polymer materials

Other polymer materials including polyimide-PEO copolymer and polyurethane-PEO copolymer were also synthesized as alternatives to Pebax®. The aim was to obtain polymers with very high molecular weight, and reduce the thickness of the membrane for achieving higher CO$_2$ permeance. The structures of these two polymers are shown in Figure 2.14.

Both polymers had the similar structure to the Pebax® structure. In the two polymer structures, the PEO acted as the soft segment, while polyimide or polyurethane served as
the hard segment. The polyimide-PEO copolymer was synthesized by two steps: end-capping and chain-extension [72,73]. During the end-capping reaction, two molecules of pyromellitic dianhydride (PMDA) reacted with one molecule of poly(ethylene glycol) (PEG) diol. In the chain-extension step, 4,4’-Methylenedianiline (MDA) was used as the chain-extender to extend the length of the polymer chain. The polyurethane-PEO copolymer was synthesized by following the similar procedure [74,75], except that during the end-capping step, methylene diphenylisocyanate (MDI) instead of dianhydride reacted with PEG diol. 4,4’-Methylene-bis(2-chloroaniline) (MOCA) was used as the chain-extender during the chain-extension step. Although these two copolymers were synthesized, the viscosity of the polymer solution was low, which means thin membranes could not be obtained. The transport measurement of the membranes prepared by these two copolymers was beyond the scope of this research. For future work, it will be promising if copolymers with high molecular weights can be synthesized. This can help obtaining a solution with a high viscosity at a low concentration, which can allow for the preparation of much thinner membranes with higher CO$_2$ permeance.

2.5. Conclusions

A new Pebax$^\text{®}$ 1657/zeolite Y composite membrane was successfully synthesized. With the help of a nano zeolite Y layer on top of the PES substrate, the adhesion between the Pebax$^\text{®}$ 1657 layer and the substrate was improved, which was confirmed by the fact that the contact angle of the substrate reduced from 30° (bare PES) to 3° (zeolite Y
layer/PES). This better adhesion could allow for the preparation of much thinner membranes, which provided a higher CO₂ permeance while maintaining a good CO₂/N₂ selectivity. Moreover, the zeolite Y layer showed a smaller interparticle pore size (~10 nm) compared to the pore size of the bare PES substrate (~72 nm). This smaller pore size reduced the penetration of the Pebax® 1657 solution into the pores underneath, which could further reduce the mass transfer resistance, leading to a higher CO₂ permeance. PDMS was proved to be effective for covering the defects of the thin Pebax® 1657 layer, which could help maintaining a good CO₂/N₂ selectivity of the composite membrane.

The membrane preparation conditions such as the spinning speed of the spin-coating, solution concentration and composition of the Pebax® 1657 blend with EO-containing small molecules, were also studied and optimized. Finally, the resulting composite membrane with a thin Pebax® layer (less than 500 nm) showed a CO₂ permeance of 940 GPU and a CO₂/N₂ selectivity of 30 at 57°C, which was stable for 24 h.
Table 2.1. Composite membrane performances with different Pebax® layer compositions.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Selective Layer Composition*</th>
<th>CO₂ Permeance (GPU)</th>
<th>CO₂/N₂ Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pebax®</td>
<td>342</td>
<td>32</td>
</tr>
<tr>
<td>2</td>
<td>Pebax®/PEG200 50/50</td>
<td>795</td>
<td>35</td>
</tr>
<tr>
<td>3</td>
<td>Pebax®/PEG-DME500 50/50</td>
<td>839</td>
<td>31</td>
</tr>
<tr>
<td>4</td>
<td>Pebax®/PEG-DME500 25/75</td>
<td>940</td>
<td>30</td>
</tr>
</tbody>
</table>

*Pebax® layer coating conditions: 2 wt.% solution and 3000 rpm spinning speed.
Table 2.2. Comparison of performances of composite membranes with and without the zeolite Y layer.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Pebax® Layer Composition</th>
<th>Zeolite Y Layer (with/without)</th>
<th>CO₂ Permeance (GPU)</th>
<th>CO₂/N₂ Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Pebax®/PEG200 50/50 ≤1 ≤</td>
<td>w</td>
<td>795</td>
<td>35</td>
</tr>
<tr>
<td>5</td>
<td>Pebax®/PEG200 50/50 ≤1 ≤</td>
<td>o</td>
<td>1420</td>
<td>10</td>
</tr>
<tr>
<td>4</td>
<td>Pebax®/PEG-DME500 25/75 ≤1 ≤</td>
<td>w</td>
<td>940</td>
<td>30</td>
</tr>
<tr>
<td>6</td>
<td>Pebax®/PEG-DME500 25/75 ≤1 ≤</td>
<td>o</td>
<td>1615</td>
<td>8</td>
</tr>
<tr>
<td>7</td>
<td>Pebax®/PEG200 50/50 ≤2 ≤</td>
<td>w</td>
<td>610</td>
<td>38</td>
</tr>
<tr>
<td>8</td>
<td>Pebax®/PEG200 50/50 ≤2 ≤</td>
<td>o</td>
<td>527</td>
<td>37</td>
</tr>
<tr>
<td>9</td>
<td>Pebax®/PEG-DME500 25/75 ≤2 ≤</td>
<td>w</td>
<td>754</td>
<td>30</td>
</tr>
<tr>
<td>10</td>
<td>Pebax®/PEG-DME500 25/75 ≤2 ≤</td>
<td>o</td>
<td>661</td>
<td>30</td>
</tr>
</tbody>
</table>

1 Pebax® layer coating conditions: 2 wt.% solution and 3000 rpm; Pebax® layer thickness: ~ 400 nm.

2 Pebax® layer coating conditions: 2.5 wt.% solution and 3000 rpm; Pebax® layer thickness: ~ 500 nm.
Table 2.3. Comparison of performances of composite membranes with and without water vapor.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Testing Condition (Dry/Wet)</th>
<th>Water Content in both Feed and Sweep Gas</th>
<th>CO₂ Permeance (GPU)</th>
<th>CO₂/N₂ Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>11 dry</td>
<td></td>
<td>0 %</td>
<td>912</td>
<td>29</td>
</tr>
<tr>
<td>11 wet</td>
<td></td>
<td>17 %</td>
<td>867</td>
<td>30</td>
</tr>
</tbody>
</table>

Pebax® layer composition: Pebax®/PEG-DME500 25/75; Pebax® layer coating conditions: 2 wt.% solution and 3000 rpm.
Figure 2.1. Chemical structures of Pebax® 1657, PEG and PEG-DME.
Figure 2.2. Schematic of Pebax®/zeolite Y composite membrane structure.
Figure 2.3. Schematic of the preparation procedure of the Pebax®/zeolite Y composite membrane.
Figure 2.4. SEM image of the cross-section morphology of the composite membrane:
(A) zeolite Y layer, (B) Pebax® layer and (C) PDMS cover layer.
Figure 2.5. Comparison of CO$_2$/N$_2$ selectivities and substrate contact angles with and without the zeolite Y layer (Pebax® layer thickness: ~ 400 nm; compositions: Pebax®/PEG200 50/50 or Pebax®/PEG-DME500 25/75 and coating conditions: 2 wt.% solution and 3000 rpm spinning speed).
Figure 2.6. Comparison of membrane performances with and without the zeolite Y layer (Pebax® layer thickness: ~ 500 nm; compositions: Pebax®/PEG200 50/50 or Pebax®/PEG-DME500 25/75 and coating conditions: 2.5 wt.% solution and 3000 rpm spinning speed).
Figure 2.7. SEM images of the surface morphology of (a) bare PES substrate and (b) zeolite Y layer/PES substrate.
Figure 2.8. Comparison of membrane performances with and without the PDMS cover layer (Pebax® layer compositions: Pebax®/PEG200 50/50 or Pebax®/PEG-DME500 25/75 and coating conditions: 2 wt.% solution and 3000 rpm spinning speed).
Figure 2.9. Effects of Pebax® layer spinning speed on the CO₂ permeance and CO₂/N₂ selectivity of the composite membrane (Pebax® layer composition: Pebax®/PEG-DME500 25/75; total solid concentration: 2 wt.%).
Figure 2.10. Effects of Pebax® layer spinning speed on the CO₂ permeance and CO₂/N₂ selectivity of the composite membrane (Pebax® layer composition: Pebax®/PEG200 50/50; total solid concentration: 2 wt.%).
Figure 2.11. Effects of Pebax®/PEG-DME500 (25/75) blend solution concentration on the CO$_2$ permeance and CO$_2$/N$_2$ selectivity of the composite membrane (spinning speed: 3000 rpm).
Figure 2.12. Effects of Pebax®/PEG200 (50/50) blend solution concentration on the CO$_2$ permeance and CO$_2$/N$_2$ selectivity of the composite membrane (spinning speed: 3000 rpm).
Figure 2.13. Membrane performance during the 24 h stability test at 57°C (Pebax® layer composition: Pebax®/PEG-DME500 25/75 and coating conditions: 2 wt.% solution and 3000 rpm spinning speed).
Figure 2.14. Chemical structures of polyimide-PEO copolymer and polyurethane-PEO copolymer.
Chapter 3 : Amine-Containing Polymer/Inorganic Composite Membranes for CO$_2$ Separation from Flue Gas

3.1. Summary

In this chapter, amine-containing polymer/zeolite Y composite membranes were successfully synthesized for CO$_2$/N$_2$ separation from flue gas. The polyvinylamine (PVAm) with a high molecular weight was synthesized and used as the fixed-site carrier for CO$_2$ 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 CO$_2$/N$_2$ 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 CO$_2$ 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 CO\textsubscript{2} permeance up to ~1100 GPU and a CO\textsubscript{2}/N\textsubscript{2} mixed gas selectivity of at least 200 at the typical flue gas temperature of 57°C. Based on this separation performance, a preliminary techno-economic analysis showed a capture cost of $37.5/tonne CO\textsubscript{2} captured (based on 2007 dollar) for a two-stage air-sweep membrane process, indicating that this membrane has great potential for reaching the U.S. Department of Energy (DOE) capture target of ≤ $40/tonne CO\textsubscript{2} captured.

3.2. Introduction

Although solution-diffusion membranes have been widely studied for CO\textsubscript{2} capture from flue gas, they usually showed a low CO\textsubscript{2}/N\textsubscript{2} selectivity due to the Robeson upper bound [24,25]. The current state-of-the-art Polaris\textsuperscript{TM} membranes from Membrane Technology and Research (MTR) Inc. for CO\textsubscript{2} capture from flue gas have shown high CO\textsubscript{2} permeances of more than 1000 GPU [15]. However, the CO\textsubscript{2}/N\textsubscript{2} selectivity was only around 20 – 50 at 30°C. At the typical temperature for flue gas stream (57°C), the CO\textsubscript{2}/N\textsubscript{2} selectivity of the Polaris\textsuperscript{TM} membrane will be even lower (less than 30). In Chapter 2, the Pebax\textsuperscript{®}/zeolite Y composite membranes showed a CO\textsubscript{2} permeance up to 940 GPU and a selectivity of up to 30 at 57°C. Based on this performance, especially due to the low CO\textsubscript{2}/N\textsubscript{2} selectivity, it could not meet the DOE target of ≤ $40/tonne CO\textsubscript{2} captured. Therefore, membranes with a much higher selectivity are required to reduce
the capture cost and to make membrane technology more competitive compared to other conventional technologies for the application of post-combustion carbon capture.

