CO$_2$ FACILITATED TRANSPORT MEMBRANES FOR HYDROGEN
PURIFICATION AND FLUE GAS CARBON CAPTURE

DISSertation

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Abstract

Membrane technology is a promising alternative to aqueous amine scrubbing process for CO\textsubscript{2} separation and capture, because of its superior energy efficiency and cost effectiveness. CO\textsubscript{2} facilitated transport membrane, based on the reversible reaction between amine carriers and CO\textsubscript{2}, is a good candidate membrane to achieve both high permeability and high selectivity. In this research, facilitated transport membranes with controlled compositions were synthesized and studied for H\textsubscript{2} purification for fuel cell applications and CO\textsubscript{2}/N\textsubscript{2} separation for flue gas carbon capture.

In Chapter 2, the water vapor transport mechanism of CO\textsubscript{2} facilitated transport membranes is elucidated. In Chapter 3, various approaches are discussed for improving membrane performance at a high temperature (120°C) with a low water vapor partial pressure (~0.54 atm) on the feed side. The best CO\textsubscript{2}/H\textsubscript{2} separation performance (CO\textsubscript{2} permeance of 146 GPU and CO\textsubscript{2}/H\textsubscript{2} selectivity of 107) was obtained on the membrane with the incorporation of a fluoride-containing polyelectrolyte and a quaternary ammonium hydroxide into an amine-containing membrane, which was about 80% higher than the performance of crosslinked poly(vinyl alcohol) based membranes containing amine carriers. Chapter 4 mainly discusses the CO\textsubscript{2}/N\textsubscript{2} separation performance of different types of amine-containing membranes for flue gas carbon capture. In Chapter 5, steric hindrance effect is demonstrated on polyvinylamine-based membranes. Poly(N-methyl-N-vinylamine) membranes showed almost 4 times of the performances of unhindered
polyvinylamine membranes at 102°C with 80% water vapor content on the feed side. Chapter 6 addresses the oxidative stability of two types of facilitated transport membranes, including the amine-containing membranes and hydroxide- and fluoride-containing membranes.

In conclusions, the water vapor transport property and oxidative stability studied in this work were rarely reported in the literature, yet important to industrial applications of CO₂ facilitated transport membranes. Different membrane compositions were developed to improve membrane performance at high temperature and low water partial pressure. The membranes containing quaternary ammonium hydroxide and amine carriers at appropriate amounts demonstrated an outstanding membrane performance, which indicated the excellent synergy of amine-catalyzed CO₂-hydroxide reaction in CO₂ facilitated transport. In addition, sterically hindered polyvinylamines were synthesized and studied, indicating that poly(N-methyl-N-vinylamine) could be the next-generation fixed-site carrier for CO₂ facilitated transport.
Dedicated to my husband Xiaochong, and my parents
Acknowledgments

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Publications


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Membrane separation is a promising technology for CO$_2$ separation and capture because of its energy efficiency, small footprint and operational simplicity. CO$_2$ facilitated transport membrane is an important group of membranes for CO$_2$ separation. In this chapter, the facilitated transport mechanism is described in conjunction with the chemical reactions of CO$_2$ and amine carriers. A wide range of facilitated transport membranes is discussed, including amine-based fixed-site carrier membranes, amine mobile carrier-containing membranes, and other facilitated transport membranes with different types of carriers and/or inorganic fillers to further improve the performance of facilitated transport membranes.
1.2. Polymer membranes for gas separation

CO₂ separation from other gases, such as N₂, H₂ and CH₄, has become increasingly critical to environment protection and fuel production. In particular, CO₂ capture from flue gas in coal-fired power plants is of great importance to the reduction of the greenhouse gas emission. Meanwhile, CO₂ separation from syngas and natural gas is also essential for increasing the energy efficiency of industrial fuel production and fuel cell applications. Conventional technologies of CO₂ separation include amine scrubbing and pressure swing adsorption. Amine scrubbing process, though the most mature technology for CO₂ separation, is limited by amine loss and handling of corrosive liquids, etc. [1]. Another obvious limitation of amine scrubbing and pressure swing adsorption is that a two-step process is needed for both of them and each step is governed by thermodynamic equilibrium [1-3]. As an alternative technology to amine scrubbing and pressure swing technology, membrane separation has received increasing attention due to its energy efficiency, operational simplicity and small footprint. Moreover, membrane separation by nature is a kinetic process. Permeability is the product of solubility and diffusivity. Although solubility is a thermodynamic equilibrium property, diffusivity is a kinetic phenomenon. Overall, the membrane process can overcome the thermodynamic equilibrium capacity limitation. Meanwhile, both flat-sheet and hollow-fiber membranes can be fabricated into the configuration of compact membrane modules, which makes the membrane separation possess a small footprint and operational simplicity. All the above
advantages make the membrane separation more promising, compared to conventional CO₂ separation technologies.

A membrane is generally defined as a thin barrier between the feed and permeate sides, which selectively allows the permeation of the target component from the feed side to the permeate side [4]. For gas separation, the membrane performance is usually characterized by the following two parameters: the first one is the permeability $P_i$, which is defined as

$$P_i = \frac{N_i}{(\Delta p_i/\ell)} \quad (1.1)$$

The common unit of $P_i$ is Barrer, $(1 \text{ Barrer} = 10^{-10} \text{ cm}^3 \text{ (STP)} / (\text{cm}^2 \cdot \text{s} \cdot \text{cm Hg})$. $N_i$ is the steady-state flux of component $i$. $\Delta p_i$ is the partial pressure difference of component $i$ between the feed and permeate sides, which is considered as the driving force in most gas separation scenarios for component $i$ to transport from the feed side to the permeate side. $\ell$ is the membrane thickness. $(P_i/\ell)$ is referred to as the permeance, and its common unit is the gas permeation unit (GPU, $1 \text{ GPU} = 10^{-6} \text{ cm}^3 \text{ (STP)} / (\text{cm}^2 \cdot \text{s} \cdot \text{cm Hg})$). Permeance is the indicator of the transport rate of a certain component through the membrane. The second parameter is selectivity (also referred to as separation factor), which is defined as

$$\alpha_{ij} = \frac{y_i/y_j}{x_i/x_j} \quad (1.2)$$

$y_i$ and $y_j$ are the molar fractions of components $i$ and $j$ on the permeate side, respectively whereas $x_i$ and $x_j$ are the molar fractions of components $i$ and $j$ on the feed side, respectively. Selectivity is the indicator of the extent of the separation of the target
component \( i \) from the other component \( j \) by the membrane. In many gas separation applications, the partial pressure on the permeate side is very small and thus can be neglected compared to that on the feed side. Under such conditions, the separation factor is equal to the ideal selectivity, which is defined as the ratio of the permeability of the gas components \([4]\):

\[
\alpha_{ij}^* = \frac{P_i}{P_j}
\]  

(1.3)

Membranes for \( \text{CO}_2 \) separation can be mainly categorized into inorganic membranes (e.g., silica membranes and zeolite membranes) and polymeric membranes. Because of their size-sieving property, inorganic membranes can demonstrate excellent selectivity. But difficulties exist in the continuous fabrication of defect-free inorganic membranes because of the brittleness of inorganic materials \([5]\). Polymeric membranes are much more favorable in terms of the ease of scale-up, because of the inherent flexibility of polymer materials. A summary of various types of membranes for \( \text{CO}_2 \) capture, ranging from polymeric membranes, inorganic membranes to ionic liquid membranes and facilitated transport membranes, can be found in a recent review article in 2015 by Kai and Duan \([6]\).

Generally, gas transport through polymeric membranes follows the solution-diffusion mechanism \([4]\). In such membranes, gas molecules first dissolve in the membranes at the interface of the feed side and the membrane, and then diffuse across the membrane to the permeate side. Permeability is the product of gas solubility and diffusivity \([4]\). The key shortcoming of solution-diffusion membranes is the trade-off between permeability and selectivity, governed by the Robeson upper bound \([7,8]\).
1.3. Facilitated transport membranes

However, things are different inside facilitated transport membranes. The facilitation of CO₂ transport is accomplished by the “carrier” inside a facilitated transport membrane, which can reversibly react with CO₂. At the feed-side interface of the membrane, CO₂ reacts with the carrier and forms a CO₂-carrier reaction product, which diffuses along its concentration gradient to the permeate side of the membrane. Owing to a lower CO₂ partial pressure on the permeate side, CO₂ is released from the CO₂-carrier reaction product to the permeate side, while regenerating the carrier that can then react with another CO₂ molecule on the feed side. Therefore, a major part of CO₂ is transported by the carriers inside the membranes in addition to the physical solution-diffusion as other non-reactive gases, such as N₂, H₂, CH₄, and CO [9]. As a result, both high permeability and selectivity can be obtained without being governed by the Robeson upper bond. The steady state flux of CO₂ through a facilitated transport membrane can be expressed as follows [10]:

\[
N_A = \frac{D_{AB}(C_{AB,1m}-C_{AB,m2})}{\ell} + \frac{D_A(C_{A,1}-C_{A,2})}{\ell}
\]  

\text{(1.4)}

\(N_A\) represents the total flux of CO₂ through a facilitated transport membrane at the steady state. \(D_{AB}\) and \(D_A\) are the diffusion coefficients of the CO₂-carrier reaction product and CO₂, respectively, inside a facilitated transport membrane. \(C_{AB,1m}\) and \(C_{AB,m2}\) are the concentrations of the CO₂-carrier reaction product at the feed-side and permeate-side
interfaces of the membrane, respectively. $C_{A,1}$ and $C_{A,2}$ are the concentrations of CO$_2$ which is dissolved at the feed-side and permeate-side interfaces of the membrane, respectively.

The advantage of facilitated transport membranes becomes even more favorable when applied for CO$_2$ capture from low CO$_2$ pressure streams, e.g., flue gas in coal-fired power plants, for which the CO$_2$ concentration in the flue gas is only about 14 vol.%. This can be explained in terms of the “carrier saturation” phenomenon [4], which occurs when CO$_2$ partial pressure or concentration is high such that CO$_2$ can react with all of the carrier molecules available in the membrane. This represents the maximum facilitation that the available carrier molecules can attain. Any further increase in the CO$_2$ partial pressure can only increase the flux through the solution-diffusion mechanism, which is minimal in comparison with the facilitated transport flux. On the other hand, when the CO$_2$ partial pressure is low, the CO$_2$ can only react with a small portion of the carrier molecules available in the membrane such that there are more carrier molecules available in the membrane for reaction with the CO$_2$, resulting in much enhanced facilitation of CO$_2$.

The carriers of facilitated transport membranes can be small and mobile molecules, referred to as mobile carriers, or functional groups anchored onto polymer backbones, which are the so-called fixed-site carriers. For a mobile carrier, the reaction product of CO$_2$ and mobile carrier diffuses inside the membrane. For a fixed-site carrier, CO$_2$ transport is governed by the “hopping” mechanism [11]. The fixed-site carrier can increase the membrane stability because of its polymeric nature and is stable inherently in the membrane. On the other hand, the mobile carrier may enhance the CO$_2$ flux because of its high mobility compared to the fixed carrier. However, it is prudent to select the mobile
carrier that has no volatility such as a salt, e.g., amino acid salt, so that it can stay put inside the membrane. A combination of fixed-site and mobile carriers should provide good membrane stability along with good CO₂ facilitation.

Supported liquid membrane, as the earliest form of the facilitated transport membrane, is composed of a porous substrate with its pores filled with a carrier-containing liquid [13-18]. The major drawback of the SLM is the loss of carriers. In order to minimize the carrier loss, scientists developed ion-exchange membranes, where the charged carrier species was immobilized onto the counterions on the polymer backbone by the electrostatic force [19-22]. But, the stability of the ion-exchange membranes was still not adequate because of charge neutralization, and their fluxes were low because of their large membrane thicknesses, in addition to the case that the polymers used in membranes were not soluble in water, which limited the potential of the membranes to achieve high separation performance. Quinn et al. developed polyelectrolyte membranes, in which the polymer that contained high ionic content was water-soluble [23-26]. The most commonly used ion for polyelectrolyte membranes is fluoride (F⁻). Fluoride cannot directly react with CO₂, but it can enhance the basicity of water molecules, and thus catalyze the hydration of CO₂ to form bicarbonate (HCO₃⁻). The enhanced basicity of water arises from the hydrogen bonding between F⁻ and water molecules in the hydrated fluoride ion [24]. The incorporation of a fluoride salt, such as CsF, demonstrated a significantly improved CO₂ separation performance [25]. It should be noted that the counter ion may influence the negative charge density on F⁻, thus impacting the strength of the hydrogen bonding between F⁻ and water molecules [25]. Based on this point, the counter ion may play a role on the
basicity of water molecules, hence affecting the CO$_2$ separation performance. In other words, the counter ion, which can enhance the hydrogen bonding of F$^-$ and water molecules, may lead to a better CO$_2$ separation performance. Meanwhile, the counter ion may also influence the membrane homogeneity. Quinn et al. investigated the effects on CO$_2$ separation performances of KF and CsF salts, respectively. They found that the membrane with KF exhibited large, non-selective gas fluxes indicative of defects, which might be caused by the crystallization of KF because of the low solubility of KF in water [25].

In recent years, the amine-containing facilitated transport membranes, which are homogeneous and in solid phase, have gained intensive attention. Deng et al. reviewed the CO$_2$ facilitated transport membranes and mixed matrix membranes with nanoparticles incorporated into polyamine membranes, in which the selection of fixed-site carrier membranes was discussed and the interaction of nano-silica particles in polymer membranes was elaborated [27]. This present review focuses on the work of amine-based fixed-site carrier (polyamine) membranes, mobile carrier-containing membranes, and other facilitated transport membranes with different types of carrier species and/or inorganic fillers to further improve the performance of facilitated transport membranes.

Inspired by the amine scrubbing process, in which CO$_2$ is absorbed by amine solvent (e.g., alkanolamine), amine and its derivatives are the most commonly used carriers for facilitated transport membranes. The reaction between CO$_2$ and amines can be described with the zwitterions-mechanism, which was originally proposed by Caplow [28] and reintroduced by Danckwerts [29]. The reaction is usually described as a two-step
reaction. In the first step (Eq. (1.5)), which is believed as the rate-controlling step, CO₂ reacts with amine to form a zwitterion, as an intermediate. The zwitterion is deprotonated rapidly by another molecule of amine itself to form a carbamate ion and a protonated amine (Eq. (1.6)). The overall reaction (Eq. (1.7)) shows clearly that the stoichiometric loading of CO₂ is one mole of CO₂ per two moles of amine, i.e., 0.5 mole of CO₂ per mole of amine.

It should be noted that the amine is unhindered.

\[
\text{CO}_2 + \text{R-NH}_2 \rightleftharpoons \text{R-NH}_2^+\text{COO}^- \quad (1.5)
\]

\[
\text{R-NH}_2^+\text{COO}^- + \text{R-NH}_2 \rightleftharpoons \text{R-NH-COO}^- + \text{R-NH}_3^+ \quad (1.6)
\]

\[
\text{CO}_2 + 2\text{R-NH}_2 \rightleftharpoons \text{R-NH-COO}^- + \text{R-NH}_3^+ \quad (1.7)
\]

A sterically hindered amine is defined as a primary amine with the amino group attached to a tertiary carbon atom or a secondary amine with the amino group attached to a secondary or tertiary carbon atom [30]. For a sterically hindered amine, the carbamate ion is not stable due to the incorporation of a bulky substituent group to the nitrogen site, and it is thus converted into the bicarbonate ion (Eq. (1.8)). Therefore, the stoichiometric CO₂ loading is doubled, with one mole of CO₂ per mole sterically hindered amine, which is the theoretical maximum CO₂ loading [31].

\[
\text{CO}_2 + \text{R-NH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^- + \text{R-NH}_3^+ \quad (1.8)
\]

1.4. Polyamine fixed-site carrier membranes

Fixed-site carrier membranes are usually referred to as the membranes consisting of pure fixed-site carriers or the blends of polymer matrix and fixed-site carriers. The
chemical structures of the most commonly used polyamine fixed-site carriers, namely polyvinylamine (PVAm), polyallylamine (PAAm), and polyethylenimine (PEI), are illustrated in Figure 1.1.

As shown in Figure 1.1, each repeating unit of PVAm has an amino group attached directly onto the polymer backbone. PVAm has the highest content of primary amino groups of any polymers [32]. Therefore, it has been widely adopted as the fixed-site carrier in facilitated transport membranes.

Hägg et al. did extensive research on polyvinylamine-based fixed-carrier membranes for the separation of CO\textsubscript{2} from CH\textsubscript{4} or N\textsubscript{2} [33-45]. The polyvinylamine they used in the beginning was obtained by acrylamide polymerization followed by the Hofmann reaction of polyacrylamide [33]. They investigated the effect of molecular weight on CO\textsubscript{2}/CH\textsubscript{4} separation performance and found that the CO\textsubscript{2} permeance did not have significant change whereas CH\textsubscript{4} permeance dropped dramatically with increasing the molecular weight from 20,000 to 80,000; this resulted in the CO\textsubscript{2}/CH\textsubscript{4} selectivity improved by 10 times. The decrease in CH\textsubscript{4} permeance could be explained by the restricted chain mobility due to the increased molecular weight, which resulted in the reduction of CH\textsubscript{4} diffusivity inside the membrane. However, CO\textsubscript{2} permeance was not impacted by the molecular weight change. These results indicated that the transport of CO\textsubscript{2} inside polyvinylamine membranes followed the facilitated transport mechanism whereas the transport of CH\textsubscript{4} followed the solution-diffusion mechanism.

In order to improve the membrane mechanical strength and selectivity, Hägg et al. blended in NH\textsubscript{4}F as a crosslinking agent, which resulted in the “physical crosslinking” via
hydrogen bonding. Meanwhile, because of the aforementioned facilitation role of fluoride ion on CO₂ transport and high density of hydrogen bonding introduced by NH₄F, the CO₂/CH₄ selectivity was dramatically increased [33,45].

For fixed-site carrier membranes, the molecular weight of fixed-site carrier is also critical for the mechanical strength of the membranes, film forming ability and the possibility to prepare thin membranes in order to improve the permeance. Later, higher molecular weight polyvinylamine (340,000) was obtained by the purification of the commercial PVAm product by Hägg et al. and used to prepare fixed-site carrier membranes. At 2-bar feed pressure and 25°C, the membranes with a thickness of 1.2 μm demonstrated 103.7 GPU and 197 CO₂/N₂ selectivity [35].

The molecular weights of many fixed-site carriers are not sufficiently high to provide decent mechanical strength and film forming ability. Moreover, some polyamines are easy to crystallize resulting from the regularity in their chain structures. To tackle the above issues, researchers have found that it is an effective approach to blend fixed-site carriers with another hydrophilic high molecular weight polymer, which is mainly served as the polymeric matrix. The most widely used polymeric matrix for facilitated transport membranes is polyvinylalcohol (PVA) [10,12]. PVA itself does not contain the functional groups that can react with CO₂. But because of the abundant hydroxyl groups, PVA is highly hydrophilic and compatible with amines, making it a good candidate as the polymeric matrix to accommodate the amine carriers. And it can form hydrogen bonding with amino groups, which can increase the mechanical strength of the membrane as well as film-forming ability [10,12]. Using this approach, Hägg et al. could obtain CO₂/CH₄
selectivity of 35 and CO₂ permeance of 111 GPU at 2 bars, 25°C and relative humidity around 90% with a thickness of 300 nm [36]. The incorporation of PVA not only improved the mechanical strength of the membranes but also affected the swelling behavior of the membranes as well as water retention inside the membranes. Hägg et al. studied the swelling behavior of PVA/PVAm blend membranes by varying the relative humidity for gas separation measurements. They found that the swelling degree of the membrane containing 20 wt.% PVA and 80 wt.% PVAm increased exponentially with relative humidity. A CO₂ permeance of 307.4 GPU and CO₂/N₂ selectivity of 160 were obtained at the relative humidity of 95% [39]. This could be explained by the role of water on CO₂ facilitated transport in amine-containing membranes [46]: (1) the membrane swelled in the presence of H₂O, thus accelerating the CO₂ “hopping” in the fixed-site carrier membrane, and (2) in the CO₂-amine reaction, zwitterion and carbamate ion can be hydrolyzed by water, thus accelerating the formation of carbamate ion and the regeneration of the free amine carrier as shown in Eqs. (1.9) and (1.10), respectively [10,31]:

\[
\text{R-NH}_2^+\text{COO}^- + \text{H}_2\text{O} \rightleftharpoons \text{R-NH-COO}^- + \text{H}_3^+\text{O} \quad (1.9)
\]
\[
\text{R-NH}_2\text{COO}^- + \text{H}_2\text{O} \rightleftharpoons \text{R-NH}_2^- + \text{HCO}_3^- \quad (1.10)
\]

In order to further improve the separation performance of PVAm-based fixed-site carrier membranes, Hägg et al. investigated the effect of pH of PVAm coating solution on membrane performance [43]. According to their results, the pH of PVAm coating solution could affect the protonation of amino groups of PVAm and the solubility of CO₂ in the PVAm membranes. The number of free amino groups increased with increasing the pH, thus leading to an improved CO₂/N₂ separation performance. Later, Hägg et al. optimized
the fabrication procedures and preparation conditions of their PVA/PVAm blend membranes with respect to CO₂/CH₄ separation [45]. In their work, a CO₂ permeance of 215 GPU (CO₂/CH₄ selectivity of about 37) was obtained with 80 wt.% PVAm in the dry membranes and a CO₂/CH₄ selectivity of 45 (CO₂ permeance of about 178 GPU) was obtained with 67 wt.% PVAm in the dry membranes. The membrane performance was stable for over 5 months.

Polyallylamine (PAAm) is another common fixed-site carrier for CO₂ transport [10,12,47,48]. Wang et al. synthesized polyallylamine by free radical polymerization and blended 20 wt.% PAAm into the PVA matrix to prepare membranes [48]. They achieved the highest CO₂ permeance of about 26 GPU and CO₂/CH₄ selectivity of 58 at 0.1 MPa feed gas pressure and 25°C [48].

In addition to PVAm and PAAm, PEI is also a common polyamine used as the fixed-site carrier [49-52]. Matsuyama et al. blended PEI with PVA to prepare membranes and used heat treatment to enhance the crosslinking of the membranes and improve the selectivity of CO₂/N₂ up to 230 at 25°C and a CO₂ partial pressure of 0.065 atm [52].

