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journal homepage: [www.elsevier.com/locate/memsci](http://www.elsevier.com/locate/memsci)Facilitated transport membranes containing amino-functionalized multi-walled carbon nanotubes for high-pressure CO<sub>2</sub> separationsLuca Ansaloni<sup>a,b</sup>, Yanan Zhao<sup>a</sup>, Benson T. Jung<sup>c</sup>, Kartik Ramasubramanian<sup>a,1</sup>, Marco Giacinti Baschetti<sup>b</sup>, W.S. Winston Ho<sup>a,c,\*</sup><sup>a</sup> William G. Lowrie Department of Chemical and Biomolecular Engineering, The Ohio State University, 151 West Woodruff Avenue, Columbus, OH 43210-1350, United States<sup>b</sup> Dipartimento di Ingegneria Civile, Chimica, Ambientale e dei Materiali (DICAM), Alma Mater Studiorum-Università di Bologna, via Terracini 28, 40131 Bologna, Italy<sup>c</sup> Department of Materials Science and Engineering, The Ohio State University, 2041 College Road, Columbus, OH 43210-1178, United States

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## ABSTRACT

In the present work, high-performance mixed matrix membranes containing amines have been developed for effective CO<sub>2</sub> removal at high pressures (15–28 bar) and high temperatures (103–121 °C). The membrane was synthesized by compatibly embedding amino-functionalized multi-walled carbon nanotubes (AF-MWNTs) as mechanical reinforcing fillers in the crosslinked polyvinylalcohol-polysiloxane/amine blend. The surface functionalization of MWNTs allows strong coupling with the hydrophilic membrane matrix to form a nano-reinforced facilitated transport membrane, which achieved exceptional CO<sub>2</sub> selectivity and permeability via the facilitated transport mechanism as well as attractive membrane stability via the incorporation of MWNTs. The synthesized membranes exhibited an average CO<sub>2</sub> permeability of 957 Barrers coupled with high selectivities vs. H<sub>2</sub> (56), CH<sub>4</sub> (264), and N<sub>2</sub> (384) at 107 °C and 15 bar. The effects of AF-MWNT loading, high molecular weight species content, selective layer thickness, feed pressure, relative humidity, and temperature on membrane performance were thoroughly studied for a fundamental understanding of membrane properties. Furthermore, a mathematical model has been used to describe and explain the thickness-dependent CO<sub>2</sub> transport behavior in the membrane. The combination of high CO<sub>2</sub> permeability and good selectivities vs. CH<sub>4</sub>, H<sub>2</sub>, and N<sub>2</sub>, along with enhanced mechanical stability, makes the membrane a promising candidate for the gas separation applications at high pressures.

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## 1. Introduction

Natural gas is an important source for energy production nowadays. The natural gas purification industry offers a large market opportunity for gas separation technologies [1]. Although several contaminants are present in raw natural gas composition, carbon dioxide always constitutes the major impurity and its removal is of fundamental importance to meet the pipeline specification (< 2% of the total composition), increase the heating value of natural gas, minimize pipeline corrosion, and cut down energy costs for compression and delivery [2,3]. In addition, the removal of CO<sub>2</sub> is also an important separation step in other

processes, e.g., the purification of shifted syngas to produce H<sub>2</sub> as fuel gas for gas turbines or fuel cells [4].

In addition to the available technologies such as potassium carbonate or amine absorption, pressure or temperature swing adsorption, and cryogenic distillation, polymeric membranes offer a potentially efficient strategy due to intrinsic advantages such as low energy consumption, small footprint, reduced waste production, and good processability [5]. The industrial viability of this technology relies strongly on robust materials that exhibit high permeability and selectivity along with necessary mechanical, thermal and chemical stabilities when exposed to typical operating conditions [6].

Facilitated transport (FT) membranes represent a unique group of polymer membranes. In FT membranes, the gas transport behavior is dominated by the facilitated transport mechanism, which exploits the fast chemical reactions between CO<sub>2</sub> and basic compounds (also called “carriers”) at the feed gas/membrane interface to enhance CO<sub>2</sub> trans-membrane flux [7].