Facilitated transport membranes was a good choice because they can provide a much higher CO₂/N₂ selectivity (100 – 1500) due to the reversible reaction between CO₂ and the reactive amino group-containing carrier in the membrane [26-41,76,77]. In a facilitated transport membrane, CO₂ molecules react with the amine carrier first, and then diffuse through the membrane either as CO₂-mobile carrier reaction products or by hopping from one site of fixed-site carrier to another. At the permeate side of the membrane which has a lower CO₂ partial pressure, the CO₂ molecules can be released from the CO₂-carrier reaction products. On the other hand, N₂ molecules can only permeate through the membrane by the solution-diffusion mechanism. Consequently, a high CO₂/N₂ selectivity can be achieved by facilitated transport mechanism. The most common reactions between CO₂ and amine carriers are shown below.

\[
\begin{align*}
\text{CO}_2 + 2 \text{R-NH}_2 & \rightleftharpoons \text{R-NH}_3^+ + \text{R-NH-COO}^- \quad (3.1) \\
\text{CO}_2 + \text{R-NH}_2 + \text{H}_2\text{O} & \rightleftharpoons \text{R-NH}_3^+ + \text{HCO}_3^- \quad (3.2) \\
\text{CO}_2 + \text{CO}_3^{2-} + \text{H}_2\text{O} & \rightleftharpoons 2 \text{HCO}_3^- \quad (3.3)
\end{align*}
\]

As can be seen, water also plays a great role for the CO₂-amine reaction.

In this Chapter, an amine-containing polymer/zeolite Y composite membrane for CO₂/N₂ separation was designed and synthesized. First, zeolite Y with an average particle size of around 40 nm was deposited onto the PES substrate using a vacuum-assisted dip-coating method (similar to what was described in Chapter 2). For the polymer layer, PVAm with a high molecular weight was synthesized and acted as the
fixed-site 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. The thin amine selective layer had an average thickness of 100 – 200 nm. The transport of CO₂ through the amine selective layer is based on the facilitated transport mechanism.

3.3. Experimental

3.3.1. 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 ~ 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.
3.3.2. Synthesis of PVAm and amine-containing mobile carriers

PVAm was synthesized by following the procedure in the literature [35,78]. The synthesis route is shown in Figure 3.1. 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 prepared 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 Figure 3.2.

3.3.3. Membrane preparation

The amine-containing polymer/zeolite Y composite membranes were synthesized by following two steps. First, zeolite Y with a particle size of around 40 nm, which was synthesized by following the procedure in the literature [63,64], was deposited onto the PES300 substrate using a vacuum-assisted dip-coating method [65,66]. After that, 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.

3.3.4. Gas transport performance measurements

Gas transport performance measurements were conducted by using a permeation apparatus described in a previous paper [27]. 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 cm$^2$. 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% CO$_2$ and 80% N$_2$ 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, CO$_2$ permeance and CO$_2$/N$_2$ selectivity were calculated to characterize the membrane transport performance.

3.3.5. 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).

3.4. Results and discussion

3.4.1. PVAm synthesis

As the fixed-site carrier in the selective polymer layer, PVAm not only provides amino groups for CO\textsubscript{2}/N\textsubscript{2} 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 CO\textsubscript{2} permeance. Moreover, thinner membranes can be obtained from the solution with a low concentration and a high viscosity, which can lead to a higher CO\textsubscript{2} permeance.
Table 3.1 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.

3.4.2. Membrane morphology via SEM

The SEM image in Figure 3.3 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. Figure 3.4 shows the cross-section of another composite membrane with
a thicker amine layer. The thickness of the amine layer as shown in Figure 3.4 was around 350 nm.

3.4.3. Correlation between amine layer thickness and coating knife gap setting

As mentioned, the knife-coating method was used for the amine layer coating in this work. Amine layers with different thicknesses were obtained by using different gap settings of the coating knife. Figure 3.5 shows the linear correlation between the amine layer thickness and the gap setting of the coating knife. The dry amine layer thicknesses shown in Figure 3.5 were measured by SEM. The concentration of the amine-containing coating solution in this work was kept at around 10 wt.%. The empirical equation for the relationship between the wet coating thickness and the amine layer thickness was then obtained:

\[ l \times \rho_{\text{dry}} = 0.5 \times c \times \rho_{\text{solution}} \times l_{\text{gap}} \]  

(3.4)

where \( l \) (µm) is the dry amine-containing polymer layer thickness, \( \rho_{\text{dry}} \) (g/cm³) is the density of the dry amine-containing polymer layer, \( \rho_{\text{solution}} \) (g/cm³) is the density of the coating solution, \( c \) (by weight) is the total solid concentration of the amine coating solution, and \( l_{\text{gap}} \) (µm) is the gap setting of the coating knife. The amine layer thicknesses mentioned in this research were all calculated based on the correlation as shown in Equation 3.4, which agreed well with the SEM measurements, as shown in Figure 3.5.
3.4.4. Effects of mobile carrier amount on membrane separation performance

For the facilitated transport mechanism, the CO$_2$ transport of the fixed-site carrier is limited by the mobility of the CO$_2$-carrier reaction products. Therefore, the incorporation of mobile carriers becomes necessary to help enhancing the CO$_2$ transport. Figure 3.6 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 CO$_2$ permeance and CO$_2$/N$_2$ selectivity were observed to be lower without the mobile carriers in the membrane composition, which proved that the mobile carriers played a big role in improving the transport performance.

In this work, different amounts of mobile carriers (KG, LiG or PG) were incorporated into the PVAm solution to form the coating solution. From Figure 3.7 to Figure 3.9, it can be concluded that with either kind of the mobile carriers, a higher mobile carrier amount resulted in a higher CO$_2$ permeance, while the CO$_2$/N$_2$ 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 Figure 3.10, with 70 wt.% PG in the solid content of the amine-containing polymer layer, both the CO$_2$ permeance and the CO$_2$/N$_2$ selectivity showed a decreasing trend after the 6-h test. Besides, the CO$_2$/N$_2$ 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 12 h, which is shown in Figure 3.11.

3.4.5. 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. Figure 3.12 shows the comparison of the CO₂ permeances of the composite membranes with various kinds of the mobile carriers. As can be seen, 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
reaction products are higher. Due to these two reasons, a higher CO$_2$ permeance was obtained from the composite membrane with LiG as the mobile carrier than that with KG as the mobile carrier.

3.4.6. Influence of amine-layer thickness on membrane performance

A thinner selective layer can lead to a higher CO$_2$ 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. Figure 3.13 shows the trend of increasing CO$_2$ permeance with decreasing selective layer thickness. All the membranes shown in Figure 3.13 were prepared with the 65/35 PG/PVAm composition for the amine-containing polymer layer. The highest CO$_2$ permeance was around 1100 GPU, which was obtained from the composite membrane with an amine-containing polymer layer thickness of 100 nm.

Lower CO$_2$/N$_2$ selectivity was obtained from the membranes with an amine-containing polymer layer thickness of less than 100 nm. Figure 3.14 shows the CO$_2$ transport performances of the membranes with the amine-containing polymer layer thicknesses of 100 nm, 80 nm and 50 nm, respectively. It can be clearly seen that although the CO$_2$ permeance kept increasing with thinner amine layers, there was a significant decline of the CO$_2$/N$_2$ 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 CO$_2$/N$_2$ selectivity.

3.4.7. 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. Figure 3.15 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 CO$_2$ 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 in 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 Figure 3.15 exhibited a CO$_2$/N$_2$ selectivity in the range of 150 – 220. No obvious effect of the zeolite Y layer on the CO$_2$/N$_2$ selectivity was observed from this study.

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

Figure 3.16 showed the 24 h stability test of the amine-containing polymer/zeolite Y composite membrane. The membrane showed an average CO$_2$ permeance of 1100 GPU and a CO$_2$/N$_2$ 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 CO$_2$ permeance or CO$_2$/N$_2$ selectivity. The membrane stability in the presence of SO$_2$ and O$_2$ will be studied in the future.

3.5. 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 CO$_2$ permeance by minimizing the mass transfer resistance. However, this effect only applied for membranes with an amine-containing polymer layer thickness of $\geq$ 200 nm. When the membrane was thinner, this effect was opposite and the membrane without the zeolite Y layer had a higher CO$_2$ 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 CO$_2$ permeance of around 1100 GPU and a CO$_2$/N$_2$ selectivity of more than 200. Based on this separation performance, a techno-economic analysis showed a capture cost of $37.5/tonne CO$_2$ captured (based on 2007 dollar) for a two-stage air-sweep membrane process to achieve 90% CO$_2$ recovery and 95% purity of the CO$_2$ product, indicating that this membrane has great potential for reaching the DOE (U.S. Department of Energy) capture target of $\leq$ $40/tonne CO_2$ captured.
Nomenclature

\( c \) concentration of amine coating solution

\( l \) dry amine layer thickness

\( l_{gap} \) coating knife gap setting

\( \overline{M}_w \) weight average molecular weight

Greek letters

\( \rho \) density

\( \rho_{dry} \) density of the dry amine-containing polymer layer

\( \rho_{solution} \) density of coating solution
Table 3.1. Comparison of the PVAm synthesized in this work and Lupamin® 9095.

<table>
<thead>
<tr>
<th></th>
<th>Lupamin® 9095</th>
<th>Synthesized PVAm</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_w$</td>
<td>340,000</td>
<td>719,000</td>
</tr>
<tr>
<td>Viscosity of 3 wt.% polymer solution (cp)</td>
<td>50</td>
<td>486</td>
</tr>
<tr>
<td>Hydrolysis</td>
<td>Basic</td>
<td>Acidic</td>
</tr>
<tr>
<td>Byproduct</td>
<td>Sodium formate salts</td>
<td>None</td>
</tr>
</tbody>
</table>
Figure 3.1. Synthesis route of high-molecular-weight PVAm.
Fixed carrier:

Polyvinylamine (PVAm)

Mobile carriers (small aminoacid salts):

Potassium glycinate (KG)
Lithium glycinate (LiG)
Piperazine glycinate (PG)

Figure 3.2. Chemical structures of PVAm, KG, LiG and PG.
Figure 3.3. 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.
Figure 3.4. 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.
Figure 3.5. Correlation between the dry amine layer thickness and the coating knife gap setting (coating solution concentration: 10 wt.%).
Figure 3.6. Comparison of the composite membrane separation performances with and without mobile carriers (membrane thickness: ~ 100 nm).
Figure 3.7. Transport performances of membranes with different KG amounts in the total solid composition (membrane thickness: ~ 100 nm).
Figure 3.8. Transport performances of membranes with different LiG amounts in the total solid composition (membrane thickness: ~100 nm).
Figure 3.9. Transport performances of membranes with different PG amounts in the total solid composition (membrane thickness: ~ 100 nm).
Figure 3.10. Membrane stability with 70 wt.% PG in the total solid composition of the amine layer (membrane thickness: ~ 100 nm).
Figure 3.11. Membrane stability with 65 wt.% PG in the total solid composition of the amine layer (membrane thickness: ~ 100 nm).
Figure 3.12. Comparison of CO₂ permeances of the composite membranes with various kinds of mobile carriers (membrane thickness: ~ 100 nm).
Figure 3.13. Membrane transport performances with different amine layer thicknesses (membrane solid composition: 65/35 PG/PVAm).
Figure 3.14. Comparison of membrane transport performances with different amine layer thicknesses (less than 100 nm).
Figure 3.15. Influence of the zeolite Y layer on membrane transport performance (membrane solid composition: 65/35 PG/PVAm).
Figure 3.16. Membrane transport performances during 24 h stability test at 57°C (membrane solid composition: 65/35 PG/PVAm).
Chapter 4: High-Molecular-Weight Polyvinylamine/Piperazine Glycinate

Membranes on Bare Polymer Substrates for CO₂ Separation from Flue Gas

4.1. Summary

In this chapter, high-molecular-weight polyvinylamine (PVAm)/piperazine glycinate (PG) membranes were successfully synthesized for CO₂/N₂ separation from flue gas. PVAm samples with different molecular weights were synthesized through free radical polymerization by adjusting the monomer concentration and initiator amount. The obtained PVAm showed both a higher molecular weight and a higher solution viscosity than the commercially available PVAm (Lupamin® 9095, from BASF Corporation). The high viscosity of the PVAm solution at a low concentration allowed for the preparation of much thinner membranes. It could also help reducing penetration of the polymer solution into the pores of the substrate, and further minimizing the mass transfer resistance. Consequently, a high CO₂ permeance could be obtained from thin membranes with the thickness of 100 – 200 nm. In the membrane, PVAm acted as the fixed-site carrier for CO₂ facilitated transport whereas PG was incorporated into the PVAm polymer matrix and served as the mobile carrier. The PVAm/PG blend solution was coated onto different
substrates including polyethersulfone (PES) and polysulfone (PSf) substrates. Sodium dodecyl sulfate (SDS) surfactant was incorporated in the coating solution to improve the adhesion between the membrane layer and the substrate in some cases. The resultant PVAm/PG membranes exhibited a high CO₂ permeance of about 1100 GPU and a high CO₂/N₂ mixed gas selectivity of more than 140 at the typical flue gas temperature of 57°C along with 17% water vapor.