Among the aforementioned three polyamines (PVAm, PAA, PEI), PVAm has the highest amino group concentration. Since the majority of the amino groups in PEI are secondary and tertiary amine, PEI has a relatively lower reaction rate with CO₂, compared with PVAm and PAAm. Because the amino groups in PVAm are attached directly to the backbones, the steric hindrance degree of the primary amino groups in PVAm is higher than that in PAAm. The steric hindrance degree can be expressed by Taft’s steric hindrance parameter $\Sigma \text{Es}$ [53]. According to the group contribution method for the $\Sigma \text{Es}$ calculation,
the steric hindrance degree of PVAm is 0.93, whereas the steric hindrance degree of PAAm is only 0.43. As mentioned in the first section, a sterically hindered amine has a higher CO₂ loading capacity, thus is a more effective CO₂ carrier than an unhindered amine. Sterically hindered amines are mostly used in amine-scrubbing processes, in which small molecules of sterically hindered amines are used, e.g., 2-amino-2-methyl-1-propanol (AMP) [54,55]. Zhao and Ho were the first to demonstrate the steric hindrance effect in solid membrane phase. In their work, unhindered polyallylamine was modified into sterically hindered polyamines, namely poly-N-isopropylallylamine, poly-N-isobutylallylamine, and poly-N-tert-butylallylamine, and blended with a crosslinked PVA matrix to prepare the fixed-site carrier membranes containing 30 wt.% crosslinked PVA and 70 wt.% polyamine fixed-site carrier. Among those polyamines, the moderately hindered poly-N-isopropylallylamine exhibited the greatest CO₂ facilitation, showing a dramatic 440% enhancement in CO₂ permeability along with a 135% increase in CO₂/H₂ selectivity and a 311% increase in CO₂/N₂ selectivity compared to polyallylamine as the fixed-site carrier. Their work shows a promising direction on the exploration of new generation polyamine-based fixed-site carriers [56].

Fixed-site carriers are not limited to the above polyamines. Wang et al. synthesized poly(N-vinyl-γ-sodium aminobutyrate-co-sodium acrylate) and prepared fixed-site carrier membranes [57]. Through crosslinking with metal ions, their membranes could demonstrate a CO₂/N₂ ideal selectivity of 524.5. Feng et al. synthesized poly(N,N-dimethylaminoethyl methacrylate) by free radical bulk polymerization, and coated onto polysulfone substrates, followed by crosslinking with p-xylylene dichloride in a heptane
solution [58]. Their facilitated CO₂ transport was based on the amino groups in poly(N,N-dimethylaminoethyl methacrylate).

Some research on fixed-site carrier membranes also focused on the technique of membrane synthesis via interfacial polymerization [59-63], which is mostly used in the preparation of reverse osmosis membranes. Wang et al. adopted the interfacial polymerization of water-soluble triethylenetetramine (TETA) and hexane-soluble trimesoyl chloride (TMC) followed by heat treatment for the development of novel fixed-site carrier membranes [60-63]. They found that heat treatment was a successful way in stabilizing membrane performance with pressure. They obtained a CO₂ permeance of 13.3 GPU and CO₂/CH₄ selectivity of 94.1 at 1.1 atm feed pressure and a CO₂ permeance of 12.8 GPU and CO₂/CH₄ selectivity of 40.5 at 5 atm feed pressure [60]. The CO₂ separation performance of membranes prepared by interfacial polymerization can be tuned by changing the amine-based water-soluble monomers. Wang et al. developed a fixed carrier membrane containing tertiary amino groups by the interfacial polymerization of 3,3′-Diamino-Ν-methyldipropylamine (DNMDAm) and TMC [61]. This membrane showed a CO₂ permeance of 118 GPU and a CO₂/CH₄ selectivity of 37 at 1.1 atm feed pressure. It should be noted that the CO₂ separation performance of fixed-site carrier membranes prepared by interfacial polymerization can be greatly affected by the membrane morphology determined by the interfacial polymerization conditions. Wang et al. investigated the relationships among the membrane preparation conditions, membrane structure and separation performance, and found that the choice of organic solvent and the monomer concentrations in aqueous and organic phases could all play an important role in
membrane morphology [62]. Their finding has provided a basis for the controlled preparation of fixed-site carrier membranes by interfacial polymerization. Some key gas transport measurement results of polyamine fixed-site carrier membranes are shown in Table 1.1.

1.5. Amine-based mobile carriers

Because of the low mobility of fixed-site carriers, the separation performance of that type of membrane is rather limited. Therefore, the incorporation of a mobile carrier is advantageous for significantly improving the separation performance of facilitated transport membranes [10,12,49-51]. Alkanolamines are the mostly widely used amine solvents for CO₂ separation in aqueous amine scrubbing processes. Feng et al. introduced various alkanolamines, including monoethanolamine (MEA), 2-amino-2-methyl-1-propanol (AMP), diethanolamine (DEA) and N-methylidethanolamine (MDEA), as mobile carriers into a polyvinylalcohol polymer matrix to prepare facilitated transport membranes [64,65]. They found that the membranes containing DEA demonstrated the best permselectivity among all the alkanolamines used in their work. A CO₂/N₂ ideal selectivity of 100 was obtained on their DEA containing membranes at 23°C, and the membranes could remain stable for 5 weeks. Another group of amine-based mobile carrier is alkylamine, e.g., ethylenediamine (EDA) [66,67,68]. Wang et al. blended EDA into their synthesized PVAm and obtained a CO₂ permeance of 607 GPU and a CO₂/N₂ selectivity of 106 at 22°C for the membrane with the EDA/PVAm weight ratio of 3 [67]. Wang et al.
later incorporated piperazine (PZ) into PVAm. With the PZ/PVAm weight ratio of 1.43, a remarkably high CO$_2$ permeance was obtained for an ultrathin membrane [68].

The drawback of alkanolamine and alkylamine as mobile carriers is the carrier leakage caused by the high volatility of those types of small-molecule amines. Some amine-containing dendrimers were introduced as mobile carriers because of the reduced volatility of the amine carriers. Wang et al. synthesized pentaerythrityl tetraethylenediamine (PETEDA) dendrimer and used as the mobile carrier to blend with polyvinylalcohol. They could incorporate PETEDA up to approximately 79 wt.% in the dry membrane and achieved a CO$_2$ permeance of 81 GPU and CO$_2$/CH$_4$ selectivity of 52 at about 2 atm and 20°C [69]. However, the low diffusivity of dendrimers limited their application as mobile carriers of high efficiency.

Amino acid is another commonly used mobile carrier for CO$_2$ facilitated transport as well [10,12,49-51]. Recently, Ho et al. developed polymeric facilitated transport membranes, consisting of crosslinked polyvinylalcohol as the polymer matrix, polyamine as the fixed-site carrier and amino acid salts as the mobile carriers [10,12,46,49-51,70-73]. The advantage of amino acid salts as mobile carriers is the good diffusivity and negligible volatility. Moreover, the presence of salts can increase the ionic strength of the membrane, which can help to reduce the solubility of non-polar gases in the membrane. Following the earlier work of Ho [49,50], Tee and Ho synthesized facilitated transport membranes using polyethylenimine (PEI) as the fixed-site carrier and $N,N$-dimethylglycine (DMG) salts as the mobile carriers blended in the highly hydrophilic crosslinked polyvinylalcohol (PVA) matrix [51]. Zou and Ho further improved the work by using polyallylamine (PAAm) as
the fixed-site carrier and 2-aminoisobutyric acid potassium salt (AIBA-K) as the mobile carriers in the crosslinked PVA, and they obtained a CO₂ permeability of >6000 Barrers along with a very high CO₂/H₂ selectivity of about 200 – 400 and an extraordinarily high CO₂/N₂ selectivity of 500 – 1500 for membrane thicknesses of 30 – 60 μm [10].

Zhao and Ho used the moderately hindered poly-N-isopropylallylamine as the fixed-site carrier and AIBA-K as the mobile carrier and obtained a CO₂ permeability of over 6500 Barrers, a CO₂/H₂ selectivity of more than 300, and a CO₂/N₂ selectivity of at least 650 at 110°C and a feed pressure of 2 atm. Their membrane also showed a good stability of at least 430 h at 110°C and 2 atm [12]. Tong et al. used commercial polyvinylamine (Lupamin®) as the fixed-site carrier and AIBA-K as the mobile carrier and obtained a CO₂ permeability of 3000 Barrers at 120°C and a CO₂/H₂ selectivity of over 180. They also investigated water vapor transport properties across facilitated transport membranes and found that the nanoporous polysulfone substrates provided the main mass transfer resistance to water vapor transport [46]. Chen and Ho synthesized high molecular weight PVAm as the fixed-site carrier and polymer matrix along with various amino acid salts (lithium glycinate, potassium glycinate, and piperazine glycinate) incorporated as mobile carriers. They achieved a CO₂ permeance of 1100 GPU and a CO₂/N₂ selectivity of 210 at 57°C with a 200-nm thick selective layer containing 35 wt.% PVAm and 65 wt.% piperazine glycinate [73]. The chemical structures of above amino acid salts used in Ho et al.’s work are shown in Figure 1.2. Among the four mobile carriers in Figure 1.2, DMG-Li is a tertiary amine, which has the lowest reaction rate. Glycine-Li has the smallest molecular size and is linear, making it with the highest diffusivity. AIBA-K is a sterically
hindered amine and thus has a high CO$_2$ loading capacity. Piperazine-glycinate is the only one that has two amino groups in one molecule, resulting in the highest CO$_2$ permeance membrane among those investigated by Ho et al. [73].

Matsuyama et al. incorporated ionic liquids containing amino acids as the anionic portion and used the amino acids as mobile carriers [74,75]. But, the cationic portion of the ionic liquids was very bulky, leading to low CO$_2$ transport performance. They also incorporated 2,3-diaminopropionic acid (DAPA) into a polyvinylalcohol-polyacrylic acid copolymer matrix and achieved 938 GPU and CO$_2$/N$_2$ selectivity of 1070 at 125°C and 300 KPa for a feed gas consisting of 3.6 mol% CO$_2$, 32.9 mol% N$_2$ and 63.5 mol% H$_2$O [76]. Some key gas transport measurement results of amine mobile carrier-containing membranes are summarized in Table 1.2.

1.6. Other facilitated transport membranes

Though most of the facilitated transport membrane work for CO$_2$ separation and capture focuses on amine-based carriers, enzyme as a biomimetic catalyst for the CO$_2$-water reaction has also attracted considerable interest. It should be noted that enzyme cannot directly react with CO$_2$, but in a similar way as fluoride (F$^-$), it can catalyze the hydration of CO$_2$. Carbonic anhydrase (CA) is the most commonly enzyme for CO$_2$ absorption, since it has the fastest catalysis rate as known so far [77-80]. The limitation of enzyme CA is its short lifetime, which may lead to the instability of the membrane. Deng et al. developed a mimic enzyme that was more stable than natural enzyme CA and
incorporated it into a membrane contactor [81]. They showed good potential for such a membrane contactor to be applied for CO\textsubscript{2} capture from a low CO\textsubscript{2} concentration stream.

Facilitated transport membranes in mixed matrix configuration have also been investigated. Xing and Ho incorporated fumed silica particles into facilitated transport membranes containing crosslinked PVA and amine carriers, and demonstrated a good stability at 107°C and 15 atm [82]. Zhao and Ho incorporated 2 wt.% multi-walled carbon nanotubes (MWNTs), and they obtained a CO\textsubscript{2}/H\textsubscript{2} selectivity of 43 and a CO\textsubscript{2} permeability of 836 Barrers at 1.52 MPa (15 atm or 220 psi) and 380.2 K (107°C) [83]. Such performance was maintained with no significant change for 444 hours. Hägg et al. blended 1 wt.% carbon nanotubes (CNTs) into PVAm/PVA membranes for high-pressure gas transport measurements [84]. They found that at 10 – 15 bar, the CO\textsubscript{2} permeance was more than doubled in the CNT reinforced PVAm/PVA membrane compared with the counterpart PVAm/PVA membrane. Ansaloni et al. incorporated amino-functionalized MWNTs and improved the CO\textsubscript{2} permeability to 957 Barrers, CO\textsubscript{2}/H\textsubscript{2} selectivity to 56, and CO\textsubscript{2}/N\textsubscript{2} selectivity to 384 at 107°C and 15 bar [85]. Their amino-functionalization of MWNTs was believed to improve the compatibility between MWNTs and the facilitated transport membranes. Wang et al. incorporated the imidazolate framework ZIF-8 into PVAm membranes and found an improvement on the CO\textsubscript{2}/N\textsubscript{2} separation performance [86]. In addition, Wang et al. incorporated hydrotalcite channels in PEI based fixed-site carrier membranes, which provided unobstructed channels for mobile carriers movement. By using this approach, Wang et al. were able to achieve very high CO\textsubscript{2} permeance with good CO\textsubscript{2}/N\textsubscript{2} selectivity at the feed pressure of 1.1 bar [87].
1.7. Significance and summary of this research

There has been intensive research on the CO\textsubscript{2} facilitated transport membranes for various CO\textsubscript{2} separation and capture applications. In this research, different properties of facilitated transport membranes were studied that have rarely been reported, including water vapor transport property, oxidative stability and the factors that can affect the water retention capability of facilitated transport membranes.

Most of the studies on CO\textsubscript{2} facilitated transport membranes focused on their CO\textsubscript{2} separation performances. In fact, water vapor is present in many industrial applications where CO\textsubscript{2} facilitated transport membranes are applied for CO\textsubscript{2} removal. But the water vapor transport property of CO\textsubscript{2} facilitated transport membranes was rarely studied. In Chapter 2, the transport mechanism of water vapor in facilitated transport membranes was elucidated, and the approaches to mitigate the water vapor transport were investigated and provided.

In Chapter 3, different types of CO\textsubscript{2} facilitated transport membranes were studied for the application of hydrogen purification at a high temperature (120°C) and a low water partial pressure (~0.54 atm). It was found that under those conditions, the water retention capability of the membrane played a more important role in CO\textsubscript{2}/H\textsubscript{2} separation performance than the content of amine in the membrane. An interesting finding was that the hydroxide-containing species could help to improve amine-containing membrane performance significantly, though the reaction rate constant of CO\textsubscript{2} and hydroxide is much
lower than that of CO₂ and amine. The membrane composition was modified and improved by incorporating a fluoride-containing polyelectrolyte and quaternary ammonium hydroxide to improve the water retention capability of the membrane.

Chapter 4 mainly discusses the application of different types of amine-containing membranes for flue gas carbon capture, including crosslinked poly(vinyl alcohol) based membranes prepared by spin coating and high-molecular-weight polyvinylamine based thin membranes prepared by knife casting. The incorporation of a highly permeable gutter layer and a cover layer was found to improve CO₂/N₂ separation performance significantly for membranes prepared by spin-coating. In this chapter, the carrier saturation phenomenon was also demonstrated by the comparison of amine-containing membranes with different concentrations of CO₂ in the feed gas.

In Chapter 5, the effect of steric hindrance is discussed for polyvinylamine fixed-site carrier membranes. Sterically hindered polyvinylamines were synthesized and optimized with respect to the degree of steric hindrance. The effect of temperature on the enhancement of membrane performance by amine steric hindrance was also investigated. Poly(N-methyl-N-vinylamine) membranes demonstrated a CO₂ permeability of 6804 Barrers, a CO₂/N₂ selectivity of 350, and a CO₂/H₂ selectivity of 162 at 102°C with an 80% water vapor content on the feed side, which were almost 4 times of the performances of unhindered polyvinylamine membranes. Therefore, sterically hindered poly(N-methyl-N-vinylamine) can be considered as the next-generation fixed-site carrier for facilitated transport membranes.
In some applications, oxygen is present in the feed gas (e.g., flue gas) and/or in the sweep gas (e.g., air sweep), therefore oxidative stability is a key criterion to evaluate the membrane performance for those applications. Chapter 6 addresses the oxidative degradation issue of facilitated transport membranes. Oxidative stability was investigated, and the suitability of different types of facilitated transport membranes for various oxygen-present applications was discussed.
Table 1.1. CO₂ separation performances of polyamine fixed-site carrier membranes.\(^a\)

<table>
<thead>
<tr>
<th>Membrane Type</th>
<th>Feed Gas Composition(^b)</th>
<th>Operating Conditions(^c)</th>
<th>CO₂ Permeance (GPU)</th>
<th>CO₂ vs. Gas Permeability (Barrers)</th>
<th>CO₂ vs. Gas Selectivity(^d)</th>
<th>Ref. No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVAm (340,000 Mw)</td>
<td>10% CO₂, 90% N₂</td>
<td>25 °C, 2 bar, ~100% RH</td>
<td>103.7 GPU</td>
<td>197</td>
<td>35</td>
<td></td>
</tr>
<tr>
<td>PVAm/PVA</td>
<td>10% CO₂, 90% N₂</td>
<td>25 °C, 2 bar, 95% RH</td>
<td>307.4 GPU</td>
<td>160</td>
<td>39</td>
<td></td>
</tr>
<tr>
<td>PVAm/PVA</td>
<td>10% CO₂, 90% CH₄</td>
<td>25 °C, 2 bar, ~100% RH</td>
<td>178 GPU</td>
<td>45</td>
<td>45</td>
<td></td>
</tr>
<tr>
<td>PAAm/PVA</td>
<td>10% CO₂, 90% CH₄</td>
<td>25 °C, 1 bar, ~100% RH</td>
<td>26 GPU</td>
<td>58</td>
<td>48</td>
<td></td>
</tr>
<tr>
<td>PEI/PVA</td>
<td>6.5% CO₂, 93.5% N₂</td>
<td>25 °C, 1 bar, ~100% RH</td>
<td>850 Barrers</td>
<td>160</td>
<td>52</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>650 Barrers(^e)</td>
<td>230(^e)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PAAm-C₃H₇</td>
<td>20% CO₂, 40% H₂, 40% N₂</td>
<td>110 °C, 2 bar, H₂O % f: 40.5%, H₂O % f: 57.6%</td>
<td>297 Barrers</td>
<td>H₂: 40</td>
<td>56</td>
<td></td>
</tr>
<tr>
<td>VSA-SA/ metal ion</td>
<td>50% CO₂, 50% CH₄</td>
<td>20 °C, 1.1 bar, ~100% RH</td>
<td>9.2 GPU</td>
<td>524.5(^*)</td>
<td>57</td>
<td></td>
</tr>
<tr>
<td>TMC-TETA IP(^f)</td>
<td>10% CO₂, 90% CH₄</td>
<td>32 °C, 1.1 bar, ~100% RH</td>
<td>13.3 GPU</td>
<td>94.1</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>32 °C, 5.1 bar, ~100% RH</td>
<td>12.8 GPU</td>
<td>40.5</td>
<td></td>
</tr>
<tr>
<td>DNMDAm- TMC IP(^f)</td>
<td>10% CO₂, 90% CH₄</td>
<td>25 °C, 1.1 bar, ~100% RH</td>
<td>118 GPU</td>
<td>37</td>
<td>61</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>173 GPU</td>
<td>70</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) The highest performances are shown in the table when various gas transport measurement results were reported in the work.
Table 1.1: Continued

b The feed gas composition refers to the composition on a dry basis.

c The pressure indicated in the table is the feed pressure; Permeate pressure is about 1 atm unless otherwise described; “RH” stands for relative humidity; “H₂O % ᵇ” stands for water content on the feed side; “H₂O % ᵇ” stands for water content on the permeate side.

d “*” indicates ideal selectivity.

e The results of 650 Barrers and 230 selectivity were obtained by heat treatment under a higher temperature than the results of 850 Barrers and 160 selectivity.

f “IP” stands for interfacial polymerization.
Table 1.2. CO₂ separation performances of amine mobile carrier-containing membranes.ᵃ

<table>
<thead>
<tr>
<th>Amine Carriers</th>
<th>Feed Gas Compositionᵇ</th>
<th>Operating Conditionsᶜ</th>
<th>CO₂ Permeance (GPU) / Permeability (Barrers)</th>
<th>CO₂ vs. Gas Selectivityᵈ</th>
<th>Ref.</th>
<th>No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAAm; AIBA-K (K₂CO₃-KHCO₃)</td>
<td>20% CO₂, 40% H₂, 40% N₂</td>
<td>120 °C, 2 bar,</td>
<td>9710 Barrers</td>
<td>H₂: 523</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>H₂O % r: 59%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>H₂O % p: 85%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PAAm-C₃H₇; AIBA-K</td>
<td>20% CO₂, 40% H₂, 40% N₂</td>
<td>110 °C, 2 bar,</td>
<td>6577 Barrers</td>
<td>H₂: 340</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>H₂O % r: 40.5%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>H₂O % p: 57.6%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVAm; AIBA-K (K₂CO₃-KHCO₃)</td>
<td>10% CO, 40% H₂, 50% CO₂</td>
<td>120 °C, 1 bar,</td>
<td>3000 Barrers</td>
<td>H₂: 180</td>
<td>46</td>
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<tr>
<td></td>
<td></td>
<td>H₂O % r: 66.7%</td>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td></td>
<td>H₂O % p: 57.6%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PEI; DMG-Li</td>
<td>20% CO₂, 40% H₂, 40% N₂</td>
<td>90 °C, 1 bar, ~100% RH</td>
<td>~1700 Barrers</td>
<td>H₂: ~46</td>
<td>51</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DEA</td>
<td>Pure CO₂ or Pure N₂</td>
<td>23 °C, 1.7 bar, ~100% RH</td>
<td>~8 GPU</td>
<td>100*</td>
<td>64</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVAm; EDA</td>
<td>20% CO₂, 80% N₂</td>
<td>22 °C, 1 bar, ~100% RH</td>
<td>607 GPU</td>
<td>106</td>
<td>67</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PETEDA</td>
<td>10% CO₂, 90% CH₄</td>
<td>20 °C, 2 bar, ~100% RH</td>
<td>81 GPU</td>
<td>52</td>
<td>69</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVAm; Gly-PZ</td>
<td>20% CO₂, 80% N₂</td>
<td>57 °C, 1.1 bar, ~100% RH</td>
<td>1100 GPU</td>
<td>210</td>
<td>73</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DAPA</td>
<td>9.9% CO₂, 90.1% N₂, H₂O % r: 63.5%</td>
<td>125 °C, 3 bar,</td>
<td>938 GPU</td>
<td>1070</td>
<td>76</td>
<td></td>
</tr>
</tbody>
</table>