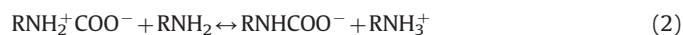
The reaction between amines and CO<sub>2</sub> can be described by the zwitterion mechanism as shown in Eqs. (1) and (2). In the first

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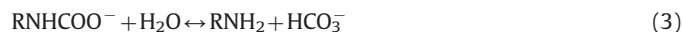
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step, a single amine molecule reacts with one CO<sub>2</sub> molecule to form a zwitterion intermediate, which is then deprotonated by a secondary amine to generate a carbamate ion.



For unhindered amines, the carbamate ion formed is rather stable, resulting in an overall reaction ratio of one mole of CO<sub>2</sub> to two moles of amines [8]. On the other hand, if the amine is sterically hindered, the bulky group on the amine moiety makes the carbamate ion unstable, which undergoes hydrolysis very quickly to give a bicarbonate ion and a free amine molecule as shown by Eq. (3):



As a result, the amine steric hindrance effect doubles the reaction sites available per unit volume of membrane matrix theoretically, hence enhancing the CO<sub>2</sub> transport rate across the membrane [9].

KOH can also act as a CO<sub>2</sub> carrier, reacting with CO<sub>2</sub> to produce potassium carbonate and potassium bicarbonate (K<sub>2</sub>CO<sub>3</sub> and KHCO<sub>3</sub>) based on a different reaction mechanism given by the following equation [10]:



After the reaction, the reaction products (i.e., carbamates, bicarbonates, K<sub>2</sub>CO<sub>3</sub>, and KHCO<sub>3</sub>) carrying CO<sub>2</sub> leave the feed gas/membrane interface and diffuse across the membrane selective layer along their concentration gradients. Only a small portion of CO<sub>2</sub> as well as the other non-reacting gaseous species (i.e., H<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>) is transported across the membrane based on the solution-diffusion mechanism at a much lower flux.

Due to the fast, specific chemical reaction, facilitated transport membranes are able to couple high CO<sub>2</sub> trans-membrane flux and very good selectivity, going beyond the tradeoff limit between permeability and selectivity of solution-diffusion membranes [11–14]. Furthermore, the facilitated transport performance has demonstrated a close correlation with the type of amine carriers. Amine carriers can be classified into two groups. A mobile carrier is a small-molecule carrier with a bonded CO<sub>2</sub> reactive site, which is able to move freely across the selective layer. A fixed-site carrier is defined as a carrier having a long-chain polymer backbone with pendant CO<sub>2</sub> reactive sites that has limited mobility around its equilibrium position in the membrane. Zhao and Ho have reported that the facilitated transport membrane containing only fixed-site carriers (poly-N-isopropylallylamine) achieved a CO<sub>2</sub> permeability slightly higher than 300 Barrers (1 Barrer = 1 × 10<sup>-10</sup> cm<sup>3</sup> (STP) cm cm<sup>-2</sup> s<sup>-1</sup> cmHg<sup>-1</sup> or 3.364 × 10<sup>-16</sup> mol s<sup>-1</sup> m<sup>-1</sup> Pa<sup>-1</sup>) along with a CO<sub>2</sub>/H<sub>2</sub> selectivity close to 45 and a CO<sub>2</sub>/N<sub>2</sub> selectivity of 340 at 2 bar and 110 °C [9]. In another publication, the same group replaced part of the fixed-site carriers with mobile carriers and obtained a dramatically improved membrane performance (i.e., CO<sub>2</sub> permeability of 6500 Barrers and CO<sub>2</sub>/H<sub>2</sub> selectivity of 340) under the same test conditions [15]. Similar results were also obtained by Zou et al. using facilitated transport membranes of a different composition with both mobile and fixed-site carriers [16]. These results highlight the significant contribution of mobile carriers to facilitated transport membrane performance.