4.2. Introduction

In Chapter 3, it was mentioned that facilitated transport membranes showed much higher CO₂/N₂ selectivities than solution-diffusion membranes. Amine-containing polymer/inorganic composite membranes were successfully synthesized in Chapter 3, and showed a CO₂ permeance of up to 1100 GPU and a CO₂/N₂ selectivity of more than 140. However, there were several limitations for the further scale-up fabrication of this composite membrane. First of all, the inorganic material has a high cost. It took a long time for the synthesis of zeolite Y particles with certain particle size although rapid synthesis of zeolite-Y was studied [64,79]. The effectiveness of the zeolite nanoparticle layer for improving the transport performance of the composite membranes needs further investigation. Second, it was difficult to prepare a defect-free zeolite-Y layer, which might cause a low CO₂/N₂ selectivity of the composite membrane. Another limitation for the scale-up membrane fabrication was the high cost of the Millipore Biomax PES substrate. In this chapter, to overcome those limitations, amine-containing membranes
were prepared on top of bare polymer substrates instead of zeolite-Y layers. Different polymer substrates were used to replace the expensive Millipore PES substrate.

In this chapter, facilitated transport membranes were synthesized with polyvinylamine (PVAm) as the fixed-site carrier and piperazine glycinate (PG) as the mobile carrier. Since the CO\textsubscript{2} permeance is affected adversely by the membrane thickness, a higher CO\textsubscript{2} permeance can be obtained with a lower membrane thickness. To achieve a lower thickness of the membrane, a polymer matrix with a higher molecular weight is advantageous. First of all, it can provide a stronger polymer matrix for the membrane. Second, with a higher molecular weight, a higher viscosity of the polymer solution can be achieved even at a low solution concentration. Furthermore, the high viscosity can help reducing penetration of the coating solution into the pores of the substrate, further minimizing the mass transfer resistance of CO\textsubscript{2} transport through the membrane. Overall, with the high-molecular-weight PVAm, a high CO\textsubscript{2} permeance can be expected from the membrane.

In this chapter, high-molecular-weight PVAm was synthesized to obtain thin membranes with high CO\textsubscript{2} permeance. According to the literature [34,35,78,80], PVAm can be synthesized by free radical polymerization. For free radical polymerization, the molecular weight of the polymer increases with higher monomer concentration and lower initiator concentration [81,82]. In this chapter, various monomer concentrations and initiator amounts were used to obtain PVAm with different molecular weights. After the synthesis of PVAm, the aminoacid salt PG was incorporated into the polymer solution to serve as the mobile carrier, which could enhance the mobility of the CO\textsubscript{2}-carrier reaction.
product. In Chapter 3, the effects of different aminoacid salts on membrane transport performance were investigated, and PG was found to perform better than other mobile carriers including potassium glycinate and lithium glycinate. Therefore, PG was used as the mobile carrier in the membrane matrix.

The membrane in this chapter was prepared by a knife-coating method, which is similar to the one used in Chapter 3. The PVAm/PG coating solution was coated on top of different substrates including polysulfone (PSf) substrates and polyethersulfone (PES) substrates. In some cases, the adhesion between the coating solution and the substrate was not good. Therefore, sodium dodecyl sulfate (SDS) as the surfactant was incorporated into the coating solution to improve the adhesion between the amine solution and the substrate, and to minimize the defects of the membrane.

4.3. Experimental

4.3.1. Materials

Glycine (98.5%), piperazine (99%), n-vinylformamide (NVF, 98%), α,α’-azodiisobutyramidine dihydrochloride (AIBA, 97%), sodium dodecyl sulfate (SDS, 99%), 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 substrate (Biomax PES) with a molecular weight cut off of 300 kDa was purchased from EMD Millipore (Billerica, MA). The Biomax PES substrate was soaked in deionized water for overnight and then in IPA for 30 min to remove the glycerol in the pores before usage. Another kind of PES substrate (Lab-fabricated PES) was fabricated in our lab by a phase-inversion technique with controlled pore size and porosity. The NL polysulfone substrate (NL PSf) was kindly provided by NL Chemical Technology, Inc. (Mount Prospect, IL). TriSep polysulfone substrate (TriSep PSf) was purchased from TriSep Corporation (Goleta, CA). All the substrates had a similar structure, which contained a porous PES or PSf layer on top of a nonwoven fabric of polyester. The surface morphologies including the average pore size and the porosity of the four substrates are listed in Table 4.1.

4.3.2. Synthesis of PVAm

High-molecular-weight PVAm was synthesized by following the similar procedure to the one described in Chapter 3. NVF as the monomer was first purified by vacuum distillation to remove any inhibitor. Then, purified NVF was added in water to form a solution with different monomer concentrations. The solution in a 250 mL 3-neck round-bottom flask under nitrogen protection was preheated to 50°C in a water bath. AIBA as the initiator at a predetermined initiator/monomer ratio was added to the solution. Then,
the polymerization was carried out under nitrogen at 50°C for 3 h. After the polymerization, the polymer solution was transferred to a 2 M HCl aqueous solution to carry out the acidic hydrolysis at 70°C for 5 h. Subsequently, 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. Then, the dry polymer was dissolved in water with reflux at 60°C for overnight to form a 3 wt.% solution. Strong base anion-exchange resin was added to the polymer solution for ion-exchange. Finally, vacuum filtration was used to remove the resin after the pH of the polymer solution reached 10.

4.3.3. Synthesis of PG mobile carrier

The mobile carrier of aminoacid salt PG was 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, piperazine at the stoichiometric amount was added to react with glycine to form the aminoacid salt. The reaction took place at room temperature for 2 h, and then the homogeneous PG mobile carrier solution was obtained.

4.3.4. Membrane preparation

After the syntheses of both PVAm and PG, the PG mobile carrier solution was incorporated into the PVAm solution with a 65/35 PG/PVAm weight ratio, which formed
the so-called coating solution. In some cases, 5 wt.% SDS surfactant in the total solid composition was added to the coating solution to improve the adhesion between the solution and the substrate.

The PVAm/PG membrane was prepared by a knife-coating method. On top of different flat-sheet substrates, the coating solution was coated using a GARDCO adjustable micrometer film applicator (Paul N. Gardner Company, Pompano Beach, FL) with a controlled gap setting. The same empirical equation (as described in Chapter 3) was used for controlling the thickness of the dry membrane by adjusting the gap setting of the coating knife.

\[
l \times \rho_{dry} = 0.5 \times c \times \rho_{solution} \times l_{gap}
\]

where \( l \) (µm) is the dry PVAm/PG layer thickness, \( \rho_{dry} \) (g/cm\(^3\)) is the density of the dry PVAm/PG layer, \( \rho_{solution} \) (g/cm\(^3\)) is the density of the coating solution, \( c \) (by weight) is the total solid concentration of the coating solution, and \( l_{gap} \) (µm) is the gap setting of the coating knife.

After the coating, the membrane was dried in a fume hood at room temperature for overnight before testing. The chemical structures of the components in the resultant membrane, including PVAm, PG and SDS, are shown in Figure 4.1. The structure of the PVAm/PG membrane is shown in Figure 4.2. As can be seen from Figure 4.2, the polymer substrate contains a nonwoven fabric, which provides the mechanical strength to the membrane, and a porous PES or PSf layer. A thin amine layer containing PVAm and PG was coated on top of the substrate.
Gas transport performance measurements were conducted by using a permeation apparatus as shown in Figure 4.3, which was modified from a set-up described in a previous paper [27]. First, the PVAm/PG membrane was loaded into a stainless-steel rectangular permeation cell with an effective membrane area of 2.7 cm². Then, the membrane cell was placed in a temperature-controlled oven (Bemco Inc. Simi Valley, CA). The oven temperature was set at 57°C, which is the typical flue gas stream temperature. The simulated flue gas containing 80% N₂ and 20% CO₂ was used as the feed gas at a flow rate of 60 cc/min, and argon was used as the sweep gas at a flow rate of 30 cc/min. Both the feed gas and sweep gas were humidified when passing through 150 mL water in a 2 L stainless-steel humidifier (Swagelok, Westerville, OH) filled with 60% (by volume) packing of glass Raschig rings. After leaving the humidifier, 17% water content was achieved at 57°C for both feed gas and sweep gas. Then, both gas streams passed through the respective second stainless-steel vessel, to minimize any liquid water entrainment before reaching the membrane cell. The second stainless-steel vessel with a 500 mL volume contained no water, and it was filled with 60% (by volume) packing of glass Raschig rings. A countercurrent flow configuration was used through the membrane cell to offer the maximum driving force. After leaving the cell, water vapor in both streams was knocked out in two respective condensers. The testing pressures were adjusted by the two near-ambient pressure regulators. The feed side pressure was set at 1.5 psig, and the sweep side pressure was set at 1.0 psig. 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). SUPELCO Carboxen® 1004 micropacked GC column (Sigma-Aldrich, St. Louis, MO) was used for the GC analysis. CO₂ permeance and CO₂/N₂ selectivity were calculated from the GC analysis to characterize the membrane transport performance.

In this work, 57°C was used as the testing temperature for most cases. However, 102°C was also used to investigate membrane separation performance at high temperature, which will be discussed in Section 4.4.6.

4.3.6. Characterization of PVAm and membrane properties

The chemical structure of the synthesized PVAm was characterized by Fourier transform infrared (FTIR) attenuated total reflectance (ATR) spectroscopy using a Nicolet 470 Fourier transform infrared spectrometer (Thermo Electron Co., Waltham, MA). The viscosity of the 3 wt.% PVAm solution was measured using Brookfield Digital Viscometer DV-E (Brookfield Engineering Laboratories, Inc., Middleboro, MA). 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 cross-section morphology of the synthesized membranes was observed by scanning electron microscope (SEM) using FEI Nova NanoSEM400 (FEI Company, Hillsboro, OR).
4.4. Results and discussion

4.4.1. FTIR characterization of synthesized PVAm

The FTIR spectrum of the synthesized PVAm is shown in Figure 4.4. The strong and wide absorption band between 3500 cm\(^{-1}\) and 2800 cm\(^{-1}\) was considered to be the stretching vibrations peak of primary amine groups [83-87]. The peak at 2950 cm\(^{-1}\) was assigned to the stretching vibration absorption of C-H bond. The peak at 1580 cm\(^{-1}\) was attributed to the bending vibration absorption of N-H bond of the primary amine groups. The peak at 1650 cm\(^{-1}\) should be attributed to the stretching vibrations of C=O bond in amide groups, indicating that the acidic hydrolysis was not complete, which means that there were still some amide groups which had not been transformed to amino groups.

4.4.2. Effects of PVAm synthesis conditions on polymer molecular weight and polymer solution viscosity

As mentioned, PVAm with a higher molecular weight was advantageous for the membrane transport performance. First, PVAm provides the mechanical strength as the polymer matrix of the membrane, which means a stronger and more stable membrane will be obtained from a higher molecular weight polymer. Second, with higher molecular weight, the polymer solution will be more viscous at the same concentration, and the adhesion between the coating solution and the substrate will be better. This can help
maintaining a good CO₂/N₂ selectivity of the membrane. Moreover, higher viscosity can also help reducing the penetration of the polymer solution into the pores of the substrate, which can further reduce the mass transfer resistance and improve the CO₂ permeance of the membrane.