ᵃ The highest performances are shown in the table when various gas transport measurement results were reported in the work.
Table 1.2: Continued

b The feed gas composition refers to the composition on a dry basis.

c The pressure indicated in the table is the feed pressure; Permeate pressure is about 1 atm unless otherwise described; “RH” stands for relative humidity; “H₂O %" stands for water content on the feed side; “H₂O %p” stands for water content on the permeate side.

d “*” indicates ideal selectivity.
Figure 1.1. Chemical structures of polyvinylamine, polyallylamine and polyethylenimine.
Figure 1.2. Chemical structures of the mobile carriers in Ho et al.’s work [10,12,46,51,73].
Nomenclature

\( l \)    membrane thickness

\( N_i \)    steady-state flux of species \( i \)

\( P_i \)    permeability of species \( i \)

\( \Delta p_i \)    partial pressure difference across the membrane

\( x \)    mole fraction in the retentate stream, dimensionless

\( y \)    mole fraction in the permeate stream, dimensionless

Greek letters

\( \alpha_{ij} \)    Selectivity of species \( i \) over species \( j \)
Chapter 2: Water vapor and CO₂ transport through amine-containing facilitated transport membranes

2.1. Summary

Amine-containing CO₂ facilitated transport membranes have great potential to be applied for hydrogen purification from synthesis gas. In some applications, the humidity of the retentate stream is required as well as the purity of hydrogen. The membranes are highly hydrophilic, and they exhibit not only high CO₂ permeance but also high water vapor permeance. In this work, the transport of water vapor and CO₂ through the membranes composed of an amine-containing selective layer and a microporous polysulfone substrate was investigated. From the experiments conducted, water vapor permeance appeared to be independent of the selective layer thickness, indicating that the substrate is the controlling factor of the mass transfer resistance to water vapor transport. Moreover, water vapor permeance appeared to reduce linearly with increasing the number of the substrate layers. But, CO₂ permeance and CO₂/H₂ selectivity did not change significantly as the number of the substrate layers increased. These results indicated that the CO₂ separation performance is governed by the selective layer as expected. In addition, the membranes synthesized from Lupamin® containing 34% polyvinylamine and 66% salt...
(sodium formate) demonstrated better CO₂ separation performance than those from pure polyvinylamine, presumably due to better water retention capability of the salt than polyvinylamine.
2.2. Introduction

In this work, PVA was chosen as the polymer matrix and crosslinked by glutaraldehyde as reported in previous work [51,70–72]. AIBA-K and DMG-K were used as the mobile carriers. Polyvinylamine synthesized by our group following the procedures reported in the literature [68] and Lupamin® were used as the fixed-site carriers. The membranes synthesized were composed of mobile and fixed carriers in the crosslinked PVA matrix supported on a microporous polysulfone substrate. The amine-containing CO₂ facilitated transport membranes are highly hydrophilic and permeable to water. However, there has been limited work on water vapor transport through the facilitated transport membranes. Hence, water permeation as well as CO₂/H₂ separation was investigated in this work. The main aim of this work was to determine the controlling factor for water vapor transport through the facilitated transport membranes. The relationship between water vapor permeance and the number of polysulfone substrate layers was also investigated. Furthermore, a comparison on CO₂/H₂ separation between commercial Lupamin® and synthesized polyvinylamine was carried out.
2.3. Experimental

2.3.1 Materials

Lupamin® (containing 34 wt.% polyvinylamine (PVAm) and 66 wt.% salt (mainly sodium formate)) was donated by BASF AG, (Germany). 2-Aminoisobutyric acid (99.46%) was purchased from CHEM-IMPEX International. Poly (vinyl alcohol) (Poval S-2217, 92% purity, 87 mol% - 89 mol% hydrolyzed, Mw = 150,000) was donated by Kuraray America Inc. (Houston, TX), and the polymer chain contains 98 wt.% vinylalcohol and 2 wt.% 2-(acrylamido)-2-methylpropane sulfonic acid sodium salt. Potassium hydroxide (pallets, ≥85%) and glutaraldehyde solution (50 wt.% solution in H2O) were purchased from Aldrich Chemical Company (St. Louis, MO). Dimethylglycine was obtained from MacKenzie Company (Los Angeles, CA). All chemicals were used as received without purification.

Microporous polysulfone supports (thickness = 145 µm including non-woven fabric support and average pore size = ~9 nm) were purchased from TriSep Corporation. A gas mixture of certified grade (10% CO, 40% H2 and 50% CO2) was used as the feed gas, which was purchased from Praxair Inc. (Danbury, CT). Prepurified argon and compressed air were used as sweep gases and acquired from Praxair Inc.
2.3.2. Membrane preparation

Flat sheet CO₂-selective composite membranes were prepared by casting the solutions containing crosslinked polyvinylalcohol (XL-PVA) with the crosslinking agent glutaraldehyde, KOH and amine carriers onto the polysulfone support. The preparation of XL-PVA solution was as follows: 3 g PVA was dissolved in 18 g deionized water at room temperature under stirring overnight. 1.4 g potassium hydroxide in aqueous solution was added to catalyze the crosslinking reaction of PVA and glutaraldehyde (crosslinking reagent). The crosslinking reaction was carried out at 80°C for 2.5 hours under stirring, and the obtained XL-PVA solution was 19 wt.% in solid content. The clear aqueous PVA solution turned dark brown in color with a significant increase in viscosity caused by crosslinking.

The amine carrier solution was prepared by mixing aqueous fixed-site carrier solution and aqueous mobile carrier (AIBA-K or DMG-K) solution with the desired concentration of total solids to avoid instantaneous gelling after mixing it with the crosslinked PVA solution. Instantaneous gelling was believed to be caused by the interaction of the polyamine with the aldehyde groups. The mobile carrier solution was obtained by dropwise adding KOH solution into amino acid (AIBA or DMG) solution and then overnight stirring.

The casting solution was obtained by dropwise adding the amine carrier solution into the XL-PVA solution. The viscosity of the casting solution increased gradually under stirring due to water evaporation by nitrogen purge and the reaction between aldehyde
groups in the XL-PVA solution and amino groups in the carriers. After casting the solution onto the polysulfone support using a GARDCO adjustable micrometer film applicator (Paul N. Gardner Company, Pompano Beach, FL) with a controlled gap setting, the membrane was dried and cured at 120°C for 6 h in a muffle furnace (Thermolyne 30400, Thermo Scientific, Waltham, MA) for the complete removal of water and complete crosslinking reaction for PVA with glutaraldehyde. The total thickness of the membrane including the polysulfone support was measured by a Mitutoyo electronic indicator (Model 543-252B, Mitutoyo America Corporation, Aurora, IL) with an accuracy of ±0.5 μm. The thickness of the dry active separation layer was obtained by subtracting the measured polysulfone support thickness from the measured total thickness of the membrane including the polysulfone support. The dry active layer thickness was controlled at about 10 – 25 μm.

2.3.3. Water vapor permeation measurement

The measurement of water vapor transport flux was based on the total amounts of water collected from retentate side and permeate side knockouts for a given period of permeation time. The water vapor permeance was obtained from the water flux permeating from the feed side to the sweep side divided by the difference of water partial pressures, in the feed side and the sweep side, based on the log-mean driving force model.
2.3.4. Gas transport measurement

Gas permeation apparatus shown in Figure 2.1 was used to conduct the gas transport performance test. A membrane was mounted in a rectangular stainless-steel gas permeation cell, with an active transport area of 3.4 cm$^2$, which was placed inside an oven (BEMCO Inc., Simi Valley, CA) with good temperature control of about ±1 °C. Inside the cell, feed gas and sweep gas flows were counter-current. The feed side pressure was controlled by a back pressure regulator and set at around 1 psig. The sweep side pressure was set close to 1 atm. Dry gas flow rates of feed gas and sweep gas were controlled at 60 cc/min and 30 cc/min, respectively, by mass flow controllers (Brooks Instrument, Hatfield, CA). Liquid water was injected by Varian ProStar delivery modules (Model 210, Varian Inc., Palo Alto, CA) at 0.09 cc/min and 0.01 cc/min for feed side and sweep side, respectively. After injection, liquid water was vaporized and well-mixed with the dry gas in each of the humidifiers, and the humidified feed and sweep gases flew into the testing cell. The water contents for the feed side and sweep side were 66.7% and 30%, respectively. After the membrane cell, the retentate stream and permeate stream left the oven and were cooled down in their corresponding water knockouts to ambient temperature to let water condensed. The resulting retentate and permeate gas streams were injected, respectively, into the Agilent 6890N gas chromatograph (Agilent Technologies, Palo Alto, CA) for gas composition analysis. The GC column used was SUPELCO Carboxen® 1004 micropacked (Sigma-Aldrich, St. Louis, MO).
The testing conditions, including feed pressure and water content, were based on a certain commercial application intended for our membranes. The stage-cut of the tests was below 5% for both water and CO₂.

The gas transport performance of the membrane at steady state was evaluated by two parameters: permeability and selectivity [4]. Permeability, $P_i$, is defined as:

$$P_i = \frac{N_i}{\Delta p_i / \ell}$$  \hspace{1cm} (2.1)

where $N_i$ is denoted for the steady state flux of species $i$ across the membrane; $l$ is the thickness of selective layer; $\Delta p_i$ stands for the partial pressure difference of species $i$ between the retentate and permeate sides of the membrane, which is also the driving force for gas permeation. In this work, $\Delta p_i$ is determined by logarithmic mean method as in Eq. (3.2):

$$\Delta p_i = \frac{(p_{i,feed\ in} - p_{i,sweep\ out}) - (p_{i,feed\ out} - p_{i,sweep\ in})}{\ln(p_{i,feed\ in} - p_{i,sweep\ out}) - \ln(p_{i,feed\ out} - p_{i,sweep\ in})}$$  \hspace{1cm} (2.2)

Selectivity, denoted as $\alpha_{ij}$, is defined as:

$$\alpha_{ij} = \frac{y_i / y_j}{x_i / x_j}$$  \hspace{1cm} (2.3)

where $x$ and $y$ are the mole concentrations of the gas components on the feed and permeate sides of the membrane, respectively. The common unit of $P_i$ is Barrer, (1 Barrer $= 10^{-10}$ cm³(STP) • cm/(cm² • s • cm Hg)). The common unit of permeance is GPU (gas permeation unit) (1 GPU $= 10^{-6}$ cm³(STP)/(cm² • s • cm Hg)).
2.4. Results and discussion

2.4.1. Water vapor transport of CO₂ facilitated transport membranes

The CO₂-selective facilitated transport membranes synthesized in this work were polyvinylalcohol based, and they were highly hydrophilic. Therefore, they were highly permeable to water as well as CO₂ in the presence of amine carriers.

The results of water vapor permeance in terms of different active separation layer thicknesses are shown in Figure 2.2. The water vapor permeation data were obtained under the conditions listed in Table 2.1, which showed that the temperature used was 120°C. As shown in Figure 2.2, the water vapor permeance results appeared to be independent of the active separation layer thickness. Hence, the different degrees of PVA crosslinking, which controlled the swelling of the active separation layer, did not influence the water vapor permeance results. These results indicated that the mass transfer resistance of the substrate is the controlling factor to water vapor transport. These results demonstrated the similar trends investigated by Lin et al. on Pebax® thin-film-composite membranes applied for H₂O/CH₄ separation [93].
2.4.2. Relationship between water vapor permeance and the number of polysulfone substrate layers

Following the same method to calculate water vapor permeance (Section 2.3.3), we characterized the relationship between water vapor permeance and the number of polysulfone substrate layers using a given amine-containing membrane (30 wt% XL-PVA (100% crosslinking degree), 23 wt% Lupamin®, 11 wt% KOH, 36 wt% DMG-K). The schematic of three membrane configurations with one, two and three layers of the polysulfone substrate is illustrated in Figure 2.3. For the membrane configurations with two and three layers of the polysulfone substrate, one and two layers of the polysulfone substrate were placed underneath the membrane coated on top of the polysulfone substrate, respectively. In other words, the one and two layers of the polysulfone substrate were placed underneath the polysulfone substrate of the membrane. The water vapor permeance results for these three membrane configurations at 102°C are depicted in Figure 2.4. As depicted in this figure, the water vapor permeance appeared to reduce linearly with the number of polysulfone substrate layers. The increase in the number of polysulfone layers could be modeled as the support with a higher effective thickness, leading to a higher mass transfer resistance to water vapor transport. These results confirmed the finding shown in Figure 2.2 that the mass transfer resistance of the substrate is the controlling factor to water vapor transport.
2.4.3. Effect of the number of polysulfone substrate layers on CO₂ separation

For the three membrane configurations with one, two and three layers of the polysulfone substrate described above, their CO₂ separation performances were also obtained from the same permeation measurements of water vapor transport described in the above section. The CO₂ separation results as a function of the number of polysulfone substrate layers are listed in Table 2.2. As listed in this table, CO₂ separation performance in terms of CO₂ permeance and CO₂/H₂ selectivity did not change significantly as the number of polysulfone substrate layers increased from one to two and then three. These results indicated that the CO₂ separation performance is governed by the selective layer of the amine-containing membrane as expected, i.e., the thickness of the selective layer.

2.4.4. Effect of water retention capability on CO₂ separation

Water plays a vital role in the facilitated transport of CO₂ by amine carriers. In the facilitated transport of CO₂ inside the membrane, H₂O helps in two ways: (1) the hydration of CO₂ favors the reaction of CO₂ and amines and (2) the membrane swells in the presence of H₂O, thus accelerating the diffusion of the CO₂/amine reaction product in the membrane. In the reaction of amine and CO₂, zwitterion and carbamate ion are hydrolyzed by water, thus accelerating the formation of carbamate ion and the regeneration of free amine carriers as shown in Eqs. 1.9 and 1.10 in Chapter 1.
We investigated the effect of water retention capability of the membranes with the same composition except replacing pure polyvinylamine, synthesized by our group according to the procedure reported in the literature [68], by commercial Lupamin® containing 34% polyvinylamine and 66% salt (sodium formate). The membrane compositions were: 30 wt.% XL-PVA (80 mol% crosslinking degree), 23 wt.% synthesized polyvinylamine (or Lupamin®), 11 wt% KOH, and 36 wt% AIBA-K. The CO₂ separation performance results are listed in Table 2.3. The same weight amount of pure polyvinylamine and Lupamin® corresponded to a higher amine molar content of fixed-site carrier in pure polyvinylamine relative to Lupamin®, due to the presence of the salt in Lupamin®. Even though the fixed-site carrier based amine content (molar basis) was higher with pure polyvinylamine, the separation performance of the membrane containing pure polyvinylamine was lower than that of the membrane containing Lupamin® as shown in this table. As a result, the presence of the salt in Lupamin® was believed to retain more water in the membrane matrix because of a relatively higher ionic interaction by the presence of the salt. Thus, more water retention was believed to contribute to the higher separation performance with Lupamin® as the fixed site carrier.

The average water permeance for Lupamin® was around 3200 GPU (ranging from 2250 – 4000 GPU) as shown in Figure 2.2. As the water permeance was controlled by the polymeric substrate, not the selective layer containing polyamine, the water vapor permeance for pure polyvinylamine should be within the above range for Lupamin®.
2.5. Conclusions

The CO₂ facilitated transport membranes studied in this work were synthesized by incorporating commercial Lupamin® or synthesized polyvinylamine as the CO₂ fixed-site carrier, and AIBA-K or DMG-K as the mobile carrier into the crosslinked PVA membrane matrix. Water vapor transport was studied and exhibited independent of active separation layer thickness. With increasing the number of polysulfone substrate layers from one to two and then three, water vapor permeance appeared to reduce linearly. These results showed that the mass transfer resistance of the substrate is the controlling factor to water vapor transport. But, CO₂ separation performance in terms of CO₂ permeance and CO₂/H₂ selectivity did not change significantly as the number of polysulfone substrate layers increased. These results indicated that the CO₂ separation performance is governed by the selective layer of the amine-containing membrane as expected. The CO₂ separation performance was improved by using Lupamin® instead of pure polyvinylamine, because of better water retention capability of Lupamin®.
Table 2.1. Gas transport measurement conditions for Figure 2.2.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Gas Flow Rate (on dry basis, cm$^3$/min)</th>
<th>Water Content (mol%)</th>
<th>Pressure (psig)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Feed</td>
<td>Sweep</td>
<td>Feed</td>
</tr>
<tr>
<td>120</td>
<td>60</td>
<td>30</td>
<td>66.7</td>
</tr>
</tbody>
</table>

\textsuperscript{a} A gas mixture consisting of 10\% CO, 40\% H$_2$ and 50\% CO$_2$ on dry basis and the prescribed water content was used as the feed gas, which was also the feed gas for water vapor transport measurements.
Table 2.2. CO\textsubscript{2} separation performance as a function of the number of polysulfone substrate layers.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Number of Polysulfone Substrate Layer</th>
<th>CO\textsubscript{2} Permeance (GPU)</th>
<th>CO\textsubscript{2}/H\textsubscript{2} Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>105</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>113</td>
<td>89</td>
</tr>
<tr>
<td>3</td>
<td>110</td>
<td>91</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Gas transport measurement conditions were the same as Table 2.1 except 102°C was used instead of 120°C.
Table 2.3. Membrane performance comparison between synthesized polyvinylamine and commercial Lupamin®.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Fixed-Site Carrier</th>
<th>CO\textsubscript{2} Permeability (Barrers)</th>
<th>CO\textsubscript{2}/H\textsubscript{2} Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthesized Polyvinylamine</td>
<td>2300</td>
<td>140</td>
</tr>
<tr>
<td>Lupamin®</td>
<td>3000</td>
<td>180</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Gas transport measurement conditions were the same as Table 2.1. A gas mixture consisting of 10% CO, 40% H\textsubscript{2} and 50% CO\textsubscript{2} on dry basis and the prescribed water content was used as the feed gas, which was also the feed gas for water vapor transport measurements. The membrane compositions were: 30 wt% XL-PVA (80 mol% crosslinking degree), 23 wt% Lupamin® (or synthesized polyvinylamine), 11 wt% KOH, 36 wt% AIBA-K.
Figure 2.1. Schematic of the gas permeation apparatus (originally drawn by Dr. Jian Zou [10]).
Figure 2.2. H$_2$O permeance-separation layer thickness data for CO$_2$/H$_2$ separation using 3 different membrane compositions: (▲) 30 wt% XL-PVA (15% crosslinking degree), 23 wt% Lupamin®, 11 wt% KOH, 36 wt% AIBA-K, (●) 30 wt% XL-PVA (80% crosslinking degree), 23 wt% Lupamin®, 11 wt% KOH, 36 wt% AIBA-K, and (■) 30 wt% XL-PVA (100% crosslinking degree), 23 wt% Lupamin®, 11 wt% KOH, 36 wt% DMG-K. The tests were conducted at 120°C.
Figure 2.3. Membrane schematic with one, two and three layers of the polysulfone substrate.
Figure 2.4. Water vapor permeance vs. the number of polysulfone substrate layers at 102°C.
Nomenclature

\( l \) \hspace{1cm} \text{membrane thickness}

\( N_i \) \hspace{1cm} \text{steady-state flux of component } i

\( P_i \) \hspace{1cm} \text{permeability of component } i

\( \Delta p_i \) \hspace{1cm} \text{partial pressure difference of component } i \text{ across the membrane}

\( p_{i, \text{feed in}} \) \hspace{1cm} \text{partial pressure of component } i \text{ at the inlet of feed side}

\( p_{i, \text{feed out}} \) \hspace{1cm} \text{partial pressure of component } i \text{ at the outlet of feed side}

\( p_{i, \text{sweep in}} \) \hspace{1cm} \text{partial pressure of component } i \text{ at the inlet of sweep side}

\( p_{i, \text{sweep out}} \) \hspace{1cm} \text{partial pressure of component } i \text{ at the outlet of sweep side}

\( x_i \) \hspace{1cm} \text{molar fraction of component } i \text{ in the retentate stream}

\( x_j \) \hspace{1cm} \text{molar fraction of component } j \text{ in the retentate stream}

\( y_i \) \hspace{1cm} \text{molar fraction of component } i \text{ in the permeate stream}

\( y_j \) \hspace{1cm} \text{molar fraction of component } j \text{ in the permeate stream}

Greek letter

\( \alpha_{ij} \)  \hspace{1cm} \text{selectivity of component } i \text{ over component } j
Chapter 3: New CO$_2$ facilitated transport membranes for H$_2$ purification

3.1. Summary

It has been shown in Chapter 2 that the H$_2$O vapor content has strong influence on the performance of amine-containing membranes. This chapter discusses the transport results of reducing the H$_2$O vapor content on the feed side to 54%, i.e., 0.54 atm water vapor pressure for the total feed side pressure of 1 atm (at 120°C). Such a low water vapor partial pressure has never been studied by our group for amine-containing membranes. At this low water vapor content, the membrane with the same composition in an earlier study reported in Chapter 2 showed a CO$_2$ permeance of 50 GPU with a CO$_2$/H$_2$ selectivity of 78. This performance was much lower than the CO$_2$ permeance of 200 GPU along with the CO$_2$/H$_2$ selectivity of 180 with 67% H$_2$O vapor content on the feed side. These results exhibited the significant effect of water vapor content on membrane performance. In order to improve the water retention capability of the membrane, the membrane composition was modified by increasing the amount of KOH and incorporating CsF salt in the membrane. The resultant membrane performance was improved to have the CO$_2$ permeance of 81 GPU with a CO$_2$/H$_2$ selectivity of 129.
Another new facilitated transport membrane was synthesized as an attempt to further increase the water retention capability. High-molecular-weight polyvinylamine (PVAm) was crosslinked by ethylene glycol diglycidyl ether (EGDGD), and the crosslinked PVAm (XL-PVAm) was used to replace the crosslinked polyvinylalcohol (XL-PVA). A highly hydrophilic polyelectrolyte, polydiallyldimethyl-quaternaryammonium fluoride (PDADMQ-F), was incorporated in the membrane. The effects of PVAm crosslinking degree, PVAm content, PDADMQ-F/mobile carrier ratio, and mobile carrier species were investigated, and the optimal membrane composition was identified, exhibiting a CO$_2$ permeance of 101 GPU and CO$_2$/H$_2$ selectivity of 108. Another mobile carrier, tetramethylquaternaryammonium hydroxide (TMAOH) was incorporated into the membrane to further improve the membrane performance. Indeed, the membrane performance was improved to have the CO$_2$ permeance of 146 GPU and CO$_2$/H$_2$ selectivity of 107. This could be explained by the superior water retention capability of TMAOH and the amine-catalyzed reaction of CO$_2$ and hydroxide ion.
3.2. Introduction

Hydrogen is an important building-block for the production of chemicals, such as ammonia, and widely used in hydrogenation and hydrotreating in refineries. Also, with the greater demand for high-efficiency and clean power generation, there is an increasing need to convert conventional fuels to syngas or hydrogen. The most commonly used technologies for high-purity hydrogen production are pressure swing adsorption and amine solvent absorption. The main disadvantages of those technologies include low energy efficiency due to sorbent regeneration or stripping of amine solvent as well as the complexity associated with the operation of those processes. As a kinetic process, membrane-based separation is not limited by the thermodynamic equilibrium solubility and thus can reduce the energy consumption significantly, making it a promising technology for cost-effective hydrogen purification.