Normally, facilitated transport membranes experience a performance drop (both CO<sub>2</sub> permeability and selectivity) with an increased feed pressure, due to the characteristic “carrier saturation” phenomenon of facilitated transport membranes [17]. For a given membrane, the total number of amine carriers available for the reaction with CO<sub>2</sub> is fixed. Under an increasing feed pressure or CO<sub>2</sub> partial pressure, more and more amine carriers are involved in

the reactions, leading to an increasing CO<sub>2</sub> flux. When all the carriers are reacted, the CO<sub>2</sub> flux approaches to a nearly constant value with a minor increase due to the physical solution-diffusion transport. Further increasing feed pressure or CO<sub>2</sub> partial pressure thus results in a drop of CO<sub>2</sub> permeability [18]. Meanwhile, the solution-diffusion fluxes of other penetrants (i.e., H<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>) increase linearly with feed pressure, resulting in decreased CO<sub>2</sub> selectivities. Bai and Ho reported good results of crosslinked polyvinylalcohol-based (PVA-based) FT membranes, including a CO<sub>2</sub> permeability of about 300 Barrers and a CO<sub>2</sub>/H<sub>2</sub> selectivity of 18 at 106 °C and a feed pressure of 29 bar [19]. Xing and Ho synthesized FT membranes containing fumed silica as reinforcing fillers and showed very promising results, including a CO<sub>2</sub> permeability of 1296 Barrers and a CO<sub>2</sub>/H<sub>2</sub> selectivity of 87 at 107 °C and a feed pressure of 15 bar [20].

In spite of the outstanding separation performance, facilitated transport membranes still suffer from the instability issue, especially for high-pressure gas separations. Few publications have reported long-term stable performances of facilitated transport membranes for more than 400 h under low pressures (~2 bar) with different types of carriers [15,21]. At high pressure and high temperature conditions, the polymeric selective layer loses rigidity and becomes susceptible to compaction, causing a continuous decrease in the membrane separation performance over time [22,23]. Operated at 15 bar and 106 °C, the crosslinked PVA-based FT membrane without nanofillers underwent a continuous performance drop over 500 h, resulting in a total reduction of 13.1% in the CO<sub>2</sub> permeability and 19.6% in the CO<sub>2</sub>/H<sub>2</sub> selectivity [23]. SEM images showed that the selective layer thickness was compressed by 50% after the 500-h test [23]. This instability issue clearly represents a serious threat to the viability of facilitated transport membranes for high-pressure gas separations.

The present work aims at demonstrating that facilitated transport membranes are able to exhibit desirable performances for high-pressure gas separation applications. For this reason, a new type of facilitated transport membrane with enhanced anti-compaction property and separation performance has been developed for high-pressure gas separations. Several strategies were used to manipulate the key membrane properties, especially mechanical strength, to obtain stable, efficient selective materials for CO<sub>2</sub> removal. Rigid multi-walled carbon nanotubes (MWNTs) were incorporated in the membrane matrix to enhance the overall membrane mechanical strength [24]. To maximally harness the outstanding mechanical and thermal properties, the naturally hydrophobic graphene wall of MWNTs was bonded with amine moieties to increase the affinity with the highly hydrophilic polymeric matrix and ensure a homogeneous dispersion in the membrane structure. Polyamines of high molecular weights were used as fixed-site carriers, whereas aminoacid potassium salt and potassium hydroxide were used as mobile carriers. The potassium hydroxide was used to catalyze the crosslinking of polyvinylalcohol and retained in the membrane. The reactive moieties available on both mobile and fixed carriers molecules made the main contribution to CO<sub>2</sub> facilitated transport. Crosslinked polyvinylalcohol–polysiloxane (PVA–POS) was used as matrix polymer to provide membrane structural integrity and thus membrane stability under high pressures up to 28 bar.

Two gas mixtures simulating natural gas and shifted syngas compositions were used as feed gases for membrane gas permeation tests in order to evaluate the potential applications of this membrane material for natural gas sweetening and H<sub>2</sub> purification. For a fundamental understanding of material properties, the membrane performance was studied and optimized by tuning key fabrication and operation parameters. Finally, a mathematical model, proposed by Noble et al. [25], was used to describe the thickness-dependent gas transport behavior of the synthesized membranes.

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