In this work, PVAm samples with different molecular weights were synthesized through free radical polymerization by adjusting the monomer concentration and the initiator amount (or initiator/monomer ratio). Figure 4.5 shows the correlation between the 3 wt.% polymer solution viscosity and the synthesis conditions including the monomer concentration and the initiator/monomer ratio. At the same polymer solution concentration (3 wt.%), a higher viscosity indicated that the synthesized polymer had a higher molecular weight. From Figure 4.5, it can be seen that with 40 wt.% monomer concentration, the viscosity of the polymer solution was higher than that with 30 wt.% monomer concentration at the same initiator/monomer ratio. In this work, 50 wt.% monomer concentration was also used for the polymerization. However, the reaction took place too fast, and there was gel formation during the polymerization. Another trend which can be seen from Figure 4.5 is that the PVAm solution viscosity increases with a lower initiator/monomer ratio. However, when the initiator/monomer ratio was less than 0.14 wt.%, there was a significant reduction of the polymer solution viscosity. It could be due to the fact that the initiator concentration was too low, so that it was difficult to initiate the polymerization reaction, which led to a lower molecular weight of the polymer.
In this work, two main types of the synthesized PVAm were used to prepare membranes. The weight average molecular weights of synthesized PVAm (a) and PVAm (b) were measured by DLS, which were 719,000 and 1,200,000, respectively. The synthesis conditions, the viscosity of 3 wt.% polymer solution and the molecular weights of the two polymers are listed in Table 4.2. To compare the synthesized PVAm with the commercially available PVAm, the viscosity of 3 wt.% polymer solution and the molecular weight of Lupamin® 9095 (from BASF Corporation) are also listed in Table 4.2. As can be seen, the synthesized PVAm showed a much higher molecular weight than Lupamin®. Besides, the viscosity of the 3 wt.% synthesized PVAm solution was significantly higher than that of 3 wt.% Lupamin® solution. Moreover, Lupamin® was obtained by basic hydrolysis using sodium hydroxide, therefore a large amount of byproduct (sodium formate salt) was formed in the polymer product, which can damage the stability of the membranes due to the salting-out problem. In contrast, since acidic hydrolysis was used instead of basic hydrolysis in this work, no byproduct was formed. All of these factors indicated that the high-molecular-weight PVAm synthesized in this work was very much advantageous for the membrane transport performance compared to the commercially available Lupamin® product.

4.4.3. Membrane morphology via SEM

SEM was used to observe the cross-section morphology of the membrane. The SEM image in Figure 4.6 shows the cross-section of the PVAm/PG membrane prepared on top
of the lab-fabricated PES substrate. As can be seen, the thin PVAm/PG layer with a thickness of around 150 nm was successfully coated on top of the substrate. The sponge-like structure underneath the amine layer was the nanoporous PES layer. The nonwoven fabric, which provides the mechanical strength to the PES substrate, cannot be seen from this image with this particular magnification.

4.4.4. Effect of SDS surfactant on membrane separation performance

During the initial attempts, no surfactant was introduced in the membrane composition. However, due to the poor adhesion between the PVAm/PG solution and the substrate, some defects were formed in the thin amine layer, which caused a low CO₂/N₂ selectivity. The Millipore Biomax PES substrate was an exception, which will be discussed in Section 4.4.5. To improve the adhesion between the amine layer and the substrate, and to minimize the defects, SDS surfactant with an amount of 2 – 10 wt.% in total solid composition was incorporated in the coating solution.

One interesting observation was that after the incorporation of SDS surfactant, there was an increase of the coating solution viscosity. The effect of the SDS amount on the coating solution viscosity is shown in Figure 4.7. The coating solution with different SDS amount had a total solid concentration of 10 wt.% with a PG/PVAm weight ratio of 65/35. The PVAm used here was the one with a molecular weight of 719,000. Without SDS, the coating solution had a viscosity of 450 cp. After the incorporation of 2, 5, 8 and 10 wt.% SDS surfactant in the total membrane solid composition, the coating solution
viscosity increased to 630, 812, 830 and 835 cp, respectively. The viscosity increase with the SDS surfactant was mainly due to the interaction between the anionic SDS surfactant and the amino groups [88,89]. However, when the SDS amount was more than 5 wt.% in the total solid composition, phase separation in the coating solution was observed frequently, which could lead to a low CO$_2$/N$_2$ selectivity of the membrane.

Figure 4.8 shows the effect of SDS amount on the membrane transport performance including CO$_2$ permeance and CO$_2$/N$_2$ selectivity. All the membranes shown in Figure 4.8 were prepared on the lab-fabricated PES substrate with a thickness of ~ 150 nm. As can be seen, without SDS surfactant in the composition, the membrane showed a CO$_2$/N$_2$ selectivity of only 87. After the incorporation of 2 wt.%, 5 wt.% and 8 wt.% SDS surfactant in the total solid membrane composition, the selectivity increased to 117, 154 and 160, respectively. This indicated that SDS surfactant successfully improved the adhesion between the coating solution and the PES substrate. The selectivity was lower with 10 wt.% SDS in the total solid, which was mainly due to the phase separation after the introduction of too much amount of SDS. The phase separation in the coating solution could lead to minor defects in the amine layer and further reduce the CO$_2$/N$_2$ selectivity.

It can also be seen from Figure 4.8 that the CO$_2$ permeance of the membrane was higher with 5 wt.% SDS in the total solid than that with 2 wt.% SDS. One possible explanation was that due to the high hydrophilicity of the SDS surfactant, there was more water retained inside the membrane, which was beneficial to the CO$_2$ facilitated transport. Another explanation was that the viscosity of the coating solution was higher with the
higher SDS amount, which minimized the penetration of the amine solution into the pores of the PES substrate and reduced the mass transfer resistance. However, when the SDS amount is more than 5 wt.% in the total solid membrane composition, there was a decline of CO$_2$ permeance. The possible explanation was that the phase-separation problem might make some amine carriers ineffective for the CO$_2$ transport. Therefore, 5 wt.% SDS surfactant was used for most cases in this work, and it improved the adhesion between the amine layer and the substrate significantly.

It should be brought up here that for the PVAm with even higher molecular weight (1,200,000), no surfactant was needed to obtain a good CO$_2$/N$_2$ selectivity of the membrane. This was due to the high viscosity of the coating solution caused by the high molecular weight of the polymer, which provided a good adhesion between the amine solution and the substrate. More work will be done with this higher molecular weight PVAm in the future.

4.4.5. Effect of different substrates on membrane separation performance

As mentioned, different substrates were used for the preparation of amine membranes in this work. Table 4.3 shows the comparison of membrane transport performances with different substrates. As can be seen, the membrane on the Biomax PES from Millipore showed the best performance. Besides, no SDS surfactant was needed for this case. The reason was that the Biomax PES was more hydrophilic, compared to the other three substrates, which provided a good adhesion to the coating solution. Due to the good
adhesion, a thin membrane layer (~100 nm) could be coated on top of the substrate without any defects. Subsequently, both a high CO₂ permeance and a high CO₂/N₂ selectivity could be achieved from this substrate. In contrast, for the other three substrates, when the membrane layer was less than 150 nm, defects could be introduced to the membrane, resulting in a low CO₂/N₂ selectivity.

Although the Biomax PES provided the best membrane performance, the high cost of this substrate was a limitation for further scale-up fabrication of the membrane. Therefore, the other three alternative substrates were investigated. As is shown in Table 4.3, the membrane prepared on TriSep PSf and NL PSf substrates showed lower CO₂ permeances. This could be due to the smaller pore size and lower porosity in the PSf substrates (as shown in Table 4.1), which contributed more mass transfer resistance to the membrane. The CO₂/N₂ selectivity was also lower on the PSf substrates, which could be explained by the fact that the PSf was more hydrophobic than PES substrates. Overall, the lab-fabricated PES was a better option due to the relatively good membrane separation performance and low cost.

4.4.6. Effect of temperature on membrane separation performance

In this research, 57°C was used as the membrane testing temperature for most cases. However, 102°C was also used to investigate the membrane performance at high temperature. The two membranes shown in Table 4.4 were prepared with the same condition. PVAm with 719,000 molecular weight was used to prepare the membrane,
and 5 wt.% SDS was incorporated in the total solid membrane composition. Both membranes were prepared on the lab-fabricated PES substrate with an estimated membrane thickness of 180 nm. As can be seen, at 102°C, the membrane showed a much higher CO₂ permeance, which was more than 1800 GPU. The main reason for the high performance was that the reactivity of the amine carriers was higher at high temperature. Besides, the mobility of both mobile carriers and the CO₂-carrier reaction product was also improved at high temperature. Moreover, the higher water content at a higher temperature could also help improving the separation performance based on the facilitated transport mechanism, by which water is an important component for the amine-CO₂ reaction.

Although the membrane performed better at 102°C than at 57°C, it can introduce more operational cost due to the higher water amount required at high temperature. Besides, 57°C and 17% water content is the typical flue gas condition after the flue gas desulfurization (FGD) in coal-fired power plants. Therefore, 57°C was used in this work for most cases. The feasibility of using 102°C as the operational temperature needs further investigation.

4.4.7. Stability of PVAm/PG membrane

Figure 4.9 shows the 20 h stability test of the PVAm/PG membrane on the Biomax PES substrate with an average CO₂ permeance of 1100 GPU and a CO₂/N₂ selectivity of 290. Figure 4.10 shows the 20 h stability test of the PVAm/PG membrane on the lab-
fabricated PES substrate with an average CO$_2$ permeance of 920 GPU and a CO$_2$/N$_2$ selectivity of 160. It can be seen that the performance of both membranes was stable over the 20 h test. No sign of performance degradation was observed for either CO$_2$ permeance or CO$_2$/N$_2$ selectivity. The stable and good separation performance indicated that the synthesized PVAm/PG membrane was promising for the application of CO$_2$ capture from flue gas.

4.4.8. Effect of PVAm molecular weight on membrane separation performance

Table 4.5 shows the comparison of membrane separation performances with different PVAm molecular weights. All the membranes shown in Table 4.5 were prepared using a pilot-scale continuous coating machine in Dr. Ho’s group at The Ohio State University (OSU). As can be seen, with the same membrane thickness, a higher CO$_2$ permeance was obtained with a higher PVAm molecular weight. The most possible explanation was that with a higher PVAm molecular weight, a higher coating solution viscosity could be obtained, which minimized the penetration of coating solution into the pores of the substrates. Another advantage of the higher PVAm molecular weight is that due to the more stable polymer matrix, higher amounts of mobile carriers can be introduced to the coating solution, which can lead to higher membrane separation performances. The study of incorporating more mobile carriers in the coating solution was beyond the scope of this research, which needs further investigation in the future.
4.5. Conclusions

High-molecular-weight PVAm/PG membranes were successfully synthesized. PVAm with a higher molecular weight compared to the commercial PVAm (Lupamin®) was synthesized as the fixed-site carrier, and PG was incorporated as the mobile carrier to the membrane composition. SDS surfactant was incorporated to the coating solution to improve the adhesion between the coating solution and the substrate. Membranes with a thickness of 100 – 200 nm were coated on different substrates. The resultant membranes showed a CO$_2$ permeance up to 1100 GPU and a CO$_2$/N$_2$ selectivity of more than 140 at 57°C with 17% water vapor. The membranes showed a stable result during the 20-h stability test. With the same membrane thickness, a higher CO$_2$ permeance was obtained with a higher PVAm molecular weight due to the less penetration of coating solution into the pores of the substrates. The high-molecular-weight PVAm/PG membrane synthesized in this work showed a great potential for the application of CO$_2$ separation and capture from flue gas.
Nomenclature

\( c \) total solid concentration of amine coating solution

\( l \) dry PVAm/PG layer thickness

\( l_{gap} \) gap setting of the coating knife

Greek letters

\( \rho \) density

\( \rho_{dry} \) density of the dry PVAm/PG layer

\( \rho_{solution} \) density of coating solution
Table 4.1. Surface morphologies of different polymer substrates.