Hydrogen is primarily produced from the steam reforming of methane and the subsequent purification of synthesis gas, mainly consisting of CO₂, CO and H₂ with steam, derived from water-gas-shift (WGS) reaction. Based on the kinetic diameter differences among CO₂ (3.3Å), CO (3.76Å) and H₂ (2.89Å), scientists have developed H₂-selective membranes based mainly on the smallest size for the hydrogen molecule. The materials of H₂-selective membranes are usually metallic and inorganic materials, such as palladium and silica, etc. In spite of the high purity of the permeate H₂, those membranes suffer from the difficulty of preparing thin, defect-free and cost-effective membranes, which hinders the commercial application of this type of membrane. Another important type of
membrane for hydrogen purification is CO$_2$-selective membrane, which is usually polymeric and much easier for scale-up than those inorganic membranes. The transport mechanism of the most polymeric membranes for gas separation is solution-diffusion, which has the trade-off between permeability and selectivity [7,8]. The low CO$_2$/H$_2$ selectivity for the solution-diffusion membranes causes a large H$_2$ loss, which adds on the cost of H$_2$ purification. In order to achieve sufficient CO$_2$/H$_2$ selectivity, increasing attention has been put over the decade on facilitated transport membranes.

Compared to supported liquid membranes and ion exchange membrane, which suffer from the carrier loss and slow reaction kinetics, a hydrophilic polymer matrix based membrane containing fixed-site and/or mobile carriers have attracted increasing interests in recent years. Our group has studied various fixed-site carriers (PEI, polyallylamine (PAAm), and PVAm) and mobile carriers (KOH, lithium dimethylglycinate (DMG-Li), AIBA-K, and lithium glycinate) to blend with crosslinked polyvinylalcohol for CO$_2$/H$_2$ separation. Zou et al. incorporated PAAm as the fixed-site carrier along with AIBA-K and KOH as the mobile carriers into crosslinked PVA matrix to obtain a facilitated transport membrane, which achieved excellent CO$_2$/H$_2$ separation performance (CO$_2$ permeability of 9710 Barrers with CO$_2$/H$_2$ selectivity of 523) at 120°C and 2 bars with a feed-side H$_2$O content of 54% and a sweep-side H$_2$O content of 85% [10]. Tong et al. incorporated Lupamin® (containing 34% PVAm and 66% sodium formate salt) as the fixed-site carrier and AIBA-K as the mobile carrier and achieved CO$_2$ permeability of 3000 Barrers and CO$_2$/H$_2$ selectivity of 180 at 120°C and 1 bar with a feed-side H$_2$O content of 67% and a sweep-side H$_2$O content of 57% [46].
In this work, the required H₂O contents were 54% and 30% on the feed and sweep sides, respectively. And we found the membrane that demonstrated good performance at the 67% feed-side H₂O content [46] showed a significant performance drop at the 54% feed-side H₂O content. This performance drop should be attributed to the reduced water retention in the membrane. In order to improve the water retention capability, we developed a new facilitated transport membrane by incorporating a fluoride-containing polyelectrolyte and quaternaryammonium hydroxide into crosslinked PVAm (XL-PVAm) membranes with various aminoacid salt mobile carriers.

3.3. Experimental

3.3.1. Materials

Polyvinylalcohol (Poval S-2217, 92% purity) was donated by Kuraray America Inc. (Houston, TX). Potassium hydroxide (≥85%), (3-aminopropyl)triethoxysilane (99%), glutaraldehyde solution (50 wt.% solution in H₂O), poly(diallyldimethylammonium chloride) solution (20 wt.% in H₂O), potassium fluoride (99%), tetramethylquaternaryammonium hydroxide (TMAOH, 25 wt.% in H₂O), N-vinylformamide, 2,2'-azobis(2-methylpropionamidine) dihydrochloride, glycine (99%), piperazine (99%), and diethylene triamine (99%) were purchased from Sigma-Aldrich Corporation (St. Louis, MO). Hydrochloric acid (12.1 mol/L in H₂O), ethanol, and methanol were acquired from Fisher Scientific Inc. (Pittsburgh, PA). A600OH anion
exchange resin was kindly donated by Purolite Corporation (Bala Cynwyd, PA, USA). Ethylene glycol diglycidyl ether was purchased from Polysciences Inc. (Warrington, PA). The nanoporous polysulfone substrate (pore size = 9 nm, surface porosity = 7%) was obtained from TriSep Corporation (Goleta, CA). The gas mixture of 59.5% CO₂/26.5% H₂/14% CO used as the feed gas and prepurified argon used as the sweep gas were purchased from Praxair Inc. (Danbury, CT).

3.3.2. Preparation of XL-PVA, PDADMQ-F, and XL-PVAm

The crosslinked PVA was prepared according to our group’s previous work [12]. The preparation of polydiallyldimethylquaternaryammonium fluoride (PDADMQ-F) was conducted by ion exchange of polydiallyldimethylquaternaryammonium chloride by potassium fluoride in methanol [94]. The PDADMQ-F used in this chapter was prepared by Witopo Salim according to the above procedures. The XL-PVAm was obtained via the reaction between the amino groups in PVAm and the epoxide groups in ethylene glycol diglycidyl ether (EGDGE). The chemical structure of PDADMQ-F and XL-PVAm are illustrated in Figure 3.1. The PVAm used in this chapter was synthesized by Kai Chen in our group using inverse emulsion polymerization.
3.3.3. Membrane Preparation

The preparation of the XL-PVA based membrane followed the similar procedures reported in Chapter 2. The mobile carrier solutions of potassium glycinate (KG), piperazine glycinate (PG), and diethylene triamine glycinate (DETAG) were prepared by adding KOH, piperazine, and DETA in the stoichiometric amount into glycine aqueous solution, respectively.

The preparation of XL-PVAm membrane was carried out according to the procedures as follows: (1) PVAm was mixed with EGDGE at a certain ratio to achieve the desired crosslinking degree at room temperature for 2 h with a PVAm concentration of 1.3 wt.%, and the resultant viscosity increase was observed; (2) the mobile carrier solution (KG, PG, DETAG or TMAOH) was then gradually added into the XL-PVAm solution; (3) PDADMQ-F solution was diluted to about 7.5 wt.% and then added to the above amine-containing solution. Because of the interactions between PDADMQ-F and XL-PVAm, the viscosity of the solution was further increased. The above solution was concentrated to a proper viscosity via a mild N₂ purge and then coated onto polysulfone substrates using a GARDCO adjustable micrometer film applicator (Paul N. Gardner Company, Pompano Beach, FL) with a controlled gap setting. The thickness of the membrane was controlled at around 12 μm.
3.3.4. Gas transport measurement

The gas transport measurement of the membrane was similar to that described in Chapter 2, except for the H₂O injection rates, which were changed to 0.054 cc/min for the feed side and 0.01 cc/min for the sweep side, corresponding to the H₂O vapor contents of 54 mol% and 30 mol%, for the feed and sweep sides, respectively.

3.4. Results and discussion

3.4.1. XL-PVA based membrane performance at 54% feed-side H₂O vapor content

As reported in our previous work, the amine-containing membrane performance was strongly dependent on the water vapor contents in the feed and/or sweep streams of gas transport measurements [10,12,70]. Using the membrane in the above section that demonstrated the CO₂ permeance of about 180 – 200 GPU and CO₂/H₂ selectivity of 200 with the 67% feed-side H₂O vapor content, we could only obtain a CO₂ permeance of only 50 GPU and a CO₂/H₂ selectivity of only 78 with a 54% feed-side H₂O vapor content.

In order to improve the water retention capability of the membrane, we modified the membrane composition with increasing the amount of KOH and maintaining the same amount of an aminoacid salt mobile carrier. The new membrane composition was 20 wt.% XL-PVA, 26 wt.% Lupamin®, 18 wt.% KOH, and 36 wt.% potassium glycinate (KG). The membrane showed a CO₂ permeance of 80 GPU and a CO₂/H₂ selectivity of 128. It
indicated that KOH could help with the water retention in the membrane. In the previous chapter, it was found that Lupamin\textsuperscript{®} containing 66% sodium formate salt might have better water retention capability than pure polyvinylamine. Therefore, the above membrane composition was further modified by replacing the sodium formate contained in Lupamin\textsuperscript{®} to cesium fluoride, based on the fact that fluoride ion can form stronger hydrogen bonding with H\textsubscript{2}O [23-26]. Lab-synthesized PVAm was used, instead of the PVAm in Lupamin\textsuperscript{®}, together with CsF. Although the molar content of CsF was only 45% that of sodium formate because of the higher molar mass of CsF, the membrane still showed a CO\textsubscript{2} permeance of 81 GPU and a CO\textsubscript{2}/H\textsubscript{2} selectivity of 129. The membrane performances discussed in this section are summarized in Table 3.1. This table shows the importance of membrane composition for transport performance.

3.4.2. XL-PVAm based membrane performance with 54% feed-side H\textsubscript{2}O vapor content

3.4.2.1. Effects of crosslinking degree of PVAm

The PVAm solution used in this study had a high viscosity (3 wt.% solution shear viscosity = 7800 cp at room temperature), which could provide a good film forming capability without blending in any crosslinked PVA. Based on this viewpoint, PVAm could be used as both the fixed-site carrier and the polymer matrix in the membrane to provide mechanical strength. As a result, XL-PVA, which is not able to perform the function of CO\textsubscript{2} facilitated transport, could be eliminated from the membrane composition.
However, in order to further improve the membrane performance and stability, ethylene glycol diglycidyl ether (EGDGE) was used as the crosslinker for PVAm. By controlling the molar ratio of EGDGE to the repeating unit of PVAm, we obtained crosslinked PVAm (XL-PVAm) based membranes with different crosslinking degrees of 5 mol.%, 6 mol.%, 10 mol.%, and 12 mol.%. Furthermore, a specified amount of the fluoride-containing polyelectrolyte, polydiallyldimethylquaternaryammonium fluoride, (PDADMQ-F), was incorporated into the membrane composition to improve the membrane water retention capability. The chemical structure of XL-PVAm and PDADMQ-F are illustrated in Figure 3.1. The membrane composition used in this section was 21 wt.% PVAm, 30 wt.% PDADMQ-F, and 49 wt.% KG.

The effect of crosslinking of polyvinylamine in this work was two-fold: first, it could interrupt the packing of polyvinylamine chains, hereby creating more free volume for mobile carrier diffusion; second, it could limit the mobility of polyvinylamine chain segment, which in turn, hindered the transport of gases in the membrane. As a result, an optimal crosslinking degree should exist, which could improve both CO₂ permeance and CO₂/H₂ selectivity. The effect of PVAm crosslinking degree on membrane performance is illustrated in Figure 3.2. As illustrated in this figure, the CO₂ permeance first increased as the crosslinking degree increased and then dropped as the crosslinking degree further increased, while CO₂/H₂ selectivity showed an ascending trend as the crosslinking degree increased from 0 mol.% to 12 mol..% For hydrogen purification of this project, more emphasis was put on CO₂ permeance instead of CO₂/H₂ selectivity. Therefore, the 6 mol.%
crosslinking degree of PVAm was used in the experiments discussed in the following sections. The gas transport results discussed in this section are listed in Table 3.2.

3.4.2.2. Effects of XL-PVAm content

XL-PVAm as a high-molecular-weight polymer matrix provided the film forming ability of the membrane. Therefore, an appropriate amount of XL-PVAm could avoid the membrane structure collapse after the membrane was swollen by the moisture in the test. But, because of the high mobility, the mobile carrier is supposed to be more efficient than PVAm in terms of CO$_2$ facilitated transport. As a result, the amount of XL-PVAm in the membrane should have a certain upper limit. In this section, the effect of XL-PVAm content is discussed, and the appropriate content of XL-PVAm in the membrane is presented. To maintain the water retention capability of the membrane at a consistent level, all the membranes studied in this section contained 49 wt.% PDADMQ-F. The amount of XL-PVAm varied from 16.5 wt.% to 26.1 wt.% The resultant membrane performances are compared in Figure 3.3. As shown in this figure, the membrane containing 21 wt.% XL-PVAm demonstrated the highest membrane performance, while the membrane containing 16.5 wt.% XL-PVAm might be short of mechanical strength to maintain the membrane integrity and the one containing 26.1 wt.% XL-PVAm might not have a sufficient amount of the mobile carrier for CO$_2$ facilitated transport. The gas transport results discussed in this section are listed in Table 3.2.
3.4.2.3. Effects of PDADMQ-F and mobile carrier ratio

This section mainly discusses the influence of membrane water retention capability and mobile carrier on membrane performance. As a polyelectrolyte with abundant fluoride ions which can form strong hydrogen bonding with H\textsubscript{2}O molecules, the presence of PDADMQ-F in the membrane is able to improve membrane water retention capability significantly. Since 21 wt.% XL-PVAm was necessary to maintain membrane integrity, an increased amount of PDADMQ-F would decrease the amount of the mobile carrier in the membrane. Therefore, it is prudent to investigate the ratio of PDADMQ-F and mobile carrier to optimize the membrane performance. The effect of PDADMQ-F and KG ratio on membrane performance is illustrated in Figure 3.4. As shown in this figure, the membrane with 40 wt.% PDADMQ-F demonstrated the highest CO\textsubscript{2} permeance. This could be explained by the fact that the increase of PDADMQ-F content from 30.2 wt.% to 40 wt.% increased the water absorbed by the membrane but when the content of PDADMQ-F reached 49.1 wt.%, the content of the mobile carrier was insufficient to perform the facilitation of CO\textsubscript{2} transport. It should be noted that the membrane containing the lowest content of PDADMQ-F (30.2 wt.%) showed the highest selectivity, almost double the selectivities of the other two membranes, which could be attributed to the tight membrane structure at the low water content in the membrane. The gas transport results discussed in this section are listed in Table 3.2.

3.4.2.4. Effects of different mobile carriers
Our group has demonstrated that the membranes containing the mobile carriers, potassium glycinate (KG), lithium glycinate (LiG), and piperazine glycinate (PG), at the same weight content had different CO$_2$/N$_2$ separation performances at the typical flue gas temperature of 57°C for carbon capture [73]. The membrane containing PG showed the highest CO$_2$ permeance and CO$_2$/N$_2$ selectivity, the one containing LiG possessed the second highest CO$_2$/N$_2$ separation performance, and the lowest performance was obtained from the membrane containing KG. These results could be explained by the difference in the amino content in the different mobile carriers.

In this work, we studied the membranes with different mobile carriers as well: KG, LiG, PG, and diethylene triamine glycinate (DETAG). The coating solution containing PVAm and PDADMQ-F turned turbid upon the addition of LiG aqueous solution. This should be caused by the low solubility of LiF in water. All the membrane coating solutions containing the above-mentioned mobile carriers were homogeneous except for the one containing LiG. The comparison among the membrane performances containing KG, PG, and DETAG is illustrated in Figure 3.5. As shown in this figure, the membrane containing KG showed the highest CO$_2$/H$_2$ separation performance under the gas transport testing conditions in this work, in spite of the lowest amino content in KG. This could be explained by the fact that KG possesses the highest ionic strength, thus the highest water retention capability. These results indicated that under high temperature and low water content conditions, membrane water retention capability might play a more important role in
separation performance than the amino content in the membrane. The gas transport results discussed in this section are also listed in Table 3.2.

3.4.2.5. Effects of tetramethylquaternaryammonium hydroxide

Membranes containing different amounts of TMAOH were synthesized and investigated. The gas transport separation performances are illustrated in Table 3.3. Compared to the membrane containing 21 wt.% XL-PVAm, 39 wt.% KG and 40 wt.% PDADMQ-F, the membrane containing 9 wt.% TMAOH and 32 wt.% KG demonstrated a significant increase in CO₂ permeance but decrease in CO₂/H₂ selectivity. It indicated that the incorporation of TMAOH could assist to increase the CO₂ permeance but decrease the CO₂/H₂ selectivity, mainly because of its excellent water retention capability, which led to membrane swelling. Comparing the CO₂/H₂ selectivities of Membranes #3 and #4, it could be found that a greater amount of XL-PVAm was more favorable in terms of CO₂/H₂ selectivity than a higher crosslinking degree of XL-PVAm. It should also be noted that the CO₂ permeance of Membrane #4 was only 2 GPU lower than that of Membrane #3, although the amount of PDADMQ-F of the former was less than that of the latter. This indicated that TMAOH contributed more to membrane performance than PDADMQ-F. Since this project required that the CO₂/H₂ selectivity had to be above 100, the best performance (CO₂ permeance of 146 GPU and CO₂/H₂ selectivity of 107) was obtained on Membrane #5, which had a similar composition as Membrane #4 but a thicker membrane thickness.
3.5. Conclusions

Two types of facilitated transport membranes were successfully synthesized and characterized at 120°C and 1 atm, with 54 mol.% H₂O vapor content on the feed side: (1) XL-PVA based amine-containing membrane and (2) XL-PVAm based fluoride-containing membrane. Although amine reacts with CO₂ much faster than the reaction of CO₂ hydration catalyzed by fluoride ion, the second type of facilitated transport membrane demonstrated the best performance with a CO₂ permeance of 101 GPU and a CO₂/H₂ selectivity of 108 as a result of incorporating 40 wt.% fluoride-containing polyelectrolyte (PDADMQ-F) in the membrane to increase its water retention ability. The effects of crosslinking degree of PVAm, PVAm content in the membrane, ratio of PDADMQ-F to mobile carrier, and mobile carrier species on membrane performance were studied. The optimal membrane was composed of 21 wt.% XL-PVAm with the crosslinking degree of 6 mol%, 40 wt.% PDADMQ-F, and 39 wt.% potassium glycinate.
Table 3.1. XL-PVA based membrane performances at 54% feed-side H₂O vapor content.

<table>
<thead>
<tr>
<th>Membrane Composition (wt.%)</th>
<th>Membrane Thickness (μm)</th>
<th>CO₂ Permeance (GPU)</th>
<th>CO₂/H₂ Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>XL-PVA Fixed-site Carrier</td>
<td>KOH KG</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30 23 (Lupamin®)</td>
<td>11 36</td>
<td>12</td>
<td>52 88</td>
</tr>
<tr>
<td>20 26 (Lupamin®)</td>
<td>18 36</td>
<td>10</td>
<td>80 128</td>
</tr>
<tr>
<td>20 9 (PVAm) + 17 (CsF)</td>
<td>18 36</td>
<td>10</td>
<td>81 129</td>
</tr>
</tbody>
</table>
Table 3.2. Gas transport performances of PVAm based membranes (w/o TMAOH).

<table>
<thead>
<tr>
<th>Membrane Composition (wt.%)</th>
<th>Crosslinking Degree of PVAm (mol.%)</th>
<th>Membrane Thickness (μm)</th>
<th>CO₂ Permeance (GPU)</th>
<th>CO₂/H₂ Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVAm</td>
<td>PDADMQ-F</td>
<td>Mobile carrier</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>30</td>
<td>50, KG</td>
<td>0</td>
<td>11</td>
</tr>
<tr>
<td>20</td>
<td>30</td>
<td>50, KG</td>
<td>5</td>
<td>11</td>
</tr>
<tr>
<td>20</td>
<td>30</td>
<td>50, KG</td>
<td>6</td>
<td>12.8</td>
</tr>
<tr>
<td>20</td>
<td>30</td>
<td>50, KG</td>
<td>10</td>
<td>12</td>
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<tr>
<td>20</td>
<td>30</td>
<td>50, KG</td>
<td>12</td>
<td>11.8</td>
</tr>
<tr>
<td>16.5</td>
<td>49</td>
<td>34.5, KG</td>
<td>6</td>
<td>11</td>
</tr>
<tr>
<td>21</td>
<td>49</td>
<td>30, KG</td>
<td>6</td>
<td>12</td>
</tr>
<tr>
<td>26.1</td>
<td>49</td>
<td>24.9, KG</td>
<td>6</td>
<td>11.3</td>
</tr>
<tr>
<td>21</td>
<td>40</td>
<td>39, KG</td>
<td>6</td>
<td>10</td>
</tr>
<tr>
<td>21</td>
<td>40</td>
<td>39, PG</td>
<td>6</td>
<td>11.2</td>
</tr>
<tr>
<td>21</td>
<td>40</td>
<td>39, DETAG</td>
<td>6</td>
<td>12</td>
</tr>
</tbody>
</table>
Table 3.3. Gas transport performances of TMAOH-containing membranes.

<table>
<thead>
<tr>
<th>M#</th>
<th>Membrane Thickness</th>
<th>XL-PVAm wt.%</th>
<th>PDADMQ-F wt.%</th>
<th>KG wt.%</th>
<th>TMAOH wt.%</th>
<th>CO₂ Permeance (GPU)</th>
<th>CO₂/H₂ Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>22</td>
<td>37</td>
<td>32</td>
<td>9</td>
<td>151</td>
<td>79</td>
</tr>
<tr>
<td>2</td>
<td>13.2</td>
<td>(6% XL)</td>
<td></td>
<td></td>
<td></td>
<td>129</td>
<td>110</td>
</tr>
<tr>
<td>3</td>
<td>12.2</td>
<td>23.9</td>
<td>28.3</td>
<td>32.6</td>
<td>15.2</td>
<td>177</td>
<td>57</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(12% XL)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>12.2</td>
<td>26.6</td>
<td>23</td>
<td>33.4</td>
<td>17</td>
<td>175</td>
<td>69</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(6% XL)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>15.3</td>
<td>26.3</td>
<td>22.2</td>
<td>34</td>
<td>17.5</td>
<td>146</td>
<td>107</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(6% XL)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 3.1. Chemical structure of XL-PVAm and PDADMQ-F.
Figure 3.2. Effect of the crosslinking degree of PVAm.
Figure 3.3. Effect of XL-PVAm content.
Figure 3.4. Effect of PDADMQ-F content.
Figure 3.5. Effect of different mobile carriers.
Chapter 4: Amine-containing CO₂-selective membranes for flue gas carbon capture

4.1. Summary

The key challenge to flue gas carbon capture is the low CO₂ concentration and partial pressure, i.e., the low driving force for CO₂ separation, which demands a high CO₂ permeance of the membrane as well as its high CO₂/N₂ selectivity. Regarding this point on the CO₂ permeance, a thin thickness of the membrane is desired. In this chapter, two methods to obtain ultrathin membranes were applied, i.e., spin coating and knife casting. In order to improve CO₂/N₂ separation performance of the membrane prepared by spin coating, polydimethylsiloxane (PDMS) gutter and cover layers were incorporated. The PDMS gutter layer significantly reduced the penetration of the dilute amine-containing coating solution and the incorporation of PDMS cover layer successfully improved membrane selectivity by sealing the defects caused by poor adhesion between the hydrophobic gutter layer and the hydrophilic amine layer. The thin-composite membrane with a CO₂ permeance of 601 GPU and a CO₂/N₂ selectivity of 33 was successfully synthesized by spin coating. To prepare an ultrathin membrane by knife casting, high-molecular-weight polyvinylamine (PVAm) was synthesized and used as the polymer matrix of the membrane. Piperazine glycinate (PG) and diethylenetriamine glycinate
(DETAG) were applied as the amine mobile carriers to be blended with PVAm. The PVAm/PG membrane exhibited an average CO₂ permeance of 730 GPU with an average CO₂/N₂ selectivity of 136, whereas the PVAm/DETAG membrane showed an average CO₂ permeance of 804 GPU with an average CO₂/N₂ selectivity of 108 for the feed gas containing 20% CO₂ and 80% N₂ (on a dry basis) saturated with H₂O vapor at 57°C and 1 atm.
4.2. Introduction

The emission of greenhouse gas, mainly CO₂, from coal- and/or natural gas-fired power plants has been widely accepted as the main contributor to the global warming issue nowadays. CO₂ capture is believed to be one of the most effective approaches to mitigate greenhouse gas emission. The most mature technology for CO₂ capture is amine scrubbing, which is based on the reversible chemical reaction between amine and CO₂. The key obstacles that inhibit its further development include large energy consumption, low space efficiency, amine loss, the handling of corrosive liquid, etc. Over the recent years, intensive research has been focused on membrane-based CO₂ capture as an alternative technology to amine scrubbing, due to its large energy-efficiency, high cost-effectiveness and small footprint. In consideration of the ease for scale-up, the best candidate membrane material is polymeric one. However, most of the polymer membranes are limited by the trade-off between permeability and selectivity, i.e., the Robeson upper bond [7,8]. Amine-containing facilitated transport membranes can exceed the Robeson upper bond, due to the facilitation function performed by amine carriers, which can reversibly react with CO₂. Therefore, the facilitated transport membranes are able to achieve high CO₂ permeance and possess high CO₂/N₂ selectivity at the same time, as compared to other polymeric membranes based on the solution-diffusion mechanism.

As for membrane-based separation, the flux of a certain gas component is the product of its permeance and the driving force, i.e., the partial pressure difference of the gas component between the feed and permeate sides of the membrane. The typical flue
gas contains around 12 – 14% CO\(_2\) for coal-fired power plants and about 4 – 6% CO\(_2\) for natural gas-fired power plants, which mean that the partial pressure of CO\(_2\) in flue gas at 1 atm is less than 0.15 bar. The low driving force requires the high permeance of the membrane. In order to meet the separation target set by the Department of Energy, USA (90% CO\(_2\) capture and 95% CO\(_2\) purity), both high CO\(_2\) permeance and high CO\(_2\)/N\(_2\) selectivity are needed. In this regard, defect-free ultrathin (<1 μm) amine-containing membranes were synthesized and studied in this chapter.

Three methods are commonly used for membrane preparation in lab scale, i.e., spin coating, dip coating, and knife casting. As for spin coating and dip coating, an ultrathin membrane demands the low viscosity of the coating solution, which on the other hand causes penetration of the coating solution into the pores of the substrate. In this work, a commercial polyethersulfone substrate (Biomax PES, Millipore) was deposited with a thin layer of zeolite Y on its top and used as the substrate as a whole for the preparation of CO\(_2\)-selective membranes. The approaches to prevent penetration for spin coating and the selective layer membrane composition are discussed in the following section. As for knife casting, in order to successfully obtain ultrathin membranes without penetration, the coating solution has to be sufficiently viscous at a low concentration. High-molecular-weight polyvinylamine (PVAm) has shown its advantages in the preparation of such coating solution [68,73]. In this work, high-molecular-weight PVAm was synthesized based on the method reported previously with minor adjustment, and a new amino acid salt was used as the mobile carrier. A flat-sheet PES substrate fabricated via phase inversion
by our group according to our previous work [95] was used as the membrane support for knife casting.

4.3. Experimental

4.3.1. Materials

Zeolite Y nanoparticles (average particle size of 40 nm) were synthesized and characterized by Dr. Dutta’s group in the Department of Chemistry and Biochemistry at The Ohio State University and provided to our group for ZY-deposition. The Biomax® polyethersulfone substrate with the molecular weight cut-off of 300 kDa was purchased from EMD Millipore Corporation (Billerica, MA). The average pore size of this substrate was about 72 nm with a surface porosity of about 15%. This substrate was first soaked in deionized water overnight and then in isopropanol (IPA) for 30 minutes to remove the glycerol entrapped inside its pores before usage. Ethanol (99.5%+), and heptane (anhydrous, 99%), glutaraldehyde solution (50 wt.% solution in H₂O), potassium hydroxide (pallets, ≥85 wt.% purity), lithium hydroxide monohydrate (99.5%), glycine (99%), piperazine (99%), and diethylenetriamine (DETA, 99%) were purchased from Sigma-Aldrich (Milwaukee, WI). Isopropanol (IPA, 99.9%) was acquired from Fisher Scientific Inc. (Pittsburgh, PA). Dehesive® 944, Wacker® crosslinker V24, and Wacker® catalyst OL were kindly donated by Wacker Silicones Inc. (Adrian, MI), which were used for the preparation of polydimethylsiloxane (PDMS). Polyvinylalcohol (Poval S-2217,
92% purity, 87 – 89 mol.% hydrolyzed, Mw = 150,000) was donated by Kuraray America Inc. (Houston, TX). Lupamin® (containing 66 wt.% salts and 34 wt.% polyvinylamine, Mw = 340,000 g/mol) was donated by BASF Corporation (Wyandotte, MI).

4.3.2. Preparation of thin composite membranes by spin coating

The amine-containing membranes discussed in this section contained XL-PVA, purified polyvinylamine from Lupamin®, and the mobile carrier. As mentioned earlier, Lupamin® contained 66 wt.% sodium formate salt and 34 wt.% PVAm. The sodium formate salt was separated from PVAm by gradually pouring Lupamin® into ethanol, with PVAm precipitated out from ethanol. The PVAm solid was redissolved in H₂O, and then the above procedures were repeated for three times. XL-PVA was prepared following the similar procedures as reported in Chapter 2, with the crosslinking degree of 15 mol.%.

Lithium glycinate (LiG) was prepared by adding lithium hydroxide monohydrate into glycine aqueous solution at 70°C under a N₂ shower and mixing for 1 hour at 70°C, followed by mixing at room temperature for 2 hours. The coating solution was prepared by mixing XL-PVA solution and amine carriers at the solid content of 2 wt.%.

The procedures to prepare the thin composite membranes were as follows: (1) zeolite Y particles were deposited on the Biomax PES substrate by vacuum assisted dip coating; (2) for the membrane without a gutter layer or a cover layer, n-heptane was first applied onto the inorganic layer, followed by spin coating of amine-containing solution on top of the n-heptane treated inorganic layer; (3) for the membrane to have a gutter layer
and a cover layer, water was first applied onto the inorganic layer to prevent the penetration of PDMS gutter-layer coating solution, followed by spin coating of 5.2 wt.% PDMS gutter-layer solution, amine-containing coating solution, and 2.7 wt.% PDMS cover-layer solution in sequence. The preparation of PDMS solution involved mixing Dehesive® 944, Wacker® crosslinker V24, and Wacker® catalyst OL by the weight ratio of 100/1/0.5 in n-heptane at the desired total concentration. In order to enhance the adhesion between the hydrophilic amine layer and the hydrophobic PDMS gutter layer, the solvent of amine-containing coating solution contained around 30 wt.% ethanol and 70 wt.% deionized H₂O. The details of the spin coating procedures and drying conditions of each layer are summarized in Table 4.1.

4.3.3. Preparation of High-molecular-weight PVAm based ultrathin membranes by knife casting

The synthesis of high-molecular-weight PVAm was similar to our group’s previous work [73]: N-vinylformamide monomer was polymerized into poly(N-vinylformamide) via free radical polymerization at 50°C under a mild N₂ purge for 4 hours followed by acid catalyzed hydrolysis to obtain polyvinylamine (PVAm). The protonated PVAm (PVAm•HCl) was precipitated by pouring it gradually into an excessive amount of ethanol. The precipitant was redissolved in H₂O and precipitated once again by pouring the aqueous solution into ethanol. This step was to completely remove the byproducts generated in polymerization and hydrolysis, if any, and obtain a more narrowly distributed molecular
weight of PVAm. The rest of the procedures were the same as reported in our group’s previous work.

The preparation of coating solution was conducted by blending the PVAm solution (pH = 11.0) with mobile carrier solution. Piperazine glycinate (PG) and diethylenetriamine glycinate (DETAG) were used as the mobile carriers in this chapter. The coating solution was coated on top of a flat-sheet PES substrate (pore size = 69 nm, surface porosity = 17%) using a GARDCO adjustable micrometer film applicator (Paul N. Gardner Company, Pompano Beach, FL) with a gap setting of 4 μm. The flat-sheet PES substrate was fabricated via phase inversion by our group according to our previous work [95].

4.3.4. Gas transport measurement

The gas transport performance of a membrane synthesized was tested by using the gas permeation apparatus described in Chapter 2. A gas mixture composed of 20 vol.% CO₂ and 80 vol.% N₂ or 1 vol.% CO₂ and 99 vol.% N₂ on a dry basis was used as the feed gas for the gas transport measurement at the typical flue gas temperature of 57°C for CO₂ capture. Argon (Ar) was used as the sweep gas for the simplicity of gas chromatograph analyses. Prior to flowing the gases, 100 mL water was injected into each of the 500 mL stainless-steel humidifiers (Swagelok, Westerville, OH, USA), filled with 60% (by volume) packing of Raschig rings. The feed gas and the sweep gas were humidified by bubbling them through the abovementioned humidifiers on the feed and sweep sides,
respectively, to achieve the saturation water vapor content of 17.2% at 57°C and 1 atm, and then the humidified gases flowed into the gas permeation cell.

4.4. Results and discussion

4.4.1. Thin composite membranes by spin coating

The gas transport results for amine-containing polymer/inorganic composite membranes prepared by spin coating are illustrated in Figure 4.1. As illustrated in this figure, the membrane without a gutter layer or cover layer showed very low permeance and selectivity, which should be due to the severe penetration of the amine-containing coating solution. It should be noted that the penetration of dilute coating solution not only can lead to low permeance but also can contribute to the poor coverage with a very thin membrane thickness. The incorporation of the PDMS gutter and cover layers enhanced the CO₂ permeance and CO₂/N₂ selectivity significantly. This could be explained by the fact that the highly permeable PDMS gutter layer successfully prevented the penetration of dilute amine-containing solution into the pores and/or defects in the inorganic layer, thus reducing the mass transfer resistance. Meanwhile, the PDMS cover layer sealed the possible defects caused by poor adhesion between the hydrophilic amine layer and the hydrophobic PDMS gutter layer, thus improving the selectivity. Furthermore, the membranes containing the mobile carrier (lithium glycinate) showed even higher CO₂ permeance than the ones with
no mobile carriers. This was a result of the case that the mobile carrier was more efficient in CO$_2$ facilitated transport than the PVAm fixed-site carrier under the test conditions.

4.4.2. High-molecular-weight PVAm based thin membranes prepared by knife casting

4.4.2.1. Membrane performance comparison between PG and DETAG

In terms of ease for scale-up, spin coating is not as advantageous as knife casting. In order to prepare ultra-thin CO$_2$-selective membranes by knife casting, the coating solution should possess high viscosity at a low concentration. The PVAm synthesized in this chapter had a viscosity of 1910 cp for 3 wt.% solution. Two mobile carriers, piperazine glycinate (PG) and diethylenetriamine glycinate (DETAG), were incorporated into the membranes with the PVAm-to-mobile carrier weight ratio of 35/65, respectively.

The membrane performance results are summarized in Table 4.2. As shown in this table, the membranes with PG as the mobile carrier showed a lower CO$_2$ permeance than those with DETAG as the mobile carrier and had a higher CO$_2$/N$_2$ selectivity. This could be explained by the fact that DETAG contained more amino groups than PG at the same weight content, which could provide more amine carriers to react with CO$_2$ and form more hydrogen bonding with PVAm to interrupt the packing of PVAm chain. The latter could increase the free volume for N$_2$ diffusion, resulting in a lower CO$_2$/N$_2$ selectivity. It should be noted that the influence of mobile carriers on membrane performance could differ under different testing conditions. As discussed in Chapter 3, the membrane containing DETAG
showed both slightly higher CO₂ permeability and CO₂/H₂ selectivity than the one containing the same weight content of PG at 120°C and a 54% feed-side H₂O vapor content. This was mainly due to the fact that water retention capability of the membrane at high temperature became more important than at 57°C.

4.4.2.2. Membrane performance at 1% CO₂ in the dry feed gas

The significance of investigating the membrane performance at 1% CO₂ mainly lays in demonstrating the feasibility of applying amine-containing facilitated transport membrane for low CO₂ concentration sources after a primary flue gas carbon-capture system, which may reduce the CO₂ concentration to <1%. The separation performances of the membranes containing PG and DG at 1% CO₂ in the feed gas on a dry basis are illustrated in Table 4.3. As shown in this table, both the CO₂ permeance and CO₂/N₂ selectivity increased by reducing the CO₂ concentration in the feed gas, mainly due to more available carriers for the CO₂ molecular transport at lower CO₂ concentration conditions. Our group is still making continuous effort on studying the membrane performance with CO₂ concentration going down to 0.1%.

4.5. Conclusions

In order to obtain high CO₂ permeance and CO₂/N₂ selectivity at 57°C with a CO₂/N₂ mixture saturated with H₂O at ~1atm, two membrane coating techniques were
applied, i.e., spin coating and knife casting. The key challenge of spin coating is the penetration of dilute coating solution into the pores of the substrate. In order to minimize the penetration, a PDMS gutter layer was incorporated before amine layer coating, i.e., underneath the amine layer, and a PDMS cover layer was applied on the top of amine layer to seal the defects caused by the poor adhesion between the amine layer and the PDMS gutter layer. Though the membrane performance improved significantly after incorporating the PDMS gutter and cover layers, the CO$_2$/N$_2$ selectivity was still too low (≤33). This was mainly because of the low selectivity of the PDMS gutter layer and the presence of XL-PVA which was much less CO$_2$-selective compared to amine carriers. The synthesis of high-molecular-weight PVAm enabled us to fabricate a thin membrane using knife casting and eliminate the XL-PVA in the membrane composition. Two mobile carriers, PG and DETAG, were studied, and the latter demonstrated higher CO$_2$ permeance but lower CO$_2$/N$_2$ selectivity than the former under the test conditions investigated.
Table 4.1. Spin coating procedures and drying conditions for preparation of thin-composite membranes. a

<table>
<thead>
<tr>
<th>PDMS Gutter Layer</th>
<th>Amine-Containing Layer</th>
<th>PDMS Cover Layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spin Coating</td>
<td>Drying</td>
<td>Spin Coating</td>
</tr>
<tr>
<td>1500 rpm, 5 s</td>
<td>100°C</td>
<td>2000 rpm, 5 s</td>
</tr>
<tr>
<td>4500 rpm, 1 min</td>
<td>30 min</td>
<td>4000 rpm, 1 min</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2 h</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6000 rpm, 1 min</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30 min</td>
</tr>
</tbody>
</table>

a Spin coating involved two steps: the purpose of Step 1 at a lower spinning speed for 5 s was aimed to spread the solution evenly onto the substrate, while the purpose of Step 2 at a higher spinning speed for 1 min was to reduce the thickness of the membrane layer.
Table 4.2 Membrane performance comparison between PG and DETAG. \(^a\)

<table>
<thead>
<tr>
<th>Mobile Carrier</th>
<th>(\text{CO}_2) Permeance (GPU)</th>
<th>(\text{CO}_2/\text{N}_2) Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>PG #1</td>
<td>738</td>
<td>138</td>
</tr>
<tr>
<td>PG #2</td>
<td>721</td>
<td>133</td>
</tr>
<tr>
<td>DG #1</td>
<td>792</td>
<td>117</td>
</tr>
<tr>
<td>DG #2</td>
<td>808</td>
<td>106</td>
</tr>
<tr>
<td>DG #3</td>
<td>811</td>
<td>102</td>
</tr>
</tbody>
</table>

\(^a\) Feed gas containing 20% \(\text{CO}_2\) and 80% \(\text{N}_2\) on a dry basis
Table 4.3. Membrane performances at different CO₂ concentrations in the feed gases.

<table>
<thead>
<tr>
<th>Feed CO₂ Concentration on a Dry Basis</th>
<th>20%</th>
<th>1%</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>PG #2</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO₂ Permeance (GPU)</td>
<td>721</td>
<td>934</td>
</tr>
<tr>
<td>CO₂/N₂ Selectivity</td>
<td>133</td>
<td>149</td>
</tr>
<tr>
<td><strong>DETAG #1</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO₂ Permeance (GPU)</td>
<td>792</td>
<td>989</td>
</tr>
<tr>
<td>CO₂/N₂ Selectivity</td>
<td>117</td>
<td>126</td>
</tr>
<tr>
<td><strong>DETAG #2</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO₂ Permeance (GPU)</td>
<td>808</td>
<td>992</td>
</tr>
<tr>
<td>CO₂/N₂ Selectivity</td>
<td>106</td>
<td>110</td>
</tr>
</tbody>
</table>
Figure 4.1. Gas transport measurement results for amine-containing polymer/inorganic composite membranes prepared by spin coating.
Chapter 5: New sterically hindered polyvinylamine membranes for CO$_2$ separation and capture

5.1. Summary

Facilitated transport membranes have been intensively studied for CO$_2$ separation and capture, in which amine carriers are the key for membrane separation performance. It has been reported that sterically hindered amines possess superior CO$_2$ loading capacity over unhindered amines. In this work, we successfully introduced the effect of the steric hindrance to the nitrogen site of amine into polyvinylamine membranes. Sterically hindered poly(N-vinylamine)s, namely poly(N-methyl-N-vinylamine), poly(N-isopropyl-N-vinylamine), and poly(N-tertiary-butyl-N-vinylamine), were synthesized from modifying unhindered poly(N-vinylamine). The effect of steric hindrance on membrane performance was investigated under the typical flue gas CO$_2$ capture conditions, i.e., 57°C and ~1 atm, showing that poly(N-methyl-N-vinylamine) was the one with the optimal steric hindrance degree for the best membrane performance. Compared with unmodified polyvinylamine, poly(N-methyl-N-vinylamine) demonstrated 24% improvement on CO$_2$ permeability and 14% increase in CO$_2$/N$_2$ selectivity at 57°C. The membrane performance enhancement by amine steric hindrance was found to be greatly influenced by temperature.
At 102°C, poly(N-methyl-N-vinylamine) demonstrated a CO₂ permeability of 6804 Barrers, a CO₂/N₂ selectivity of 350, and a CO₂/H₂ selectivity of 162, which were approximately 4 times those of unmodified polyvinylamine. This work has extended the study on sterically hindered polyamines for CO₂ facilitated transport and developed a next-generation fixed-site carrier membrane.
5.2. Introduction

CO₂ separation and capture are of great significance in many industrial applications, e.g., greenhouse gas emission reduction, hydrogen purification, natural gas sweetening, etc. Amines and their derivatives are the most widely used reagents for bulk CO₂ removal, which relies on the reversible chemical reaction between basic amine and acidic CO₂ [2,4]. The state-of-the-art technology for CO₂ removal from gas mixtures is amine scrubbing, in which the pressure and/or temperature swing operations are conducted to accomplish the CO₂ absorption at high feed gas pressure and low temperature (40 – 60°C) and the CO₂ desorption at reduced pressure and high temperature (120 – 180°C). Though the most mature technology nowadays, amine scrubbing has shortcomings including thermodynamic equilibrium solubility limitation, high energy consumption, a large footprint, and severe corrosion [1,2]. Owing to its kinetic nature and solid membrane form that can avoid these shortcomings, membrane technology has emerged as a much more cost-effective process. Membrane technology is also advantageous in terms of a modular configuration, system compactness, and operational flexibility and simplicity [4]. Inspired by the reversible amine-CO₂ reaction, scientists have incorporated amines and/or their derivatives into hydrophilic polymer networks to develop CO₂ facilitated transport membranes [33-40,67-68,70-73,96,97]. In such a membrane, amine acts as the “carrier” that reacts with CO₂ and transports it in the form of CO₂-amine reaction product, while other non-reactive gases, such as N₂, H₂, CH₄, etc., can only transport across the membrane via the physical solution-diffusion mechanism [97].
Facilitated transport membranes have great potential to be applied for flue gas carbon capture, syngas purification, and natural gas sweetening. It is advantageous to apply facilitated transport membranes for flue gas carbon capture in view of low CO₂ concentration and the presence of H₂O in flue gas, which favors the reaction of CO₂ and amine. Many research groups, including ours, have developed thin composite membranes with the amine-containing selective layer for the application of flue gas CO₂ capture. Qiao et al. synthesized the high-molecular-weight poly(N-vinylamine) (PVAm), which serves as the fixed-site carrier and the polymer matrix, and they found that the PVAm membrane performance was improved significantly by blending it with an appropriate amount of piperazine [68]. Chen et al. further developed the membrane composition by incorporation of piperazine glycinate into their synthesized high-molecular-weight PVAm, and they achieved a CO₂ permeance of 1100 GPU and CO₂/N₂ selectivity of more than 200 under simulated flue gas carbon capture conditions after flue gas desulfurization, i.e., the CO₂ and N₂ gas mixture saturated with H₂O at 57°C and 1 atm [73,96]. Wu et al. investigated the SO₂ interference on membrane performance for the application of amine-containing membranes for flue gas carbon capture. Their membranes showed good stability with 1 – 3 ppm SO₂ at 57°C, which indicated the great potential for the amine-containing membranes to be applied for real flue gas carbon capture in combination of a SO₂ polishing process prior to the membrane process [95]. Recently, our group demonstrated over 200 hours of prototype spiral-wound membrane module stability with a slipstream of real flue gas containing 7±1% O₂, 0.5 – 5 ppm SO₂, and 1.5 – 4 ppm NO₂ at the National Carbon Capture Center (NCCC) in Wilsonville, AL, USA [95,98].
In addition to flue gas carbon capture, facilitated transport membranes have also been employed for the purification of syngas and natural gas [88,91,99]. In fact, the syngas and natural gas purification conditions may be more attractive for the application of amine-containing membranes, due to higher temperatures and water partial pressures, which benefit the reaction of amine and CO$_2$. The high CO$_2$/H$_2$ selectivity of an amine-containing membrane makes it more favorable for hydrogen purification regarding hydrogen loss reduction than solution-diffusion membranes, e.g., Pebax®1657, polyester-ether and polyurethane-ether membranes, which are usually used at low temperatures (~35°C) and have selectivities less than 50 [100-102]. Zou et al. applied the amine-containing CO$_2$-selective membranes for their water-gas-shift (WGS) membrane reactor and achieved a CO$_2$ permeability of greater than 6000 Barrers and a CO$_2$/H$_2$ selectivity of 200 – 300 for membrane thicknesses of 30 – 60 μm [70]. Tong et al. synthesized the membranes containing the Lupamin® PVAm as the fixed-site carrier for hydrogen purification for fuel cell applications and obtained a CO$_2$ permeance of 200 GPU along with a CO$_2$/H$_2$ selectivity of more than 180 for an average membrane thickness of 15 μm [46]. Amine-containing membranes, mechanically enhanced by nanofillers, can also be applied for high-pressure natural gas sweetening. Ansaloni et al. incorporated amino-functionalized carbon nanotubes into amine-containing membranes and achieved a CO$_2$ permeability of 957 Barrers along with a high CO$_2$/CH$_4$ selectivity of 264 at 107°C and 15 bar [85].