<table>
<thead>
<tr>
<th>Polymer Substrate</th>
<th>Average Pore Size (nm)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biomax PES</td>
<td>72.0</td>
<td>15.0</td>
</tr>
<tr>
<td>Lab-fabricated PES</td>
<td>68.0</td>
<td>16.0</td>
</tr>
<tr>
<td>NL PSf</td>
<td>12.1</td>
<td>5.3</td>
</tr>
<tr>
<td>TriSep PSf</td>
<td>10.0</td>
<td>8.0</td>
</tr>
</tbody>
</table>
Table 4.2. Comparison of high-molecular-weight PVAm synthesized in this work and Lupamin®.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Monomer Concentration (wt.%)</th>
<th>Initiator/Monomer Ratio (by weight)</th>
<th>Viscosity of 3 wt.% Polymer Solution (cp)</th>
<th>Weight Average Molecular Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVAm (a)</td>
<td>30</td>
<td>0.5/100</td>
<td>486</td>
<td>719,000</td>
</tr>
<tr>
<td>PVAm (b)</td>
<td>40</td>
<td>0.14/100</td>
<td>1,400</td>
<td>1,200,000</td>
</tr>
<tr>
<td>Lupamin®</td>
<td>N/A</td>
<td>N/A</td>
<td>50</td>
<td>340,000</td>
</tr>
</tbody>
</table>
Table 4.3. Comparison of membrane transport performances on different substrates.

<table>
<thead>
<tr>
<th>Polymer Substrate</th>
<th>SDS Amount in Total Solid (wt.%)</th>
<th>Estimated Amine Layer Thickness (nm)</th>
<th>CO₂ Permeance (GPU)</th>
<th>CO₂/N₂ Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biomax PES</td>
<td>0</td>
<td>100</td>
<td>1100</td>
<td>290</td>
</tr>
<tr>
<td>Lab-fabricated PES</td>
<td>5</td>
<td>150</td>
<td>930</td>
<td>154</td>
</tr>
<tr>
<td>NL PSf</td>
<td>5</td>
<td>150</td>
<td>768</td>
<td>132</td>
</tr>
<tr>
<td>TriSep PSf</td>
<td>5</td>
<td>150</td>
<td>690</td>
<td>123</td>
</tr>
</tbody>
</table>
Table 4.4. Comparison of membrane transport performances at different test conditions.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Water content (Feed, Sweep)</th>
<th>CO\textsubscript{2} Permeance (GPU)</th>
<th>CO\textsubscript{2}/N\textsubscript{2} Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>57</td>
<td>17%, 17%</td>
<td>843</td>
<td>142</td>
</tr>
<tr>
<td>102</td>
<td>80%, 57%</td>
<td>1815</td>
<td>175</td>
</tr>
</tbody>
</table>
Table 4.5. Comparison of membrane separation performances with different PVAm molecular weights.

<table>
<thead>
<tr>
<th>PVAm Molecular Weight</th>
<th>Amine Layer Thickness (nm)</th>
<th>CO$_2$ Permeance (GPU)</th>
<th>CO$_2$/N$_2$ Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>719,000</td>
<td>180</td>
<td>710</td>
<td>152</td>
</tr>
<tr>
<td>1,200,000</td>
<td>180</td>
<td>751</td>
<td>155</td>
</tr>
<tr>
<td>719,000</td>
<td>155</td>
<td>764</td>
<td>115</td>
</tr>
<tr>
<td>1,200,000</td>
<td>155</td>
<td>823</td>
<td>148</td>
</tr>
</tbody>
</table>
Figure 4.1. Chemical structures of PVAm, PG and SDS.
Figure 4.2. Schematic of PVAm/PG membrane structure.
Figure 4.3. Schematic of the permeation apparatus for gas transport performance measurements. 1 and 2: water reservoirs; 3 and 4: water pumps; 5 and 6: mass flow controllers; 7 and 8: humidifiers; 9 and 10: second vessels with packing; 11: the permeation cell with membrane inside; 12: oven; 13 and 14: water knockout vessels; 15 and 16: near-ambient pressure regulators; 17 and 18: pressure gauges; 19 and 20: needle valves; 21: GC.
Figure 4.4. FTIR spectrum of the synthesized PVAm.
Figure 4.5. Correlation between the 3 wt.% PVAm solution viscosity and the synthesis conditions including monomer concentration and initiator/monomer ratio.
Figure 4.6. SEM cross-section image of the PVAm/PG membrane on top of the lab-fabricated PES with a membrane thickness of ~ 150 nm.
Figure 4.7. Effect of SDS amount on coating solution viscosity.
Figure 4.8. Effect of SDS surfactant amount on membrane transport performance.
Figure 4.9. Stability of PVAm/PG membrane on Biomax PES substrate.
Figure 4.10. Stability of PVAm/PG membrane on lab-fabricated PES substrate.
Chapter 5: Testing of Pilot-Scale Membranes and Prototype Modules

5.1. Summary

In this chapter, transport performances of pilot-scale membranes and spiral-wound modules, which were prepared with the same membrane compositions described in Chapters 3 and 4, were characterized. For the pilot-scale flat-sheet membranes, both small cell test (with an effective membrane area of 2.7 cm²) and big cell test (with an effective membrane area of 342 cm² [90]) were conducted. The pilot-scale membranes and spiral-wound modules showed similar results to the lab-scale membranes (~ 800 GPU CO₂ permeance and ~ 140 CO₂/N₂ selectivity). Concentration polarization was observed from both big cell membrane tests and module tests, which indicated that a higher CO₂ permeance could be obtained with a higher feed flow rate. Several methods were used to solve the water condensation problem during the tests, including adding a Teflon support on top of the membrane for the big cell test and using a second vessel after the humidifier. Pressure drops of the spiral-wound modules were measured, which were less than 1.5 psi/m. Stability tests with O₂ and SO₂ were also investigated for spiral-wound modules. Spiral-wound modules were also tested at the National Carbon
Capture Center (NCCC, Wilsonville, AL) with real flue gas, and showed similar results to those tested in Dr. Ho’s laboratory at The Ohio State University (OSU).

5.2. Introduction

Although researchers have done a lot of work on developing membranes with good CO₂/N₂ separation performance, very few results on scale-up fabrication and pilot-scale testing of membranes were reported for CO₂ capture from flue gas [91]. In the industrial gas separation market, hollow-fiber modules are the most commonly used membrane configurations [2,3,9,92]. However, due to the high pressure drop and poor resistant to membrane fouling, hollow-fiber modules are not suitable for the application of CO₂ capture from flue gas of nearly ambient pressure. Spiral-wound modules offer low pressure drop and are robust, resistant to fouling, and economical, which are used in 95% of the reverse osmosis desalination industry [93-95]. Spiral-wound modules have a great potential for the post-combustion CO₂ capture application.

Lin et al. reported that their spiral-wound module tested at the National Carbon Capture Center (NCCC, Wilsonville, AL) showed a CO₂ permeance of 100 – 300 GPU and a CO₂/N₂ selectivity of 20 – 50 [96]. The membrane used for the module fabrication was the solution-diffusion Polaris® membrane from Membrane Technology and Research (MTR) Inc.. The spiral-wound module showed a stable result during the entire period of operation (~ 25 days). Wang et al. at Tianjin University fabricated industrial grade hollow-fiber and spiral-wound modules with facilitated transport membranes [97]. The
membrane for the module fabrication had a composition of polyvinylamine (PVAm) and piperazine, which was coated on top of polysulfone substrates. The spiral-wound modules showed a CO₂ permeance of 250 – 300 GPU and a CO₂/N₂ selectivity of 80 with an effective membrane area of 5 m².

In this chapter, transport performance measurements were conducted for both pilot-scale flat-sheet membranes and spiral-wound modules. Problems including water condensation and concentration polarization were encountered during the tests, which will be discussed. Effective solutions to those problems were also investigated. For the flat-sheet pilot-scale membranes, both small cell and big cell tests were conducted. The pilot-scale membranes from both small and big cell tests showed similar results to the lab-scale membranes. For the spiral-wound module tests, pressure drops from both feed and sweep sides were measured. The spiral-wound modules were also tested in the presence of O₂ and SO₂, and showed relatively stable results. Besides, the modules were tested at NCCC using real flue gas as the feed gas, and showed similar results to those tested at OSU.

5.3. Experimental

5.3.1. Materials

The pilot-scale membranes and modules were fabricated using the same coating solution compositions as what were described in Chapters 3 and 4. For the membranes
coated on top of zeolite Y/PES substrates, the composition of 65/35 PG/PVAm was used. For the membranes coated on bare polyethersulfone (PES) substrates, 5 wt.% sodium dodecyl sulfate (SDS) surfactant (in the total solid) was incorporated in the 65/35 PG/PVAm coating solution to improve the adhesion between the solution and the PES substrate.

The pilot-scale flat-sheet membranes were fabricated by Dongzhu Wu, Yang Han, Varun Vakharia, Witopo Salim, and Dr. Lin Zhao, using a pilot-scale continuous coating machine in Dr. Ho’s group at OSU. The fabricated pilot-scale membrane had a width of 14 inches and a length of 6 – 20 ft for each run.

The spiral-wound modules were fabricated by Witopo Salim and Varun Vakharia, using the aforementioned pilot-scale flat-sheet membranes fabricated in Dr. Ho’s group. The effective membrane areas for the spiral-wound modules were 300 – 400 cm².

5.3.2. Transport performance measurements of pilot-scale membranes

The pilot-scale flat-sheet membranes were tested using the same transport performance measurement apparatus (shown in Figure 4.3) as described in Chapters 2 – 4. Both small and big rectangular cells were used for the transport performance measurements.

For the small cell test, a small piece of membrane with an effective membrane area of 2.7 cm² was cut from the pilot-scale membrane and loaded into a small stainless-steel cell. For the big cell test, a membrane with a much larger effective membrane area (342 cm²)
was cut from the pilot-scale membrane and loaded into a big stainless-steel cell. Figure 5.1 shows the images of both the small and big cells. For tests with both the small and big cells, simulated flue gas with 20% CO₂ and 80% N₂ on dry basis before humidification was used as the feed gas, and argon was used as the sweep gas. For the small cell test, the feed and sweep flow rates were 60 cc/min and 30 cc/min, respectively, on dry basis. On the other hand, higher flow rates with a range of 133 – 2500 cc/min for both feed gas and sweep gas on dry basis were used for the big cell test. During the test, both feed and sweep streams were saturated with water vapor. The water vapor content is about 17% at the typical flue gas temperature of 57°C.

5.3.3. Transport performance measurements of spiral-wound modules

The spiral-wound modules were tested using a similar transport measurement apparatus as described in Chapters 2 – 4, except that the spiral-wound module instead of the stainless-steel cell was loaded inside the temperature-controlled oven. The schematic of the transport performance apparatus for spiral-wound modules is shown in Figure 5.2. Similarly to the big cell test, high flow rates (500 – 3000 cc/min) for both feed gas (20% CO₂ and 80% N₂) and sweep gas (argon) were used for the spiral-wound module tests at OSU.

At NCCC, spiral-wound modules were tested using real flue gas as the feed gas, and argon as the sweep gas for ease of GC analysis. 1000 cc/min flow rates were used for both feed gas and sweep gas. The flue gas composition provided by NCCC contained
approximately 12% (± 1%) CO₂, 7% (± 1%) O₂, 81% (± 1%) N₂, 0.5 – 5 ppm SO₂, and 1.5 – 4 ppm NO₂. Our gas chromatograph (GC) settings, including the GC column, were incapable of separating the oxygen concentration from the nitrogen concentration in the permeate stream sample. However, this problem was solved by using an oxygen analyzer provided by the analytical lab at NCCC to measure the oxygen concentration in the retentate stream. By using this concentration, the permeate oxygen concentration was determined from the mass balance, and accurate CO₂/N₂ selectivity of the membrane was further obtained.