Amine carriers are the key to the superior separation performance of facilitated transport membranes. The amine-CO$_2$ chemistry is commonly described by the zwitterion mechanism [28,29]. An unhindered amine reacts with CO$_2$ to first form a zwitterion (Eq. 30...
(5.1)), which can be rapidly deprotonated by another amine molecule, generating a carbamate ion and a protonated amine (Eq. (5.2)). The overall reaction indicates that the CO₂ loading of primary or secondary unhindered amine is 0.5 moles CO₂ per mole amine (Eq. (5.3)).

\[
\begin{align*}
R_1R_2NH + CO_2 & \rightleftharpoons R_1R_2NH^+COO^- \quad (5.1) \\
R_1R_2NH^+COO^- + R_1R_2NH & \rightleftharpoons R_1R_2NCOO^- + R_1R_2NH_2^+ \quad (5.2) \\
2 R_1R_2NH + CO_2 & \rightleftharpoons R_1R_2NCOO^- + R_1R_2NH_2^+ \quad (5.3)
\end{align*}
\]

Another important group of amine is sterically hindered amine, which is defined as a primary amine with the amino group attached to a tertiary carbon atom or a secondary amine with the amino group attached to at least one secondary carbon atom [103]. As for a sterically hindered amine, the carbamate ion is unstable caused by the bulky group attached to the amino group, which hinders the rotation and stretching of the C-N bond to form the carbamate ion. As a result, a free amine is released and a bicarbonate ion is formed with the presence of H₂O (as indicated in the red dotted “L” box in Eq. (5.4)). Therefore, the maximum CO₂ loading is twice of that of unhindered amine (Eq. (5.5)).

\[
\begin{align*}
R_1’R_2’NH + CO_2 + H_2O & \rightleftharpoons HCO_3^- + R_1’R_2’NH_2^+ \quad (5.5)
\end{align*}
\]

Not only sterically hindered amine possesses a higher CO₂ loading capacity, its superiority is also indicated on the overall CO₂-amine reaction rate. Though the CO₂-amine reaction rate constant of sterically hindered amine can be relatively lower than that
of unhindered amine, the free amine concentration is increased due to the higher CO$_2$ loading capacity of sterically hindered amine. Therefore, the overall reaction rate of sterically hindered amine is improved, which is determined by the second-order reaction rate constant based on free CO$_2$ concentration and free amine concentration [104]. Amine carriers exhibiting a high CO$_2$ loading capacity and reaction rate are always desirable. Thus, sterically hindered amine is an excellent candidate carrier to be applied in CO$_2$ facilitated transport membranes.

Our group has done intensive research on applying sterically hindered amine carriers. 2-Aminoisobutyric acid salts (e.g., AIBA-K), a sterically hindered amine, was used as the mobile carrier for achieving outstanding CO$_2$ separation performances [10,46,70]. As for facilitated transport membranes, the application of sterically hindered amines as fixed-site carriers is more attractive since mobile carriers may be relatively easier to lose due to the lack of covalent bonding with the polymer network. The transport mechanisms of fixed-site carrier membranes with unhindered and hindered polyamines are depicted in Figure 5.1(a) and 5.1(b), respectively. As is shown in Figure 5.1(a), CO$_2$ transport mainly relies on the “hopping” of CO$_2$ molecule from one amino group site to another, in the form of the carbamate ion, which is bonded on the polymer chains [105]. But in the case of hindered polyamine (Figure 5.1(b)), CO$_2$ transports across the membrane in the form of bicarbonate ion, which is movable and thus can diffuse much faster than CO$_2$ “hopping” along polymer chains.

Zhao and Ho for the first time applied sterically hindered amine as the fixed-site carrier in membranes by modifying unhindered polyallylamine into sterically hindered
polyamines and blending the hindered polyamines with the crosslinked polyvinylalcohol network. They found that the membrane performance was dramatically improved with the moderately hindered polyallylamine [56]. In addition to polyallylamine (PAA), polyethylenimine (PEI) and polyvinylamine (PVAm) are also commonly used fixed-site carriers. The chemical structures of these polyamines are illustrated in Figure 1.1 in Chapter 1. A large portion of the amino groups of PEI is secondary and tertiary amines. Tertiary amine is limited by the low reaction rate of CO$_2$ hydration, which makes PEI less effective than PAA or PVAm. Both PAA and PVAm contain primary amino groups alone; however, the amino group content in PAA is lower than in PVAm. Moreover, because of the amino group directly bonded to the polymer backbone, PVAm has a slightly higher degree of steric hindrance than PAA, which makes PVAm the best fixed-site carrier candidate among those three polyamines.

PVAm, as the most efficient fixed-site carrier, has attracted an increasing attention in recent years. Intensive efforts have been placed on further improving the separation performance of PVAm based membranes, including tuning the pH and hydrolysis degree of PVAm [43,106], crosslinking of PVAm with different methods [33,106], blending PVAm with multiple mobile carriers [67,68,96-99] and nanofillers to synthesize PVAm based mixed matrix membranes [86,107]. However, among all those attempts, introduction of steric hindrance effect to PVAm was rarely exploited. In this work, we synthesized high-molecular-weight PVAm and modified it into sterically hindered polyamines with different degrees of steric hindrance. Because of the chain entanglement of high-molecular-weight PVAm, PVAm not only contributed to CO$_2$ facilitated transport as a
fixed-site carrier but also provided film forming ability and mechanical strength. In our group’s previous work, 30 wt.% XL-PVA was blended with sterically hindered PAA since PAA had a very low molecular weight and was not able to form a membrane alone [56]. With the high-molecular-weight PVAm, XL-PVA can be eliminated from the membrane composition so as to rule out the influence of XL-PVA itself and/or the interaction between XL-PVA and polyamine on membrane performance. Another advantage of the sterically hindered modification of PVAm is that it only needs one methyl group for each repeating unit of PVAm to obtain sterically hindered PVAm according to the definition of sterically hindered amine. This is attractive since the amino group content of PVAm will not need to be diluted as much as for the modification of PAA. In this work, the effect of steric hindrance degree was studied, and the influence of temperature on membrane performance enhancement caused by sterically hindered PVAm was investigated. The PVAm with the optimal degree of steric hindrance can be considered as the next-generation fixed-site carrier.

5.3. Experimental

5.3.1. Materials

N-vinylformamide, 2,2’-azobis(2-methylpropionamidine) dihydrochloride, potassium hydroxide, iodomethane, 2-bromopropane, and 2-bromo-2-methyl-propane were purchased from Sigma-Aldrich (St. Louis, MO, USA). Hydrochloride acid, ethanol
and methanol were acquired from Fisher Scientific Inc. (Pittsburgh, PA, USA). A600OH anion exchange resin was kindly donated by Purolite Corporation (Bala Cynwyd, PA, USA). Polyethersulfone (PES) (Ultrason® E7020P, MW 93000) was kindly provided by BASF Corporation (Wyandotte, MI, USA). PES substrates were fabricated via phase inversion by our group according to our previous work [95]. Non-woven fabric used for PES substrate fabrication was purchased from TriSep Corporation (Goleta, CA, USA).

5.3.2. Sterically hindered polyvinylamine synthesis

The synthesis of sterically hindered polyvinylamine started with the synthesis of unhindered polyvinylamine following the procedures as previously reported [73]. First, the monomer, N-vinylformamide was purified to remove the inhibitor via vacuum distillation at 40°C. A certain amount of N-vinylformamide was dissolved in deionized H₂O at 40 wt.%. The polymerization of N-vinylformamide was initiated by 2,2'-azobis(2-methylpropionamidine) dihydrochloride at about 0.14 wt.% of N-vinylformamide. The polymerization was carried out under mild N₂ purge and at 50°C for 4 hours. After the polymerization, polyvinylformamide was obtained and hydrolyzed to convert the formamide group into amino group with HCl as the catalyst. The molar ratio of formamide group to HCl was kept at 1:2. The hydrolysis was undertaken at 80°C for 5 hours. After hydrolysis was finished, the solution was poured gradually into a 4-time volume of ethanol, and protonated polyvinylamine (PVAHCl) was precipitated out from ethanol and dried in a vacuum oven at 50°C for overnight. The dried PVAHCl was redissolved in H₂O to
have the aqueous solution of 3 wt.% PVAm•HCl, which was then deprotonated to PVAm via the anion exchange reaction using the ion exchange resin, A600OH. After the ion exchange reaction, the obtained PVAm solution had a pH of 11.0. The molecular weight of PVAm was about 1,200,000 g/mol, which was determined by dynamic light scattering characterization in our previous work [73].

Each of the sterically hindered poly(N-vinylamine)s was synthesized via the substitution reaction between PVAm and alkyl halide with KOH as the catalyst and acid acceptor as shown in Figure 5.2. [56,108-109]. In the synthesis, the obtained unhindered PVAm was dissolved in a methanol and H₂O solvent mixture (methanol/H₂O weight ratio = 80/20) containing an equivalent amount of KOH. The PVAm in the above solution was kept at 2 wt.%. An equivalent amount of alkyl halide was then added into the above solution at room temperature. For the synthesis of poly(N-methyl-N-vinylamine), the reaction was carried out in a light blocking environment. The solution containing PVAm, KOH, and alkyl halide was heated up to 55°C with reflux, and the reaction was continued for 48 hours. After the reaction, the solution was transferred into a dialysis tubing (4 nm pore size) sealed with clips at the ends. The dialysis with deionized water lasted for 4 hours under stirring with changing water every 15 minutes. Thus, the byproduct, potassium halide salt, should be removed completely. To further purify the sterically hindered polyvinylamine for removing the residual organic compound, the solution was gradually poured into ethanol/acetone (50/50 by weight) mixture (pH 2), and the protonated sterically hindered polyvinylamine was precipitated out. Following the similar procedures for the
unhindered PVAm ion exchange reaction, the sterically hindered polyvinylamine solution with a pH of 11.0 was obtained and used for membrane preparation.

5.3.3. Membrane preparation

All the polyamine solutions in this work (including PVAm and different sterically hindered PVAm solutions) with a pH of 11.0 were used for membrane preparation. The reason for controlling the consistent pH value of all the polyamine solutions in this work was that pH could affect the content of free amino groups so as to influence the CO₂ separation performance [43]. The polyamine solution was concentrated by N₂ purge at room temperature to acquire a good viscosity and then centrifuged at 8000 rpm for 5 min to remove any air bubbles. The viscous polyamine solution was then coated on top of the flat-sheet PES substrate (pore size = 69 nm, surface porosity = 17%) using a GARDCO adjustable micrometer film applicator (Paul N. Gardner Company, Pompano Beach, FL) with a controlled gap setting. The membrane was dried in the hood at room temperature for 48 hours before testing. The thickness of the dry membrane was measured by a Mitutoyo electronic indicator (Model 543-252B, Mitutoyo America Corp, Aurora, IL, USA) with an accuracy of ±0.5 μm. The membrane thickness was determined by subtracting the thickness of the substrate from the total thickness of the composite membrane. In this work, the thicknesses of all the membranes were controlled at 12±2 μm.
5.3.4. Polyamine chemical structure characterization

The chemical structures of synthesized sterically hindered polyamines and unmodified polyvinylamine were characterized by Fourier transform infrared (FT-IR) attenuated total reflectance (ATR) spectroscopy using a Nicolet iS50 Fourier transform infrared spectrometer (Thermo Fisher Scientific Inc., Waltham, MA).

5.3.5. Gas transport measurement

The testing conditions are summarized in Table 5.1 for the gas transport measurements. The feed gas and the sweep gas flowed counter-currently into the stainless-steel gas permeation cell, and the gas flow rates were controlled at 60 and 30 cm³/min by mass flow controllers (Brooks Instrument, Hatfield, PA, USA), respectively. A gas mixture composed of 20 vol.% CO₂ and 80 vol.% N₂ on a dry basis was used as the feed gas for the gas transport measurement at the typical flue gas temperature of 57°C for CO₂ capture, and a gas mixture of 20 vol.% CO₂, 40 vol.% H₂ and 40 vol% N₂ on a dry basis was used as the feed gas for the tests at > 100°C for hydrogen purification. Argon (Ar) was used as the sweep gas for the simplicity of gas chromatography analyses. Liquid water was injected into the humidifiers inside the oven by Varian ProStar delivery modules (Model 210, Varian Inc., Palo Alto, CA, USA) for gas humidification.

For the gas transport measurement at 57°C, prior to flowing the gases, 100 mL water was injected into each of the 500 mL stainless-steel humidifiers (Swagelok,
Westerville, OH, USA), filled with 60% (by volume) packing of Raschig rings. The feed gas and the sweep gas were humidified by bubbling them through the abovementioned humidifiers on the feed and sweep sides, respectively, to achieve the saturation water vapor content of 17.2% at 57°C and 1 atm, and then the humidified gases flowed into the gas permeation cell. For the gas transport measurements at >100°C, the water injection rates were controlled at 0.18 cc/min for the feed-side water content of 80 mol.% and 0.03 cc/min for the sweep-side water content of 57 mol.%. Under the testing temperature, liquid water was vaporized and well mixed with the dry gas in each of the humidifiers, and the humidified feed and sweep gases flowed into the gas permeation cell. The retentate pressure was controlled by a back-pressure regulator at 1.5 psig (measured by a pressure gauge installed on the retentate side), and the permeate pressure was set at 1.4 psig (measured by another pressure gauge on the permeate side). After the gas permeation cell, the retentate and permeate stream left the oven and were cooled down to let water condensed in their respective water knock-out vessels. The dry retentate and permeate gas samples were injected into an Agilent 6890N gas chromatograph (Agilent Technologies, Palo Alto, CA, USA) with SUPEL CO Carboxen® 1004 micro-packed column (Sigma-Aldrich, St. Louis, MO, USA) for gas composition analyses.
5.4. Results and discussion

5.4.1. Polyamine chemical structure characterization

The FT-IR spectra of the synthesized polyvinylamine, poly(N-methyl-N-vinylamine), poly(N-isopropyl-N-vinylamine), and poly(N-tert-butyl-N-vinylamine) are shown in Figure 5.3. In poly(N-methyl-N-vinylamine), poly(N-isopropyl-N-vinylamine), and poly(N-tert-butyl-N-vinylamine), the peaks at 1172 cm$^{-1}$, 1170 cm$^{-1}$, and 1183 cm$^{-1}$, respectively, should be attributed to the C-N stretching vibration in -C-NH-C- (1190 cm$^{-1}$ – 1170 cm$^{-1}$), which is not shown in polyvinylamine. This indicated that the primary amino groups in polyvinylamine were converted to secondary amino groups by their respective reactions. Meanwhile, there was a unique peak at 2779 cm$^{-1}$ in poly(N-methyl-N-vinylamine), which should be attributed to C-H stretching vibration in –NH-CH$_3$ [110]. These results indicated that the sterically hindered polyvinylamines were successfully synthesized.

5.4.2. Effect of steric hindrance degree

Using different alkylation agents as described in Section 5.3.2, polyvinylamine was modified into the sterically hindered polyvinylamines of different steric hindrance degrees. In the literature, the amine steric hindrance degree can be usually quantitatively expressed as Taft’s steric hindrance parameter, which is denoted as $\sum E_e$ and can be calculated by the
group contribution method [53]. Table 5.2 illustrates the chemical structure and the corresponding $\sum E_s$ value of each polyamine in this work. As shown in Table 5.2, as the attached alkyl group becomes bulkier, the corresponding $\sum E_s$ is in an ascending trend, indicating an increased steric hindrance degree. Meanwhile, the amino group concentration in the polyamine is in a descending trend, caused by the added alkyl groups. The corresponding amino weight content in each polyamine is also included in Table 5.2, for the discussion to follow afterwards.

The synthesized sterically hindered polyamine and unmodified polyvinylamine membranes were characterized under simulated flue gas carbon capture conditions at 57°C as shown in Table 5.1. Under the testing conditions, both CO$_2$ permeability and CO$_2$/N$_2$ selectivity were measured for all the tested membranes and plotted against $\sum E_s$ in Figure 5.4. Though the attached alkyl groups reduced the amino concentrations in the membranes, the sterically hindered polyvinylamines synthesized in this work still demonstrated improved CO$_2$/N$_2$ separation performance over the unmodified polyvinylamine. CO$_2$ permeability was improved by 24% and CO$_2$/N$_2$ selectivity was increased by 14% by modifying polyvinylamine into poly(N-methyl-N-vinylamine). These results have demonstrated the effect of steric hindrance with the incorporation of the methyl group for enhancing CO$_2$ separation performance in the solid membrane phase. Poly(N-isopropyl-N-vinylamine) and poly(N-tert-butyl-N-vinylamine) membranes showed 15% and 11% improvements on CO$_2$ permeability, respectively. The improvement in CO$_2$/N$_2$ selectivity was not as significantly as CO$_2$ permeability; only poly(N-methyl-N-vinylamine) showed an improvement of 14% while poly(N-isopropyl-N-vinylamine) and poly(N-tert-butyl-N-
vinylamine) did not show a significant change in CO₂/N₂ selectivity. This could be explained by the fact that the incorporation of alkyl groups reduced the polarity of the membrane, which raised the solubility of N₂ in the membrane. This is one of very few pieces of work that demonstrates the steric hindrance effect on CO₂ facilitated transport in the solid membrane phase [56,108].

Comparing the CO₂ separation performances of the above polyamine membranes and their corresponding steric hindrance degrees, we found that the CO₂ permeability increased first significantly with increasing the steric hindrance degree and then less pronouncedly with further increasing the steric hindrance degree. The reduced amino group content in the membranes could be one of the explanations. Moreover, it should be attributed to the lower CO₂-amine reaction rate due to the incorporation of bulky groups onto amino groups. In other words, as for poly(N-methyl-N-vinylamine), a moderately hindered polyamine, the reduced CO₂-amine reaction rate constant could be compensated by the increased free amine concentration, which overall accelerated the CO₂-amine reaction. But for severely hindered polyamines, the reaction rate constant might reduce so significantly that the CO₂-amine reaction was slow down, which resulted in the less improvement in separation performance demonstrated by poly(N-isopropyl-N-vinylamine) and poly(N-tert-butyl-N-vinylamine). The transport performances of the polyamine membranes discussed in this section are summarized in Table 5.3. Based on the gas permeation measurement results summarized in this table, poly(N-methyl-N-vinylamine) has demonstrated the most significant improvement on membrane performance, making it
a promising candidate as the next generation fixed-site carrier for CO₂ facilitated transport membranes.

5.4.3. Effect of temperature on the performance enhancement by amine steric hindrance

Though the incorporation of alkyl groups could interrupt the packing of polymer chains and hence increase the free volumes of the sterically hindered polyvinylamine membranes, the amine steric hindrance effect on membrane performance should still be mainly on the CO₂-amine reaction kinetics for the facilitated transport membranes. As well known, temperature is an important factor for chemical reaction kinetics. Therefore, the operating temperature may play a key role to some extent for the amine steric hindrance effect. As stated in Section 5.4.2, we have demonstrated the steric hindrance effect on the polyvinylamine membranes at 57°C. It is worthwhile to investigate the amine steric hindrance effect at higher temperatures. In view of practical application, such as syngas purification, which is often operated between 100 – 120°C, we conducted the gas transport measurements of the polyamine membranes synthesized in this work at 102°C, 110°C and 120°C, using the feed gas of 20%CO₂, 40%H₂, and 40%N₂ on a dry basis. Since poly(N-methyl-N-vinylamine) (PMVAm) has been identified as the sterically hindered polyamine showing the best membrane performance in Section 5.4.2, only unmodified PVAm and PMVAm membranes were tested and compared here for simplicity. CO₂/N₂ and CO₂/H₂ separation performances of PVAm and PMVAm membranes were characterized under the conditions listed in Table 5.1 for the feed gas mixture of CO₂, H₂ and N₂. The results are
plotted in Figures 5.5, 5.6 and 5.7 for CO₂ permeabilities, CO₂/N₂ selectivities and CO₂/H₂ selectivities, respectively and summarized in Table 5.4.

As shown in Figure 5.5, in spite of the steric hindrance effect, both PVAm and PMVAm membranes showed a significant increase in CO₂ permeability at high temperatures (102°C, 110°C, and 120°C) as compared to 57°C. This could be attributed to the accelerated diffusion and CO₂-amine reaction at higher temperatures. According to Figure 5.6, CO₂/N₂ selectivity also increased more dramatically at the high temperatures than at 57°C, which indicated that the significant membrane performance improvement should mainly be explained by the enhanced CO₂-amine reaction at high temperatures rather than gas diffusion acceleration. This explanation is also in line with the nature of facilitated transport membranes. In addition, Figures 5.6 and 5.7 show higher CO₂/N₂ and CO₂/H₂ selectivities at the high temperatures (102°C, 110°C, and 120°C), respectively, with the PMVAm membrane than with the PVAm membrane.

In comparison of the CO₂/N₂ separation performances at 57°C and >100°C (102°C, 110°C and 120°C), the steric hindrance effect was much more pronounced at >100°C than that at 57°C. The improvements of CO₂/N₂ separation performances at different temperatures are illustrated in Table 5.5. At 57°C, the PMVAm membrane only demonstrated 24% higher CO₂ permeability along with 14% higher CO₂/N₂ selectivity as compared to PVAm. However, when the temperature was elevated to 100 – 120°C, the PMVAm membrane demonstrated improvements at least 127% on CO₂ permeability and 153% on CO₂/N₂ selectivity as compared to the PVAm membrane. At 102°C, the PMVAm membrane demonstrated a CO₂ permeability of 6804 Barrers along with a CO₂/N₂
selectivity of 350 and a CO₂/H₂ selectivity of 162, which were 283%, 366% and 211% improvements over those of the PVAm membrane, respectively. These results indicated that the high temperatures might enhance the amine steric hindrance effect as well as the CO₂-amine reaction rate. The more pronounced steric hindrance effect at high temperatures could be explained by CO₂ and sterically hindered amine reaction mechanism. As described earlier, the carbamate ion formed between sterically hindered amine and CO₂ is not stable due to the bulky group attached to the amino group. The high temperatures could accelerate the breakdown of carbamate ion and the formation of bicarbonate. In the other words, the hydrolysis of carbamate ion enclosed in the red dotted “L” box in Eq. (5.4) is an endothermic reaction, and the reaction shifts to the direction of bicarbonate formation as temperature increases. It should be noted that the water vapor content was much higher in the high-temperature test than in the test at 57°C, which appeared to have a synergic effect with temperature on the enhancement of amine steric hindrance demonstrated at 102 – 120°C.

Figures. 5.5, 5.6 and 5.7 also indicated that as the temperature further elevated from 102°C to 120°C, both PVAm and PMVAm membrane performances dropped. This observation was in line with our group’s previous results of polyvinylalcohol-based amine-containing membranes, which could be explained by the reduced water retention capability of the membrane with a temperature increase. Besides, the improvement in membrane performance resulting from the steric hindrance effect was also lessened, e.g., the CO₂ permeability improvement of PMVAm over PVAm reduced from 283% to 127% as temperature increased from 102°C to 120°C. These results could also be explained by the
reduced water retention capability of the membrane with the temperature increase. As shown in Eq. (5.5), water plays an important role especially in the reaction of the sterically hindered amines with CO₂, which can make it a key factor for the enhancement of the amine steric hindrance effect as temperature further increases.

5.5. Conclusions

In this work, sterically hindered polyvinylamines with different degrees of steric hindrance, poly(N-methyl-N-vinylamine), poly(N-isopropyl-N-vinylamine), and poly(N-tert-butyl-N-vinylamine), were successfully synthesized. Among the synthesized sterically hindered polyamines, the poly(N-methyl-N-vinylamine) membrane demonstrated the most significant improvements in both CO₂ permeance and CO₂/N₂ selectivity, compared to the unhindered polyvinylamine, under the typical flue gas CO₂ capture conditions, i.e., 57°C and ~1 atm. With temperature elevated, the steric hindrance effect became much more pronounced and the poly(N-methyl-N-vinylamine) membrane showed 283% enhancement on CO₂ permeability, 366% increase on CO₂/N₂ selectivity and 211% improvement in CO₂/H₂ selectivity, compared to unhindered polyvinylamine membrane at 102°C. As temperature further increase from 102°C to 120°C, the membrane performance dropped; but the poly(N-methyl-N-vinylamine) membrane still showed significant improvement as compared to the polyvinylamine membrane. It indicated that water retention capability played an important role in amine-containing membrane performance. The poly(N-methyl-N-vinylamine) membrane demonstrated a CO₂ permeability of 6804 Barrers, a
CO\textsubscript{2}/N\textsubscript{2} selectivity of 350, and a CO\textsubscript{2}/H\textsubscript{2} selectivity of 162 at 102°C, which should be the best performance among the fixed-site carrier membranes reported according to our best knowledge. This work is an extension to the study of the steric hindrance effect introduced to solid-state membranes. This new sterically hindered polyvinylamine synthesized in this work can be a good candidate fixed-site carrier to be used with mobile carriers in the future.
Table 5.1. Test conditions for gas permeation measurements.

<table>
<thead>
<tr>
<th>Dry feed gas composition</th>
<th>Water content (mol.%)</th>
<th>T (°C)</th>
<th>Relative humidity (%)</th>
<th>Pressure (psig)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Feed</td>
<td>Permeate</td>
<td>Feed</td>
<td>Permeate</td>
</tr>
<tr>
<td>20% CO₂ / 80% N₂</td>
<td>17</td>
<td>17</td>
<td>57</td>
<td>~100</td>
</tr>
<tr>
<td>20% CO₂ / 40% H₂ / 40% N₂</td>
<td>102</td>
<td>80</td>
<td>57</td>
<td>61</td>
</tr>
<tr>
<td>40% N₂</td>
<td>120</td>
<td>44</td>
<td>31</td>
<td></td>
</tr>
</tbody>
</table>
Table 5.2. The chemical structure, Taft’s steric hindrance parameter $\sum E_s$ and amino group concentration of each polyamine in this work.

<table>
<thead>
<tr>
<th>Polyamine</th>
<th>Chemical Structure</th>
<th>$\sum E_s$</th>
<th>Amino Group wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyvinylamine</td>
<td><img src="image" alt="Polyvinylamine" /></td>
<td>0.93</td>
<td>37</td>
</tr>
<tr>
<td>poly(N-methyl-N-vinylamine)</td>
<td><img src="image" alt="Poly(N-methyl-N-vinylamine)" /></td>
<td>1.00</td>
<td>26</td>
</tr>
<tr>
<td>poly(N-isopropyl-N-vinylamine)</td>
<td><img src="image" alt="Poly(N-isopropyl-N-vinylamine)" /></td>
<td>1.86</td>
<td>18</td>
</tr>
<tr>
<td>poly(N-tert-butyl-N-vinylamine)</td>
<td><img src="image" alt="Poly(N-tert-butyl-N-vinylamine)" /></td>
<td>2.67</td>
<td>15</td>
</tr>
</tbody>
</table>
Table 5.3. CO₂/N₂ separation performances of different polyamine membranes at 57°C.

<table>
<thead>
<tr>
<th>Polyamine</th>
<th>Membrane #</th>
<th>CO₂ Permeability (Barrers)</th>
<th>CO₂/N₂ Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyvinylamine</td>
<td>M-1</td>
<td>220.5</td>
<td>50.4</td>
</tr>
<tr>
<td></td>
<td>M-2</td>
<td>206.4</td>
<td>47.0</td>
</tr>
<tr>
<td></td>
<td>M-3</td>
<td>212.2</td>
<td>47.7</td>
</tr>
<tr>
<td></td>
<td>M-4</td>
<td>216.3</td>
<td>48.7</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>213.9</td>
<td>48.5</td>
</tr>
<tr>
<td>Poly(N-methyl-N-vinylamine)</td>
<td>M-5</td>
<td>268.3</td>
<td>54.0</td>
</tr>
<tr>
<td></td>
<td>M-6</td>
<td>259.7</td>
<td>57.1</td>
</tr>
<tr>
<td></td>
<td>M-7</td>
<td>261.1</td>
<td>55.6</td>
</tr>
<tr>
<td></td>
<td>M-8</td>
<td>267.5</td>
<td>55.3</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>264.2</td>
<td>55.5</td>
</tr>
<tr>
<td>Poly(N-isopropyl-N-vinylamine)</td>
<td>M-9</td>
<td>247.0</td>
<td>47.9</td>
</tr>
<tr>
<td></td>
<td>M-10</td>
<td>242.4</td>
<td>47.4</td>
</tr>
<tr>
<td></td>
<td>M-11</td>
<td>245.6</td>
<td>47.2</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>245.0</td>
<td>47.5</td>
</tr>
<tr>
<td>Poly(N-tert-butyl-N-vinylamine)</td>
<td>M-12</td>
<td>239.8</td>
<td>48.6</td>
</tr>
<tr>
<td></td>
<td>M-13</td>
<td>237.5</td>
<td>48</td>
</tr>
<tr>
<td></td>
<td>M-14</td>
<td>236.2</td>
<td>48.7</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>237.8</td>
<td>48.4</td>
</tr>
</tbody>
</table>
Table 5.4. Gas transport properties of polyvinylamine (PVAm) and poly(N-methyl-N-vinylamine) (PMVAm) membranes at 102°C, 110°C and 120°C.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>CO₂ Permeability (Barrers)</th>
<th>CO₂/H₂ Selectivity</th>
<th>CO₂/N₂ Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PVAm</td>
<td>PMVAm</td>
<td>PVAm</td>
</tr>
<tr>
<td>102</td>
<td>1777</td>
<td>6804</td>
<td>52</td>
</tr>
<tr>
<td>110</td>
<td>956</td>
<td>3107</td>
<td>48</td>
</tr>
<tr>
<td>120</td>
<td>352</td>
<td>797</td>
<td>23</td>
</tr>
</tbody>
</table>
Table 5.5. Improvements in separation performance of PMVAm membranes over PVAm membranes at different temperatures.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>57</th>
<th>102</th>
<th>110</th>
<th>120</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$ Permeability Improvement (%)</td>
<td>24</td>
<td>283</td>
<td>225</td>
<td>127</td>
</tr>
<tr>
<td>CO$_2$/N$_2$ Selectivity Improvement (%)</td>
<td>14</td>
<td>366</td>
<td>345</td>
<td>153</td>
</tr>
<tr>
<td>CO$_2$/H$_2$ Selectivity Improvement (%)</td>
<td>--</td>
<td>211</td>
<td>128</td>
<td>52</td>
</tr>
</tbody>
</table>
Figure 5.1. Transport mechanisms of CO$_2$ in fixed-site carrier membranes: (a) fixed-site carrier with unhindered amino groups and (b) fixed-site carrier with hindered amino groups.
Figure 5.2. Schematic synthesis routes of sterically hindered polyvinylamines.
Figure 5.3. FT-IR spectra of polyvinylamine and sterically hindered polyvinylamines.
Figure 5.4. Gas transport properties of polyvinylamines of different steric hindrance degrees.
Figure 5.5. Effect of temperature on CO₂ permeabilities of polyvinylamine and poly(N-methyl-N-vinylamine) membranes.
Figure 5.6. Effect of temperature on CO$_2$/N$_2$ selectivities of polyvinylamine and poly(N-methyl-N-vinylamine) membranes.
Figure 5.7. Effect of temperature on CO₂/H₂ selectivities of polyvinylamine and poly(N-methyl-N-vinylamine) membranes.
Chapter 6: Oxidative stability of CO\textsubscript{2} facilitated transport membranes

6.1. Summary

Although amine oxidative degradation has been studied for amine scrubbing and adsorption with amine-containing sorbents for CO\textsubscript{2} separation and capture, CO\textsubscript{2} facilitated transport membranes as a promising alternative to amine scrubbing and adsorption were rarely studied for oxidative stability. This work for the first time reports on the oxidative stability of CO\textsubscript{2} facilitated transport membranes, including amine-containing and quaternaryammonium hydroxide- and/or fluoride-containing membranes for hydrogen purification at high temperatures using air sweep and CO\textsubscript{2} capture from flue gas in coal-fired power plants. Amine-containing membranes suffered from oxidative degradation at >100°C using humid air sweep but exhibited good stability for CO\textsubscript{2} capture from flue gas containing oxygen at 57°C. The degradation rate of amine-containing membranes was found to be greatly influenced by the temperature, i.e., the degradation rate increased with temperature elevation. Furthermore, the dropping rate of CO\textsubscript{2}/H\textsubscript{2} selectivity appeared to be higher than that of CO\textsubscript{2} permeance, indicating the increase in H\textsubscript{2} permeance caused by amine oxidation. Another type of CO\textsubscript{2} facilitated transport membrane containing quaternaryammonium hydroxide and/or fluoride instead of amines as the CO\textsubscript{2} carriers.
remained stable at 120°C with humid air sweep, showing great potential for high-temperature CO₂ separation with air sweep.
6.2. Introduction

CO\textsubscript{2} separation from other gases, such as N\textsubscript{2}, CO, H\textsubscript{2} and CH\textsubscript{4}, has become increasingly critical to environment protection and fuel production. CO\textsubscript{2} capture from flue gas in coal- and/or natural gas-fired power plants is of great importance to combat the global warming issue, which is believed to be caused by the emission of greenhouse gases, such as CO\textsubscript{2}. Meanwhile, CO\textsubscript{2} separation from synthesis gas and natural gas is also essential for increasing the energy efficiency of industrial fuel production. CO\textsubscript{2} facilitated transport membrane is an important type of membrane for CO\textsubscript{2} separation, which relies on the reversible reaction between CO\textsubscript{2} and the “carrier” incorporated in the membrane [4].

The most commonly used CO\textsubscript{2} carriers are amines and their derivatives. In such a membrane, CO\textsubscript{2} reacts with the amine in the membrane on the feed/membrane interface to form a CO\textsubscript{2}/amine reaction product, and the reaction product transports across the membrane and releases the CO\textsubscript{2} to the permeate side, where either vacuum or a sweep stream is applied. As a result, most of the CO\textsubscript{2} is transported by the amine carrier in addition to a minor part of CO\textsubscript{2} transported by physical solution-diffusion. However, other non-reactive gases, such as N\textsubscript{2}, H\textsubscript{2}, CH\textsubscript{4}, etc., can only transport across the membrane via physical solution-diffusion. The reactions between CO\textsubscript{2} and amine can be described by Eq. (6.1) for unhindered amine and Eq. (6.2) for hindered amine [4].

\[
2 \text{R}_1\text{R}_2\text{NH} + \text{CO}_2 \rightleftharpoons \text{R}_1\text{R}_2\text{NCOO}^- + \text{R}_1\text{R}_2\text{NH}_2^+ \quad (6.1)
\]

\[
\text{R}_1'\text{R}_2'\text{NH} + \text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^- + \text{R}_1'\text{R}_2'\text{NH}_2^+ \quad (6.2)
\]
In addition to those amine-containing carriers, quaternaryammonium hydroxide can react with CO$_2$ as follows [23-26]:

\[
\text{CO}_2 + \text{OH}^- \rightleftharpoons \text{HCO}_3^- \quad (6.3)
\]

Furthermore, some other ionic compounds can also act as the carriers via catalyzing the hydration of CO$_2$ instead of reacting with CO$_2$ directly like amine. Quinn et al. applied fluoride-containing polyelectrolyte and cesium fluoride salt for the synthesis of facilitated transport membranes, which contained no amine [23-26]. It is noteworthy that the fluoride ion cannot directly react with CO$_2$, but it can form strong hydrogen bonding with H$_2$O and enhance the basicity of H$_2$O molecules, which in turn accelerates the hydration of CO$_2$ (Eq. (6.4)). It should also be noted that this type of membrane should be used in CO$_2$ separation with the presence of H$_2$O vapor in the feed gas.

\[
\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^- + \text{H}^+ \quad (6.4)
\]

Facilitated transport membranes have great potential to be applied for flue gas carbon capture, syngas purification, and natural gas sweetening. Those applications not only involve the separation of CO$_2$ from N$_2$, H$_2$ or CH$_4$, but are also affected by the minor contaminants present in the feed gases. For example, SO$_x$, O$_2$ and NO$_x$ are present in flue gas, while H$_2$S and various hydrocarbons, e.g., propane and n-hexane, may exist in natural gas. These contaminants may cause degradation of the amine carriers and thus affect the long-term stability of a facilitated transport membrane in practical applications. There has been some research conducted on the investigation on the influence of various contaminants, e.g., SO$_2$, on amine-containing facilitated transport membranes for flue gas carbon capture [111-114]. But the reports on the effect of oxygen and oxidative stability
of facilitated transport membranes are quite limited. Wang et al. investigated the effect of oxygen on the membrane containing PVAm and piperazine by testing the membrane with exposure to H₂O saturated pure O₂ for 200 h. They found that the membrane performance after oxygen exposure was reduced initially and then gradually recovered back to the same as the virgin membrane after 1 hour testing [68]. Wang et al. also studied the chemical structure of fixed-site carrier membrane containing carboxylate groups before and after oxygen exposure by ATR-FTIR, and the spectra did not show obvious differences between the virgin membrane and the membrane treated with oxygen, and were in line with the CO₂/N₂ separation performance measurement results [115,116]. Hägg et al. investigated the influence of oxygen on their polyvinylalcohol (PVA)/polyvinylamine (PVAm) fixed-site carrier membrane together with other contaminants, including SO₂ and NOₓ, using 16% CO₂ 78% N₂, 5% O₂, 200 ppm SO₂, and 200 ppm NOₓ as the feed gas. Their PVA/PVAm fixed-site carrier membrane demonstrated good membrane stability for 500-h testing during a period of 90 days at 30 – 50°C and 95% RH [111].

Amine-containing membranes have shown good stability to 5% oxygen at <50°C [111]. But, the typical flue gas temperature after flue gas desulfurization (FGD) is 57°C. In this work, we summarized our group’s investigation on membrane stability for flue gas carbon capture with about 7% oxygen and at 57°C. Furthermore, the sweep gas used in most of the gas transport tests as reported in the literature was argon or other inert gas for the ease of gas chromatograph analysis. But, air sweep (21% oxygen) is used in some real-life CO₂ separation practices at >100°C for the sake of cost savings. This work for the first time addressed the oxidative stability of amine-containing membranes with air sweep at
high temperatures and the effect of temperature on membrane oxidative degradation rate. Also addressed was another type of facilitated transport membrane containing quaternary ammonium hydroxide and/or fluoride for high-temperature CO\textsubscript{2} separation from H\textsubscript{2} with air sweep as well as its oxidative stability.

6.3. Amine oxidative degradation chemistry

The oxidative degradation chemistry of amine for CO\textsubscript{2} capture has been intensively studied on amine solvents and amine sorbents [117-133]. The amine oxidative mechanisms are often described by electron abstraction and hydrogen abstraction [117,118]. The electron abstraction mechanism is essentially used to explain the oxidation of tertiary amine, e.g., MDEA (methyl diethanolamine) while the hydrogen abstraction mechanism is for primary or secondary amine, e.g., MEA (monoethanolamine) [117,118]. The main oxidation product of amine is carboxylic acid and aldehyde compounds [117-120].

Many factors could affect amine oxidative stability, including temperature, oxygen pressure, and amine species. There have been a lot of studies on comparing the oxidation rates of different amine species, such as MEA, DEA, MDEA, TEA, etc. [118]. But because of the various experimental parameters, many of those studies have drawn contradictory conclusions. An overall trend is that hindered and substituted amines are more resistant to degradation and amines with hydroxyl groups (alkanolamine) are more likely to degrade than the alkylamine [118]. Also, the loading of CO\textsubscript{2} can slow down the amine degradation. Idem et al. found that the number of degradation products and the extent of degradation of
MEA solvent decreased in this order: MEA-H₂O-O₂ > MEA-H₂O-O₂-CO₂ > MEA-H₂O-CO₂, which also explained the fact that the amine degradation occurred more in the step of stripping [120]. Oxidative degradation of amine can be mitigated by adding free radical scavengers, which can stop the radical reactions by trapping free radicals. Those radical scavengers often possess a conjugated structure for stabilizing free radicals, such as ascorbic acid and phenolic compounds [121]. Jones et al. studied the oxidation properties of amino silica sorbents and found that the alkyl linker connecting the amino group and the silica substrate played a role in the oxidative stability at 135°C [123].

6.4. Experimental

6.4.1. Materials

Polyvinylalcohol (Poval S-2217, 92% purity, 87 – 89 mol.% hydrolysis, Mw = 150,000) was donated by Kuraray America Inc. (Houston, TX). Potassium hydroxide (pallets, ≥85 wt.% purity, Mw = 56.11), glutaraldehyde solution (50 wt.% solution in H₂O, Mw = 100.12), and glycine (99%) were purchased from Sigma-Aldrich (St. Louis, MO). N,N-dimethylglycine was obtained from MacKenzie Co. (Los Angeles, CA). Lupamin® (containing 66 wt.% salts and 34 wt.% polyvinylamine, Mw = 340,000 g/mol) was donated by BASF Corporation (Wyandotte, MI).

The microporous polysulfone substrate (thickness = 145 μm including non-woven fabric support and average pore size = 9 nm) was provided by TriSep Corporation (Goleta,
CA). A gas mixture of certified grade (10% CO, 40% H₂, and 50% CO₂) was used as the feed gas, which was purchased from Praxair Inc. (Danbury, CT). Prepurified argon and compressed air were used as sweep gases and were acquired from Praxair Inc.