5.3.4. Pressure drop measurements of spiral-wound modules

The pressure drop measurements of the spiral-wound membrane modules were conducted during the module tests. As shown in Figure 5.2, the pressure drops were measured by using 4 pressure gauges with two on each of feed and sweep sides. The positions of the pressure gauges were as follows: before the module feed inlet (position 7), after the module retentate outlet (position 17), before the module sweep inlet (position 8), and after the module permeate outlet (position 18).

The pressures at the module feed and sweep outlets were set to be 1.5 psig and 1.0 psig, respectively, using the two respective near-ambient pressure regulators. The pressure difference between position 7 and position 17 (subtracting the pressure drop from the humidifier) was considered as the pressure drop for the feed side of the module. The pressure difference between position 8 and position 18 (subtracting the pressure drop...
from the humidifier) was considered as the pressure drop for the sweep side of the module. The pressure drop from the humidifier itself was measured to be around 0.2 psi at 1000 cc/min.

5.4. Results and discussion

5.4.1. Transport performances of pilot-scale membranes from the small cell tests

Transport performances of the pilot-scale flat-sheet membranes from the small cell tests are shown in Figure 5.3. The transport performances of lab-scale flat-sheet membranes and spiral-wound modules are also shown in Figure 5.3 for comparison. As can be seen, the pilot-scale membranes showed an average CO\textsubscript{2} permeance of 800 GPU and an average CO\textsubscript{2}/N\textsubscript{2} selectivity of more than 140, which were similar to the results obtained with the lab-scale membranes (700 – 930 GPU CO\textsubscript{2} permeance and more than 140 CO\textsubscript{2}/N\textsubscript{2} selectivity), except with those lab-scale membranes prepared on Millipore PES substrates (~ 1100 GPU CO\textsubscript{2} permeance and more than 140 CO\textsubscript{2}/N\textsubscript{2} selectivity).

5.4.2. Transport performances of pilot-scale membranes from the big cell tests

The transport performances of several representative pilot-scale flat-sheet membranes from the big cell tests are listed in Table 5.1. As can be seen, higher flow rates resulted in higher CO\textsubscript{2} permeances, which can be explained by the concentration polarization
effect. This effect will be explained in Section 5.4.5. The best transport performance result obtained from the big cell tests showed a CO$_2$ permeance of 680 GPU and a CO$_2$/N$_2$ selectivity of 120, which was similar to the result obtained from small cell tests (~ 750 GPU CO$_2$ permeance and 140 CO$_2$/N$_2$ selectivity). The relatively lower transport performance from the big cell test compared to the small cell test could be due to the uneven coating from the pilot-scale amine run (some part of the membrane might be thicker while other part might be thinner).

5.4.3. Transport performances and pressure drops of spiral-wound modules

The transport performances and pressure drops of representative spiral-wound modules are shown in Table 5.2. As can be seen from Table 5.2, for the same module, higher flow rates usually resulted in higher CO$_2$ permeances, which can also be explained by the concentration polarization effect. However, when the flow rate was too high (1500 – 2500 cc/min), sometimes there was a reduction of CO$_2$/N$_2$ selectivity. This can be explained by either membrane leak or module glue failure at high flow rates.

The spiral-wound modules showed an average pressure drop of less than 1.5 psi/m for both the feed and sweep sides, which have met the DOE requirement of ≤ 1.5 psi/m for pressure drop. It can also be seen from Table 5.2 that the pressure drop was usually higher with higher flow rates. To control the pressure drop at less than 1.5 psi/m, most of our modules were tested at 1000 cc/min flow rates for both feed and sweep sides.
5.4.4. Solutions to the water condensation problem

The problem of water condensation on membrane surface was observed during the initial attempts for both the big cell test and spiral-wound module test. Liquid water on top of the membrane surface was observed after the test, which should be due to the water entrainment from the humidifier to the membrane at high flow rates. Water condensation can cause a significant CO$_2$ permeance reduction, due to the fact that the effective membrane area was much less with liquid water on the membrane surface as a result of high mass transfer resistance through the liquid water layer.

Two solutions were adopted to solve the water condensation problem. For the big cell test, one solution was to add a Teflon support on top of the membrane. The Teflon support (with an average thickness of 20 μm and an average pore size of 30 nm) was provided by W. L. Gore & Associates, Inc. (Newark, DE). Due to the high hydrophobicity of the Teflon support, liquid water can be blocked and cannot go through the Teflon layer to the membrane surface. By this way, water condensation problem was successfully resolved. Table 5.3 shows the comparison of membrane transport performance with and without the Teflon support. As can be seen, after adding the Teflon layer on top of the membrane, the CO$_2$ permeance increased significantly. Although the two membranes were from different batches of the pilot-scale amine run and tested at different flow rates, the big permeance difference was considered mainly due to the water condensation effect. After the BC-8 test, a lot of liquid water (around half of the membrane area) was observed on top of the membrane surface. On the
contrary, no liquid water was observed after the BC-12 test, for which a Teflon support was applied on top of the amine membrane.

Another solution to the water condensation problem was to install another vessel with packing after the humidifier. Figure 5.4 shows the module test configuration inside the oven before the modification. Only one humidifier with 1000 mL volume was used for each side. In this case, water condensation could occur due to the water entrainment at high flow rates (1000 – 3000 cc/min) for each of the feed and sweep sides. Figure 5.5 shows the module test configuration inside the oven after the installation of a second vessel (500 mL volume) after the humidifier. Besides, the humidifier for each side was replaced with a larger one with a volume of 2000 mL. Inside the additional vessel, 60 vol.% glass Raschig rings were added. After this modification, liquid water could be trapped in the second vessel before reaching the module.

5.4.5. Concentration polarization effect

As mentioned above in Sections 5.4.2 and 5.4.3, the CO$_2$ permeance of both the membranes tested in the big cell and spiral-wound modules increased with higher feed gas flow rate. This can be explained by the concentration polarization phenomenon.

The concentration polarization effect is very common in membrane processes for liquid systems such as ultrafiltration and reverse osmosis [98-105]. In the case of gaseous systems, this effect is usually assumed to be neglected, which is based on the presumption that gas transport membranes have low fluxes and that the diffusion
coefficient is much larger in the gas phase than in the liquid phase. However, for membranes with very high permeance, this assumption is not valid any more. Researchers have done both theoretical and experimental investigations and found that the concentration polarization effect indeed existed for gas separation membranes [106-115].

As shown in Table 5.1 and Table 5.2, with the increase of the feed gas flow rate, the membrane showed a higher CO\textsubscript{2} permeance. This indicated the concentration polarization phenomenon on the feed side, i.e., the concentration of CO\textsubscript{2} in the bulk gas phase is higher than that at the membrane surface whereas the concentration of N\textsubscript{2} in the bulk gas phase is lower than that at the membrane surface as N\textsubscript{2} is rejected by the membrane while CO\textsubscript{2} permeates through the membrane much faster than N\textsubscript{2}. The concentration polarization phenomenon reduced the CO\textsubscript{2} permeance. The effects of this concentration polarization became less prominent when the feed gas flow rate increased to more than 2000 cc/min.

5.4.6. Module stability test in the presence of O\textsubscript{2} and SO\textsubscript{2} at OSU

In the flue gas composition, there are small amounts of SO\textsubscript{2} and O\textsubscript{2}, which may react with the amine carriers in the membrane and cause degradation of the membrane module performance. To investigate the effects of O\textsubscript{2} and SO\textsubscript{2} on the membrane transport performance, the spiral-wound module was tested with 3% O\textsubscript{2} and 1 – 3 ppm SO\textsubscript{2} in Dr. Ho’s laboratory at OSU. Figure 5.6 and Figure 5.7 show the stability test results. As can
be seen from Figure 5.6, the subject module (SW-67) showed an initial CO₂ permeance of around 620 GPU. After 3% O₂ was incorporated to the feed gas, the CO₂ permeance fluctuated from 580 GPU to 615 GPU. It did not show any dropping trend within the 115 h test, which can be considered relatively stable. From Figure 5.7, it can be seen that after the incorporation of 1 ppm and 3 ppm SO₂, the CO₂ permeance dropped from 600 GPU to around 580 GPU and then became stable. After removal of SO₂, the CO₂ permeance stayed at 580 GPU. The module was tested for 204 h in total and showed a relatively stable result.

5.4.7. Module stability test with real flue gas at NCCC

To investigate the membrane module performance with real flue gas, three spiral-wound modules were tested at NCCC for a total test period of one month. The flue gas composition provided by NCCC contained approximately 12% (± 1%) CO₂, 7% (± 1%) O₂, 81% (± 1%) N₂, 0.5 – 5 ppm SO₂, and 1.5 – 4 ppm NO₂. Among these components, the oxygen concentration was much higher than the typical average of 2.3% in coal-fired power plants. Our gas chromatograph (GC) settings, including the GC column, were incapable of separating the oxygen concentration from the nitrogen concentration in the permeate stream sample. However, this problem was solved by using an oxygen analyzer provided by the analytical lab of NCCC to measure the oxygen concentration in the retentate stream. By using this concentration, permeate oxygen concentration was
determined from the mass balance, and the accurate CO$_2$/N$_2$ selectivity of the membrane was obtained.

The three modules tested at NCCC showed repeatable results with $\sim$ 800 GPU CO$_2$ permeance and $\sim$ 200 CO$_2$/N$_2$ selectivity, which are shown in Table 5.4. Those results agreed well with the modules tested in the OSU lab. As shown in Figure 5.8, the first module (SW-154) was tested for 96 hours and showed a stable result at 820 GPU CO$_2$ permeance and 150 CO$_2$/N$_2$ selectivity. The second module (SW-162) was tested for 208 hours, and the third module (SW-161) was tested for 200 hours. During both SW-162 and SW-161 tests, there was a flue gas shutdown at NCCC. The shutdown durations were 60 h and 48 h for the tests of SW-162 and SW-161, respectively. Both the SW-162 and SW-161 showed an initial CO$_2$ permeance of around 800 GPU. The SW-162 showed a CO$_2$/N$_2$ selectivity of 170 before the flue gas shutdown, and the selectivity dropped to around 60 after the restart of the test following the flue gas return, which is shown in Figure 5.9. The insufficient curing of the glue used and the membrane indentations caused by the rough surface of the feed spacer might have introduced the leakage of the module and resulted in the selectivity drop. The SW-161 with a longer glue curing time showed a reasonably stable selectivity of 180 – 270 for 200 hours. However, the CO$_2$ permeance dropped to $\sim$ 630 GPU after the restart of the test following the flue gas return, which is shown in Figure 5.10. The permeance drop was presumably due to the feed gas bypass which was caused by the glue failure. Further improvement of the glue curing and minimizing membrane indentations would help to obtain more stable results.
Overall, the membrane module results obtained at NCCC achieved the same level of performance as compared to our OSU lab test results with the simulated flue gas. The modules showed \(~800\) GPU permeance and \(~200\) selectivity as well as a pressure drop of less than 1.5 psi/m. In other words, the results showed that the modules tested at NCCC behaved similarly to those in the OSU lab, indicating a great potential of the membrane modules for CO\(_2\) capture from flue gas in power plants.

5.5. Conclusions

Pilot-scale flat-sheet membranes were tested using both small and big cells. Spiral-wound modules prepared using the pilot-scale membranes were also tested. Both pilot-scale membranes and spiral-wound modules showed similar results to the lab-scale membranes (\(~800\) GPU CO\(_2\) permeance and more than 140 CO\(_2\)/N\(_2\) selectivity). The water condensation problem was found and solved by adding a Teflon support on top of the amine layer or installing a second vessel after the humidifier to trap and eliminate the liquid water droplets. The concentration polarization effect was observed for both the big cell and spiral-wound module tests. The spiral-wound module was tested in the presence of 3\% O\(_2\) and 1 – 3 ppm SO\(_2\), and showed reasonably stable results. The spiral-wound module was also tested at NCCC with real flue gas, and showed similar results to the modules tested at OSU. The promising results showed a great potential for the application of our membrane modules for CO\(_2\) capture from flue gas.
Table 5.1. Transport performances of the pilot-scale membranes from the big cell test.