6.4.2. Membrane preparation

Flat sheet CO₂-selective membranes were prepared by casting the coating solutions containing crosslinked polyvinylalcohol (XL-PVA), KOH, and amine fixed-site and mobile carriers onto the polysulfone substrate. The preparation of XL-PVA solution was as follows: 2.8 g as-received PVA was dissolved in 18 g deionized water at room temperature under minor stirring overnight and then heated up to 80°C for 80 minutes. 1.4 g potassium hydroxide in aqueous solution was added to the hot PVA solution dropwise. Then the solution was kept under vigorous stirring with the dropwise addition of glutaraldehyde solution at two batches. The amount of glutaraldehyde used was equivalent to the 100 mol.% crosslinking degree for PVA. The crosslinking reaction was carried out at 80°C for 2.5 h under vigorous stirring, and as-obtained XL-PVA solution was 18 wt.% in water. The clear aqueous PVA solution turned dark brown in color with a significant increase in viscosity, which was caused by the crosslinking of PVA with glutaraldehyde. The amine carrier solution was obtained by mixing Lupamin® solution and potassium N,N-dimethylglycinate (DMG-K) aqueous solution. The DMG-K solution was obtained by dropwise adding KOH solution into dimethylglycine solution and stirring at room temperature for 24 hours. The coating solution was obtained by dropwise adding the amine
carrier solution into a dilute XL-PVA solution. The viscosity of the coating solution increased gradually under stirring due to water evaporation by a nitrogen purge and the reaction between aldehyde groups in the XL-PVA solution and amino groups in the carriers. After casting the solution onto the polysulfone support, the membrane was dried in the fume hood at room temperature and cured in an oven at 120°C for 6 h. The membrane composition was 30 wt.% XL-PVA, 23 wt.% Lupamin®, 11 wt.% KOH, and 36 wt.% DMG-K, unless specified otherwise.

The thickness of the membranes synthesized in this work was measured by a Mitutoyo electronic indicator (Model 543-252B, Mitutoyo America Corp, Aurora, IL) with an accuracy of ±0.5 μm. The thickness of the active separation layer was obtained by subtracting the measured polysulfone support thickness from the measured total thickness of the membrane sample. The active layer thickness was controlled at about 18 μm.

6.4.3. Gas transport measurement

The gas transport performance for each of the membranes synthesized was tested by using a gas permeation apparatus reported in our group’s previous work [10]. A membrane was loaded in a rectangular stainless-steel cell with an active membrane area of 3.4 cm², which was placed inside an oven (BEMCO Inc., Simi Valley, CA) with precise temperature control of ±0.1°C. The testing conditions are summarized in Table 6.1 for the gas transport measurements. The feed gas and sweep gas flowed counter-currently into the stainless-steel gas permeation cell, their flow rates were controlled at 60 and 30 cm³/min.
by mass flow controllers (Brooks Instrument, Hatfield, PA), respectively. A gas mixture of 50 vol.% CO₂, 40 vol.% H₂, and 10 vol.% CO on a dry basis was used as the feed gas. Argon (Ar) or compressed air was used as the sweep gas. Liquid water was injected into the humidifiers inside the oven by Varian ProStar delivery modules (Model 210, Varian Inc., Palo Alto, CA).

The water injection rates were controlled at 0.09 cc/min for the feed-side water content of 67 mol.% and 0.01 cc/min for the sweep-side water content of 30 mol.% At the testing temperature, liquid water was vaporized and well mixed with the dry gas in each of the humidifiers and the humidified feed and sweep gases flowed into the gas permeation cell. After the gas permeation cell, the retentate and permeate streams left the oven and were cooled down to condense water in their respective water knock-outs. The dry retentate and permeate gas samples were injected into an Agilent 6890N gas chromatograph (Agilent Technologies, Palo Alto, CA) with SUPELCO Carboxen® 1004 micro-packed column (Sigma-Aldrich, St. Louis, MO) for gas composition analysis.

The gas transport performance of the membrane at steady state was evaluated by two parameters: permeability and selectivity [4]. Permeability, \( P_i \), is defined as:

\[
P_i = \frac{N_i}{\Delta p_i / \ell}
\]

(6.5)

where \( N_i \) is denoted for the steady state flux of species \( i \) across the membrane; \( \ell \) is the thickness of selective layer; \( \Delta p_i \) stands for the partial pressure difference of species \( i \) between the retentate and permeate sides of the membrane, which is also the driving force
for gas permeation. In this work, $\Delta p_i$ is determined by logarithmic mean method as in Eq. (6.6):

$$
\Delta p_i = \frac{(p_i, feed \ in - p_i, sweep \ out) - (p_i, feed \ out - p_i, sweep \ in)}{\ln(p_i, feed \ in - p_i, sweep \ out) - \ln(p_i, feed \ out - p_i, sweep \ in)}
$$

(6.6)

Permeance equals to $P_i/l$. Selectivity, denoted as $\alpha_{ij}$, is defined as:

$$
\alpha_{ij} = \frac{y_j}{x_j} \bigg/ \frac{x_i}{y_i}
$$

(6.7)

where $x$ and $y$ are the mole concentrations of the gas components on the feed and permeate sides of the membrane, respectively. The common unit of $P_i$ is Barrer ($1$ Barrer = $10^{-10}$ cm$^3$ (STP) • cm/(cm$^2$ • s • cm Hg)). The common unit of permeance is gas permeation unit (GPU) ($1$ GPU = $10^{-6}$ cm$^3$ (STP)/(cm$^2$ • s • cm Hg)).

6.5. Results and discussion

6.5.1. Oxidative degradation of amine-containing membranes tested with air sweep

Our group has developed amine-containing membranes, which have shown good stability with argon as sweep gas for the ease of GC analysis for laboratory research [10,12]. Figure 6.1 shows the permeance of the membrane containing 30 wt.% XL-PVA, 23 wt.% Lupamin®, 11 wt.% KOH, and 36 wt.% potassium glycinate (KG) synthesized in this work. As shown in this figure, this membrane exhibited good stability with argon as sweep gas at 120°C in terms of CO$_2$ permeance and CO$_2$/H$_2$ selectivity. Both CO$_2$ permeance and
CO₂/H₂ selectivity remained stable for the test run of about 44 hours and fluctuated at their average values of about 189 GPU and 210, respectively.

However, in some applications, air sweep is used instead of vacuum or other inert gases for the sake of cost-effectiveness. For using air sweep at high temperatures, membrane stability to oxygen is critical to the viability of the membrane process. The synthesized amine-containing membranes were tested with air sweep under 120°C and 102°C, respectively. The membrane separation performances at 120°C and 102°C are depicted in Figures 6.2 and 6.3, respectively. During the test with air sweep, the membrane performance at 120°C increased rapidly to reach steady-state and was stable for about 20 hours. But, the membrane performance started to drop at about 30 hours into the run, which should be attributed to the amine oxidative degradation. For the test at 102°C, the membrane performance dropping started at about 33 hours into the run, i.e., 3 hours later than at 120°C. Moreover, the dropping rate of membrane performance at 102°C was slower than that at 120°C, indicating that the higher temperature accelerated the oxidative degradation of amine. Similar observation was found in the case of amine absorption [120,133]. The dropping rates of membrane performance at both temperatures are listed in Table 6.2.

It should be noted that the dropping rate of CO₂/H₂ selectivity was higher than that of CO₂ permeance, as shown in Table 6.2. This indicated that H₂ permeance increased in the meantime while CO₂ permeance dropped. A potential explanation might be that the oxidation of amine destroyed the hydrogen bonding between amino groups of the carriers and the crosslinked polyvinylalcohol, which compromised the membrane integrity and
hence increased the free volume of the membrane. But CO$_2$ permeance still dropped because the major part of CO$_2$ transport relied on the facilitation by effective amine carriers. Furthermore, the separation performances in terms of CO$_2$ permeance and CO$_2$/H$_2$ selectivity at 120°C were lower than that at 102°C, which could be attributed to the stronger water retention capability of the membrane at 102°C than at 120°C. The gas transport measurement results before oxidative degradation under different conditions are summarized in Table 6.3.

6.5.2. Quateraryammonium hydroxide- and fluoride-containing membrane tested with air sweep

Since amine can react with oxygen, which results in the degradation of membrane, it is prudent to develop a new facilitated transport membrane using other types of carriers, which are stable under an oxidative environment. As described in the previous section, quaternaryammonium hydroxide can react with CO$_2$ and quaternaryammonium fluoride can catalyze the hydration of CO$_2$, which should not be reactive with oxygen at high temperatures. Based on this viewpoint, our group incorporated a quaternaryammonium hydroxide and a quaternaryammonium fluoride-containing polyelectrolyte into the crosslinked PVA-POS matrix to replace the amine mobile and fixed-site carriers, respectively [94]. The membrane showed excellent oxidative stability for over 140 hours at 120°C with air sweep and a 54 mol.% water vapor content on the feed side (feed gas composition: 59.5% CO$_2$, 26.5% H$_2$, and 14% CO on a dry basis). This stability result has
been reported by our group [94] and is hereby shown in Figure 6.4 for reference. The CO$_2$ permeance was 60 GPU, and the CO$_2$/H$_2$ selectivity was 92. The membrane thickness was 15 μm.

For comparison, an amine-containing membrane was tested under the same condition except using argon as the sweep gas instead of air. The membrane showed a CO$_2$ permeance of 80 GPU and a CO$_2$/H$_2$ selectivity of 128. This membrane contained 26 wt.% Lupamin®, 36 wt.% potassium glycinate (KG), 18 wt.% KOH, and 20 wt.% XL-PVA (any POS), and had a thickness of 10 μm. Figure 6.5 shows the CO$_2$ permeance and CO$_2$/H$_2$ selectivity results for comparison with those for the quaternaryammonium hydroxide- and fluoride-containing membrane. As shown in this figure, the amine-containing membrane had better performance than the quaternaryammonium hydroxide- and fluoride-containing membrane, which should be attributed to the slow rates of the CO$_2$-OH$^-$ reaction and CO$_2$ hydration associated with the latter membrane. It is noteworthy that the performance of the amine-containing membrane was lower at the feed-side water vapor content of 54 mol.% than at 67 mol.%, due to the reduced water retention in the membrane.

In order to improve the membrane performance with air sweep, a highly effective catalyst for CO$_2$ hydration should be incorporated into the quaternaryammonium hydroxide- and fluoride-containing membrane. Our group has improved the membrane performance significantly by the incorporation of an effective catalyst and the optimization of membrane composition, which will be reported in the near future.
6.5.3. Stability of amine-containing membrane tested with real flue gas at 57°C

In addition to the separation process with air sweep, membrane oxidative stability is also critical to flue gas carbon capture. Our group has successfully fabricated spiral-wound prototype membrane modules for flue gas carbon capture using the amine-containing facilitated transport membrane. The membrane module was tested with a slipstream of real flue gas containing 12±1% CO₂, 7±1% O₂, 0.5 – 5 ppm SO₂, and 1.5 – 4 ppm NO₂ at the National Carbon Capture Center (NCCC) in Wilsonville, AL, USA. With the presence of oxygen at 57°C, the membrane module performance was stable for a 96-hour test. The membrane stability is shown in Figure 6.6 [98]. This again indicated that the amine membrane oxidative stability was affected by the temperature. The membrane was able to show a good oxidative stability at 57°C. Also, the oxygen content in the flue gas was much lower than in the case of air sweep. It should be noted that the oxygen concentration of the flue gas used at the NCCC test, about 7%, was much higher than the typical flue gas value of 3%.

6.6. Conclusions

Although amine oxidation has been studied for CO₂ separation and capture using amine scrubbing and adsorption, but there have been very limited studies in facilitated transport membrane separation. This work has addressed the oxidative stability of facilitated transport membranes containing amines and quaternaryammonium hydroxide
and fluoride as the CO$_2$ carriers at different separation conditions. The amine-containing membrane has demonstrated good stability for flue gas carbon capture at 57°C with the flue gas containing about 7% O$_2$. But, at high temperatures (>100°C) and with air as the sweep gas, the amine-containing membrane was only able to maintain a stable performance for about 30 hours and then suffered from continuous performance drop. The performance dropping rate was found to be greatly affected by temperature, i.e., it dropped faster at a higher temperature. The permeation of the non-reactive gas, H$_2$, also became faster with membrane oxidative degradation, which might be due to the destruction of hydrogen bonding of amino groups by oxidation. Therefore, the amine-containing membrane is not applicable for a high-temperature separation process with air sweep. On the other hand, it may be applicable using a sweep gas of low-pressure waste steam or nitrogen or a vacuum on the permeate side. However, the facilitated transport membrane containing quateraryammonium hydroxide and fluoride showed good stability with air sweep at 120°C, which made it a good candidate membrane for cost-effective CO$_2$ separation using air sweep.
Table 6.1. Testing conditions of amine-containing membranes for syngas purification.

<table>
<thead>
<tr>
<th>Dry feed gas composition</th>
<th>Water content (mol.%)</th>
<th>T (°C)</th>
<th>Relative humidity (%)</th>
<th>Pressure (psig)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Feed</td>
<td>Permeate</td>
<td>Feed</td>
<td>Permeate</td>
</tr>
<tr>
<td>50% CO₂ / 40% H₂ / 10% CO</td>
<td>67</td>
<td>30</td>
<td>120</td>
<td>37</td>
</tr>
</tbody>
</table>
Table 6.2. Performance dropping rates caused by oxidative degradation at 120°C and 102°C.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Performance Dropping Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CO₂ Permeance (GPU•day⁻¹)</td>
</tr>
<tr>
<td>120</td>
<td>38</td>
</tr>
<tr>
<td>102</td>
<td>21</td>
</tr>
</tbody>
</table>
Table 6.3. Membrane performances at steady state under different conditions.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Sweep Gas</th>
<th>CO₂ Permeance (GPU)</th>
<th>CO₂/H₂ Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>120 Argon</td>
<td>189</td>
<td>210</td>
<td></td>
</tr>
<tr>
<td>120 Air</td>
<td>160&lt;sup&gt;a&lt;/sup&gt;</td>
<td>178&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>102 Air</td>
<td>205&lt;sup&gt;a&lt;/sup&gt;</td>
<td>189&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> Steady-state membrane performances before degradation.
Figure 6.1. Amine-containing membrane stability with argon sweep at 120°C (Membrane composition: 30 wt.% XL-PVA, 23 wt.% Lupamin®, 11 wt.% KOH, and 36 wt.% KG).
Figure 6.2. Membrane degradation with air sweep at 120°C.
Figure 6.3. Membrane degradation with air sweep at 102°C.
Figure 6.4. The stability plot of the quaternary ammonium hydroxide- and fluoride-containing membrane (5% TMAOH, 75% PDADMQ-F, and 20% crosslinked PVA-POS) tested with air sweep at 120°C [94].
Figure 6.5. The membrane performance comparison between the quaternary ammonium hydroxide- and fluoride-containing membrane and an amine-containing membrane at 120°C.
Figure 6.6. Membrane module stability tested with real flue gas at 57°C (membrane composition: 35 wt.% PVAm and 65 wt.% piperazine glycinate) [98].
Nomenclature

- $l$: membrane thickness
- $N_i$: steady-state flux of component $i$
- $P_i$: permeability of component $i$
- $\Delta p_i$: partial pressure difference of component $i$ across the membrane
- $p_{i, feed \ in}$: partial pressure of component $i$ at the inlet of feed side
- $p_{i, feed \ out}$: partial pressure of component $i$ at the outlet of feed side
- $p_{i, sweep \ in}$: partial pressure of component $i$ at the inlet of sweep side
- $p_{i, sweep \ out}$: partial pressure of component $i$ at the outlet of sweep side
- $x_i$: molar fraction of component $i$ in the retentate stream
- $x_j$: molar fraction of component $j$ in the retentate stream
- $y_i$: molar fraction of component $i$ in the permeate stream
- $y_j$: molar fraction of component $j$ in the permeate stream

Greek letters

- $\alpha_{ij}$: selectivity of component $i$ over component $j$
Chapter 7: Conclusions

7.1. Summary

In this research, a wide range of the properties of CO₂ facilitated transport membranes were investigated, including their water vapor transport property, CO₂/H₂ separation performance at high temperature and low water vapor partial pressure, CO₂/N₂ separation performance for flue gas carbon capture and oxidative stability. Sterically hindered polyvinylamines were successfully synthesized, which demonstrated a significant improvement in membrane performance as compared to unhindered polyvinylamine and thus had great potential to be used as the next-generation fixed-site carrier for facilitated transport membranes. The key conclusions and future directions of the work presented in Chapters 2 – 6 are summarized in the following sections:

7.2. Water vapor transport property of facilitated transport membranes

For a composite-structure membrane consisting of an amine-containing CO₂-selective layer, a nanoporous polysulfone substrate, and the backing of nonwoven fabric, the water vapor transport was found to be independent of the amine-containing layer
thickness and controlled by the substrate that provided the main mass transfer resistance to water vapor. This water transport behavior was the opposite of the case for CO\textsubscript{2} transport that was governed by the amine-containing layer thickness. Two methods were identified to mitigate the water vapor permeation through the membrane, (1) increasing the thickness of substrate thickness and (2) applying a hydrophobic layer, such as a Pebax\textsuperscript{®} layer, underneath the amine-containing layer. Method (1) was better since it had no influence on CO\textsubscript{2} transport, but method (2) could lead to a reduction in CO\textsubscript{2} permeance. Therefore, it is prudent to modify the morphology and thickness of the substrate in order to control the water vapor permeation without sacrificing the CO\textsubscript{2} permeance.

7.3. New CO\textsubscript{2} facilitated transport membranes for H\textsubscript{2} purification

H\textsubscript{2}O vapor contents in the feed and/or the sweep stream during the gas transport measurement could have great impact on amine-containing membrane performance. A low water vapor partial pressure in the feed gas could decrease the amine-containing membrane performance dramatically. In order to improve the membrane performance at the low water vapor partial pressure, the water retention capability of the membrane had to be enhanced. New facilitated transport membranes were synthesized in this work by replacing crosslinked polyvinylalcohol with crosslinked polyvinylamine and incorporating fluoride-containing polyelectrolyte into the membrane.

The effects of polyvinylamine crosslinking degree, the content of polyvinylamine in the membrane, the ratio of polyelectrolyte to amine mobile carrier, and the kind of
mobile carrier species were investigated to optimize the membrane performance. The optimized membrane demonstrated the CO$_2$ permeance of 146 GPU and the CO$_2$/H$_2$ selectivity of 107, and it contained 26.3 wt.% XL-PVAm (with a 6 mol.% crosslinking degree), 22.2 wt.% PDADMQ-F, 34 wt.% potassium glycinate and 17.5 wt.% TMAOH.

In order to further improve the membrane performance, PVAm with a higher hydrolysis degree and sterically hindered PVAm can be used as the fixed-site carriers and the polymer matrixes. Furthermore, polydiallyldimethylquaternaryammonium hydroxide (PDADMQ-OH) should be used instead of PDADMQ-F in the future, since CO$_2$ could directly react with the hydroxide ions in PDADMQ-OH for CO$_2$ facilitated transport. In addition, it is worthwhile to optimize the membrane composition by experimental design.

7.4. Amine-containing CO$_2$-selective membranes for flue gas carbon capture

The key challenge for flue gas carbon capture is the low CO$_2$ driving force, therefore a high CO$_2$ permeance of the membrane is required. In this work, two membrane-coating techniques were applied to obtain thin composite membranes with high CO$_2$ permeance. For spin coating with dilute coating solution, a PDMS gutter layer was applied to effectively prevent the penetration of dilute amine-containing coating solution into the substrate. Moreover, a PDMS cover layer was applied to seal the defects caused by the poor adhesion between the hydrophilic amine layer and the hydrophobic PDMS gutter layer. High-molecular-weight PVAm was synthesized, which enabled the fabrication of thin membranes by knife casting. Two mobile carriers, piperazine glycinate (PG) and
diethylenetriamine glycinate (DETAG), were studied and compared at different CO$_2$ concentrations in the feed gas. The membrane with DETAG as the mobile carrier exhibited significantly higher CO$_2$ permeance but lower CO$_2$/N$_2$ selectivity than that with PG as the mobile carrier.

In order to further improve the membrane performance for flue gas carbon capture, higher-molecular-weight PVAm should be synthesized to further reduce the membrane thickness and incorporate a more amount of mobile carriers. A combination of PG and DETAG can be used to enhance CO$_2$ permeance and maintain a good CO$_2$/N$_2$ selectivity. Furthermore, since the drying conditions of a thin membrane can affect its morphology, which can have significant influences on gas permeation properties of the membrane, the optimal drying temperature and relative humidity should be identified to achieve the best membrane performance.

7.5. New sterically hindered polyvinylamine membranes for CO$_2$ separation and capture

Sterically hindered polyvinylamines with different degrees of steric hindrance, poly(N-methyl-N-vinylamine), poly(N-isopropyl-N-vinylamine), and poly(N-tert-butyl-N-vinylamine), were successfully synthesized. Among the synthesized sterically hindered polyamines, the poly(N-methyl-N-vinylamine) membrane demonstrated the most significant improvements in both CO$_2$ permeance and CO$_2$/N$_2$ selectivity, compared to the unhindered polyvinylamine. As temperature elevated, the steric hindrance effect became much more pronounced. The poly(N-methyl-N-vinylamine) membrane demonstrated a
CO₂ permeability of 6804 Barrers, a CO₂/N₂ selectivity of 350, and a CO₂/H₂ selectivity of 162 at 102°C, which should be the best performance among the fixed-site carrier membranes reported in the literature.

This new sterically hindered polyvinylamine synthesized in this work can be a good candidate fixed-site carrier to be used with mobile carriers in the future. It is noteworthy that the incorporation of alkyl groups also reduces the amount of hydrogen bonding, which reduces the coating solution viscosity and influences the morphology of a thin membrane. Therefore, the effect of substitution degrees of PVAm should be investigated regarding the membrane performance for flue gas carbon capture.

7.6. Oxidative stability of CO₂ facilitated transport membranes

The oxidative stability of facilitated transport membranes was investigated for the membranes containing amines and quateraryammonium hydroxide and fluoride as the CO₂ carriers at different separation conditions. The amine-containing membrane has demonstrated good stability for flue gas carbon capture at 57°C with the flue gas containing about 7% O₂. But, at high temperatures (>100°C) and with air as the sweep gas, the amine-containing membrane suffered from a continuous performance drop after reaching the steady state for about 30 hours. Moreover, the performance dropping rate was found to be greatly affected by temperature, i.e., it dropped faster at a higher temperature. The amine oxidative degradation also decreased the intensity of hydrogen bonding, which led to the permeance increase of nonreactive gases. The facilitated transport membrane containing
quaternary ammonium hydroxide and fluoride showed good stability with air sweep at 120°C, which made it a good candidate membrane for cost-effective CO₂ separation using air sweep.
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