<table>
<thead>
<tr>
<th>Big Cell Test No.</th>
<th>Amine Thickness (nm)</th>
<th>Feed/Sweep Flow Rate (cc/min)</th>
<th>CO₂ Permeance (GPU)</th>
<th>CO₂/N₂ Selectivity</th>
<th>Small Cell Test Result</th>
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<td>150</td>
<td>180</td>
<td>657/154</td>
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<td>200</td>
<td>100</td>
<td>668/153</td>
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<td>150</td>
<td>750/140</td>
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<td></td>
<td></td>
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<td>600</td>
<td>150</td>
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<td></td>
<td></td>
<td>1000/1500</td>
<td>450</td>
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<td></td>
<td></td>
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<td>600</td>
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<tr>
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<td>750/140</td>
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<td></td>
<td></td>
<td>2500/1000</td>
<td>680</td>
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Table 5.2. Transport performances and pressure drops of spiral-wound modules.

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<th>Amine layer thickness (nm)</th>
<th>Feed/sweep flow rate (cc/min)</th>
<th>CO$_2$ permeance (GPU)</th>
<th>CO$_2$/N$_2$ selectivity</th>
<th>Pressure drop (feed/sweep, psi/m)</th>
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<td></td>
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<td>500/250</td>
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<td>1.48/1.31</td>
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<td>1000/500</td>
<td>300</td>
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Table 5.2: Continued

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Table 5.3. Comparison of membrane transport performances from the big cell test with and without the Teflon support on top of the amine membrane.

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<th>Big Cell Test No.</th>
<th>Teflon (w/o)</th>
<th>Feed/Sweep Flow Rate (cc/min)</th>
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<th>CO₂/N₂ Selectivity</th>
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<td>680</td>
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<td>680</td>
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Table 5.4. Transport performances of spiral-wound modules tested at NCCC with real flue gas.

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<th>Module No.</th>
<th>Membrane Thickness (nm)</th>
<th>CO₂ Permeance (GPU)</th>
<th>CO₂/N₂ Selectivity</th>
<th>Pressure Drop (Feed/Sweep, psi/m)</th>
<th>Module result tested at OSU</th>
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<td>820</td>
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<td>0.98/1.31</td>
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<td>SW-162</td>
<td>145</td>
<td>800</td>
<td>170→60</td>
<td>0.98/1.48</td>
<td>820</td>
</tr>
<tr>
<td>SW-161</td>
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<td>800→630</td>
<td>270→180</td>
<td>1.31/1.48</td>
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</table>
Figure 5.1. Images of (a) small stainless-steel cell and (b) big stainless-steel cell.
Figure 5.2. Schematic of gas transport performance measurements apparatus for spiral-wound module test. 1 and 2: water reservoirs; 3 and 4: water pumps; 5 and 6: mass flow controllers; 7, 8, 17 and 18: pressure gauges; 9 and 10: humidifiers; 11 and 12: second vessels with packing; 13: spiral-wound module; 14: oven; 15 and 16: water knockout vessels; 19 and 20: near-ambient pressure regulators; 21 and 22: needle valves; 23: GC.
Figure 5.3. Transport performances of flat-sheet membranes and spiral-wound modules.
Figure 5.4. Spiral-wound module test without the second vessel in the oven.
Figure 5.5. Spiral-wound module test with the second vessel in the oven.
Figure 5.6. Spiral-wound module stability test with 3% O$_2$. 
Figure 5.7. Spiral-wound module stability test with 1-3 ppm SO₂.
Figure 5.8. Spiral-wound module (SW-154) stability test at NCCC.
Figure 5.9. Spiral-wound module (SW-162) stability test at NCCC.
Figure 5.10. Spiral-wound module (SW-161) stability test at NCCC.
Chapter 6: Hydroxide-exchange Membranes for Fuel Cell Application

6.1. Summary

For fuel cell application, hydroxide-exchange membranes (HEMs) have received increasing attention compared to proton-exchange membranes (PEMs), due to the fact that low-cost catalysts can be used instead of platinum in an alkaline environment. Quaternary ammonium-based membranes were commonly used as HEMs. However, these membranes have shown low ionic conductivity, poor chemical and thermal stability. Ionic liquids are organic molten electrolytes which have high conductivity and good stability. In order to improve the conductivity and stability of HEMs, ionic liquid was incorporated to stable polymer matrixes. In this chapter, two types of polymer were synthesized and used as the polymer matrixes for HEMs. The first one is polybenzimidazole (PBI) and the other one is crosslinked polyvinylalcohol (PVA). Ionic liquid of 1-butyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide ([bmim][Tf₂N]) was incorporated into the polymer matrixes. However, it was not compatible with either PBI or PVA. Benzalkonium chloride as another ionic liquid and potassium hydroxide (KOH) were then incorporated to the polymer solution instead of [bmim][Tf₂N], and
showed a good compatibility with the polymer matrixes. The thermal stability of both PBI polymer and [bmim][Tf$_2$N] liquid was investigated by thermalgravimetric analysis (TGA). Initial conductivity of the resultant membranes including PBI/benzalkonium-OH membranes and crosslinked PVA/KOH membranes will be discussed.

6.2. Introduction

The main difference between a hydroxide-exchange membrane (HEM) fuel cell and a typical proton-exchange membrane (PEM) fuel cell is that the reactions occur in a basic environment in a HEM fuel cell. The reactions at both the cathode and anode in a HEM fuel cell are shown below.

Anode Reaction: \[ 2 \text{H}_2 + 4 \text{OH}^- \rightarrow 4 \text{H}_2\text{O} + 4 \text{e}^- \] (6.1)

Cathode Reaction: \[ \text{O}_2 + 2 \text{H}_2\text{O} + 4 \text{e}^- \rightarrow 4 \text{OH}^- \] (6.2)

Overall Reaction: \[ \text{O}_2 + 2 \text{H}_2 \rightarrow 2 \text{H}_2\text{O} \] (6.3)

In the basic environment, oxygen at the cathode converts to hydroxyl ions which are transported through the cell to the anode, where they combine with hydrogen to produce water. This can eliminate the kinetic limitations due to the slow reactions at the cathode which typically affect a PEM fuel cell. Therefore, alternative electro-catalyst can be used at the cathode in a HEM cell to replace the expensive platinum catalyst for a PEM cell.

For the optimal operation of a HEM fuel cell, it is important for the HEM to have both high hydroxyl ion conductivity and good stability in an environment at high PH. Up to date, the most commonly used HEMs are quaternary ammonium-based polymer
membranes [116-126]. Those polymers were usually prepared via quaternization of aromatic polymers, such as polysulfone and poly(phthalazinon ether sulfone ketone) (PPESK). However, these polymer membranes appeared to be unstable in alkaline environment, especially at high temperatures. To overcome this limitation, polybenzimidazole (PBI) membranes have been investigated, which are well known for their excellent chemical stability at high temperatures. Hydroxide doped PBI has been studied and shown good stability and high ionic conductivity at high PH environment and high temperatures [127,128]. However, the hydroxide salts could react with CO₂ from the oxidation stream and form carbonate precipitates [129].

Ionic liquids are promising candidates for fuel cell application. An ionic liquid is a salt in the liquid state. Sometimes the term has been restricted to salts whose melting point is below some arbitrary temperatures, such as 100°C. One benefit of the imidazolium ionic liquids is that they do not form these insoluble carbonates in large quantities due to the good solubility of CO₂ in the ionic liquids [130,131]. Ionic liquids usually have good thermal stability and low combustibility, which make them favorable for fuel cell applications.

In this research, ionic liquids were incorporated into two types of polymers including PBI and crosslinked polyvinylalcohol (PVA). Although there was a compatibility issue with the polymer and the imidazolium ionic liquid, benzalkonium-OH and KOH were successfully incorporated into both polymers as alternatives. The performance of the resultant membranes including the thermal stability and conductivity will be discussed in Section 6.4.
6.3. Experimental

6.3.1. Materials

3,3’-diaminobenzidine (DABD, 99%), 4,4’-oxybis(benzoic acid) (OBBA, 99%), polyphosphoric acid (PPA, 85 wt.% aqueous solution), dimethyl sulfoxide (DMSO, 99.5%), potassium hydroxide (KOH, 85%), benzalkonium chloride (95%), hydrochloric acid (HCl, 37%), methyl orange, and glutaraldehyde (50 wt.% aqueous solution) were purchased from Sigma-Aldrich. Polyvinylalcohol (PVA, Poval S-2217, 92%) was provided by Kuraray America Inc. (Houston, TX). 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([bmim][Tf$_2$N]) was provided by Dr. Elise B. Fox from Savannah River National Laboratory (SRNL, Aiken, SC). The chemical structures of [bmim][Tf$_2$N] and benzalkonium chloride are shown in Figure 6.1.

6.3.2. Synthesis of PBI polymer

PBI polymer was synthesized using a one-step high temperature polymerization method from DABD and OBBA, using PPA as the solvent [132-134]. Figure 6.2 shows the schematic of the PBI synthesis. The reaction took place under nitrogen protection at 80°C for 2 h and then at 200°C for 3 h. The yield of PBI was more than 99%. The synthesized PBI polymer solution (in DMSO solvent) with a total solid concentration of
3.0 – 5.0 wt.% showed a high viscosity, indicating that the PBI polymer with a high molecular weight was synthesized.

6.3.3. Preparation of PBI/benzalkonium-OH membrane

The powder-like PBI polymer was dissolved in DMSO to form a homogeneous solution. To the PBI solution, certain amount of benzalkonium chloride was added. Then the solution was poured onto a clean glass plate and coated using a GARDCO adjustable micrometer film applicator (Paul N. Gardner Company, Pompano Beach, FL) with a controlled gap setting. The membrane was dried in an oven at 80°C for 6 h and then at 120°C for 12 h. Finally, it was soaked in 1.0 M KOH solutions for the purpose of hydroxide-exchange treatment at room temperature for 24 h. The resulting membrane in hydroxide form was washed with de-ionized water and dried at 90°C for overnight. The final membrane had a thickness of 40 µm.

6.3.4. Preparation of PBI/KOH membrane

PBI polymer was first dissolved in DMSO and coated into a membrane using the similar method described in Section 6.3.3. The pure PBI membrane was soaked in 6M KOH solution for more than 24 h. After drying, the membrane was soaked in de-ionized water to release KOH into water. Then HCl solution was used for titration, using methyl orange as the indicator. The result showed that the PBI membrane successfully absorbed
KOH. The weight ratio of PBI/KOH was ~ 80/20. The final membrane had a thickness of around 25 µm.

6.3.5. Preparation of crosslinked PVA/KOH membrane

PVA was first dissolved in water under stirring at room temperature for overnight and then at 80 °C for 80 min. Then a stoichiometric amount of glutaraldehyde and a certain amount of KOH solution were added into the solution. The PVA/glutaraldehyde/KOH solution was stirred at 80°C for 2 h [27,29,135,136].

Then, the solution was coated onto a clean glass plate to form a membrane. The membrane was dried in a hood at room temperature for overnight. Then it was dried at 120°C for 6 h. After drying, the final membrane was flexible and had a thickness of approximately 50 µm.

6.3.6. Characterization of PBI polymer

The chemical structure of the synthesized PBI was characterized by Fourier transform infrared (FTIR) attenuated total reflectance (ATR) spectroscopy using a Nicolet 470 Fourier transform infrared spectrometer (Thermo Electron Co., Waltham, MA). Thermalgravimetric analysis (TGA) of the PBI polymer was performed in a PerkinElmer (Waltham, MA) Pyris 1 TGA instrument from 30°C to 950°C at a heating rate of 10°C/min under a nitrogen atmosphere (flow rate of 30 cc/min).
6.4. Results and discussion

6.4.1. FTIR characterization of synthesized PBI

The FTIR spectrum of the synthesized PBI is shown in Figure 6.3. The band between 3151 cm$^{-1}$ and 3404 cm$^{-1}$ was considered to be the stretching vibrations peak of N-H groups. The peak at 1599 cm$^{-1}$ and 1433 cm$^{-1}$ was assigned to the ring vibration of benzene and imidazole rings. The peak at 1281 cm$^{-1}$ was considered to be the C-N stretching peak of imidazole rings. The peaks at 1222 cm$^{-1}$, 1170 cm$^{-1}$ and 1040 cm$^{-1}$ should be due to the C-O-C stretching from the ether groups. No residual carbonyl characteristic peaks between 1780 and 1650 cm$^{-1}$ were observed, which indicated that the closure of the imidazole rings was complete. All of these characteristic absorption peaks indicated that PBI was successfully synthesized.

6.4.2. TGA analysis of synthesized PBI and [bmim][Tf$_2$N]

The TGA curve of the PBI membrane is shown in Figure 6.4. The curve showed that there was a weight loss before 200°C. This was due to the absorbed water in the membrane, which indicated that the membrane was not completely dried before the TGA test. At around 450°C, there was another weight loss, which indicated that the membrane was thermally stable up to around this high temperature.
The stability of ionic liquid [bmim][Tf$_2$N] was also characterized by TGA at SRNL [137]. The TGA curve of [bmim][Tf$_2$N] is shown in Figure 6.5. It can be seen that the weight loss occurred at around 400°C, which indicated that [bmim][Tf$_2$N] was thermally stable up to around this high temperature.

6.4.3. Difficulty of incorporating ionic liquid into PBI and crosslinked PVA

In the initial attempts of incorporating ionic liquids into polymer membranes, [bmim][Tf$_2$N] was used as the ionic liquid to be incorporated into the PBI or crosslinked PVA membranes. However, [bmim][Tf$_2$N] had a very low solubility in both the PBI solution with DMSO as the solvent and the crosslinked PVA solution with water as the solvent. Phase separation occurred after the solvent evaporation, which indicated that [bmim][Tf$_2$N] was not compatible with either PBI or crosslinked PVA. Therefore, another ionic liquid (benzalkonium chloride) and KOH was used to replace [bmim][Tf$_2$N], and homogeneous membranes were obtained.

6.4.4. Conductivity test of PBI/benzalkonium-OH membranes and crosslinked PVA/KOH membranes

The conductivity testing of the membranes was beyond the scope of this research. However, several membrane samples were sent to SRNL for the conductivity test, and have shown some initial results [137]. As expected, the conductivity increased with
higher relative humidity. However, in some instances such as PVA/KOH membranes at 120°C, the conductivity decreased with higher humidity. This effect can be attributed to the degradation of the membrane composition. Overall, the highest conductivity was around 10 mS/cm from the 70/30 PVA/KOH membrane, which was tested at 80°C and 70% relative humidity. When the relative humidity was higher than 70%, the PVA/KOH membrane degraded. At the same condition, the overall conductivity of PVA/KOH membranes was far superior to the PBI/benzalkonium-OH membranes. However, the PBI/benzalkonium-OH membranes showed a much better stability at higher relative humidities, at which their ionic conductivity began to approach that of the PVA/KOH membranes.

6.5. Conclusions

Hydroxide-exchange membranes were successfully synthesized using PBI and PVA as the polymer matrixes and incorporated with ionic liquids for the fuel cell application. The PBI and [bmim][Tf$_2$N] showed good stability from the TGA curves, which can improve the thermal stability of the hydroxide-exchange membranes. However, it was difficult to incorporate [bmim][Tf$_2$N] into the PBI polymer due to the poor compatibility. Instead, KOH and benzalkonium-OH were incorporated in PBI and PVA membranes to replace [bmim][Tf$_2$N], and showed good compatibility with the polymer. PVA/KOH membranes showed the highest conductivity of ~ 10 mS/cm at 80°C and 70% relative humidity. However, the membrane was not stable at higher temperatures and relative
humidities. On the other hand, the PBI/benzalkonium-OH membranes showed a lower conductivity than PVA/KOH membranes, but showed a much better stability at higher relative humidities.
Figure 6.1. Chemical structures of ionic liquids: (a) [bmim][Tf$_2$N] and (b) benzalkonium chloride.
Figure 6.2. Schematic of the PBI synthesis.
Figure 6.3. FTIR spectrum of the synthesized PBI.
Figure 6.4. TGA curve of synthesized PBI.
Figure 6.5. TGA curve of [bmim][Tf₂N].
Chapter 7: Summary and Future Work

7.1. Summary

In this research, two types of polymer membranes were successfully synthesized for different applications. The first type is CO$_2$-selective membranes for carbon capture from flue gas, and the second one is hydroxide-exchange membranes for fuel cell application.

For the first application, two subtypes of membranes were synthesized, including the ethylene oxide (EO)-containing polymer membranes (based on the solution-diffusion mechanism) and amine-containing polymer membranes (based on facilitated transport mechanism). Both of the membranes have shown promising CO$_2$/N$_2$ separation performance for carbon capture from flue gas. For the fuel cell application, different kinds of ionic liquids were incorporated to polymer matrixes including polybenzimidazole (PBI) and crosslinked polyvinylalcohol (PVA) polymers to form hydroxide-exchange membranes. The resultant membranes showed promising results in terms of conductivity and thermal stability.
7.1.1. CO₂-selective membranes for carbon capture from flue gas

From Chapter 2 to Chapter 5, polymer membranes for CO₂/N₂ separation from flue gas were discussed.

In Chapter 2, EO-containing polymer membranes were deposited onto the zeolite Y layers to form a composite membrane. Commercial polymer Pebax® (a copolymer of polyamide and PEO) was used as the polymer matrix. EO-containing small molecules including polyethylene glycol (PEG) and poly(ethylene glycol) dimethyl ether (PEG-DME) were incorporated into the polymer matrix to improve the diffusivity and solubility of CO₂ molecules. The resultant membrane showed a CO₂ permeance of 940 GPU and a CO₂/N₂ selectivity of 30 at 57°C, which was higher than the selectivities of most solution-diffusion membranes which have been reported at the same temperature. Other EO-containing polymers including polyimide-PEO copolymer and polyurethane-PEO copolymer were also synthesized. Further investigation on the transport performance of those polymer membranes is needed.

In Chapter 3, amine-containing polymer membranes were coated onto the zeolite Y layers to form a composite membrane. Polyvinylamine (PVAm) was synthesized as the polymer matrix, and different types of aminoacid salts were incorporated into the polymer solution as mobile carriers. The resultant membrane showed a CO₂ permeance of 1100 GPU and CO₂/N₂ selectivity of more than 140 at 57°C. Based on this separation performance, a preliminary techno-economic analysis showed a capture cost of $37.5/tonne CO₂ captured (based on 2007 dollar) for a two-stage air-sweep membrane.
process, indicating that this membrane has a great potential for carbon capture from flue
gas.

In Chapter 4, high-molecular-weight PVAm/piperazine glycinate (PG) membranes
were synthesized using bare polymer substrates instead of zeolite Y/PES substrates, to
reduce the cost and complicity of the inorganic layers. PVAm was synthesized with
different molecular weights by adjusting the monomer concentration and initiator
amounts during the free radical polymerization. The obtained polymer had a much
higher molecular weight than commercially available Lupamin®. The high molecular
weight allowed for the preparation of a coating solution with a high viscosity at a low
concentration, which further allowed for the fabrication of much thinner membranes.
Besides, a higher CO₂ permeance was obtained with a higher PVAm molecular weight,
due to the less penetration of coating solution into the pores of the substrates. The
resultant membranes with thicknesses of 100 – 200 nm showed CO₂ permeances of 700 –
1100 GPU on different substrates, and CO₂/N₂ selectivities of more than 140.

In Chapter 5, testing of pilot-scale membranes and spiral-wound modules was
discussed. The pilot-scale membranes and spiral-wound modules were made from the
same membrane composition described in Chapter 3 and Chapter 4. Overall, both pilot-
scale flat-sheet membranes and spiral-wound modules showed similar results to the lab-
scale membranes. Concentration polarization effect was found and discussed for both big
cell test and module test. Water condensation problem with high flow rates during the
test was solved by installing a secondary vessel after the humidifier and adding another
Teflon layer on top of the amine membrane. Module stability was investigated with SO₂
and O₂ at the OSU lab, and showed relatively stable results. Moreover, spiral-wound modules were tested at the National Carbon Capture Center (NCCC) with real flue gas, and showed similar results to those obtained at OSU.

7.1.2. Hydroxide-exchange membranes for fuel cell application

In Chapter 6, hydroxide-exchange membranes for fuel cell application were synthesized. Two types of polymer matrixes were successfully synthesized, including PBI and crosslinked PVA. Thermal stability of PBI polymer and ionic liquid of 1-butyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide ([bmim][Tf₂N]) was investigated and showed a good stability at up to 400°C. Compatibility issue was found between [bmim][Tf₂N] and both of the polymers. Benzalkonium-OH and KOH were incorporated to the polymer matrixes instead, and showed a good compatibility. The resultant membranes showed promising initial results in terms of conductivity and thermal stability.

7.2. Future work

7.2.1. CO₂-selective membranes for carbon capture from flue gas

For the EO-containing polymer membranes, several areas can be investigated for the further improvement of membrane transport performance. First of all, to achieve a higher
CO₂ permeance, gutter layers [138-146] such as polydimethylsiloxane (PDMS) and polytrimethylsilylpropyne (PTMSP) can be used to minimize penetration of the polymer solution into the pores of the substrate, and further reduce the mass transfer resistance. Second, other EO-containing polymers can be investigated, such as the polyimide-PEO copolymer and polyurethane-PEO copolymer as described in Chapter 2. However, it is important to synthesize polymers with very high molecular weights. In that case, thinner membranes can be obtained to achieve higher CO₂ permeances. In terms of the fabrication method, there was a limitation to use spin-coating for the further scale-up membrane fabrication. Therefore, either dip-coating or knife-coating should be considered as alternatives to spin-coating for the membrane fabrication. Even though dip-coating usually gave thicker membranes compared to spin-coating, an air-knife during the dip-coating process can be applied to reduce the membrane thickness. For the knife-coating method, a much more viscous solution was needed. Therefore, the synthesis of PEO copolymers with much higher molecular weights might be a better option.

For amine-containing polymer membranes, the application of a gutter layer would also help. Besides, it is important to synthesize PVAm with even higher molecular weight, which can be achieved by adjusting the synthesis conditions including the monomer concentration, initiator amount, reaction temperature and reaction time. If PVAm with a higher molecular weight can be obtained, higher CO₂ permeances will be achieved with thinner membranes. Moreover, it is possible that more mobile carriers can be incorporated with a more stable polymer matrix, which will further improve the
membrane transport performance. Another way to improve the PVAm synthesis is to improve the hydrolysis degree by using higher hydrolysis temperature and longer hydrolysis time. In that case, there will be more amino groups in the PVAm structure, which will be advantageous to the membrane transport performance.

7.2.2. Hydroxide-exchange membranes for fuel cell application

Although hydroxide-exchange membranes were successfully synthesized, there was a big issue with the compatibility between the ionic liquids and the polymer matrixes. In the future, different types of ionic liquids can be investigated and selected to obtain a good compatibility with the polymer matrixes. Different solvents can also be studied to offer a good solubility to both ionic liquids and the polymer matrixes. More investigation on the conductivity and stability of the membranes needs to be performed in the future. Significant work needs to be continued on the incorporation of ionic liquids into solid polymer membranes in order to achieve validation of their operational performance in a fuel cell.
References


