



A synergistic strategy via the combination of multiple functional groups into membranes towards superior CO₂ separation performances



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ABSTRACT

Membrane-based technology for CO₂ separation offers great potentials in environment and energy-related fields, and developing high-performance membranes is the key to improve the competitiveness of membrane process. In this work, a novel alternative strategy to enhance membrane performance was suggested via the combination of multiple functional groups into membranes, by which not only could circumvent the limitations of single functional group used, but also could achieve the synergistic effects of different functional groups. Thus, poly(diallyldimethylammonium carbonate-co-vinylamine) (P(DADMACA-co-VAm)) random copolymer containing primary amino groups, carbonate groups and quaternary ammonium groups was designed and synthesized. Then P(DADMACA-co-VAm)/polysulfone (PSf) composite membranes were developed by a simple solution casting method. Owing to the cooperative interactions of different functional groups, a notably improved gas separation performance of P(DADMACA-co-VAm) membrane was shown compared to polyvinylamine (PVAm) membrane and poly(diallyldimethylammonium carbonate) (PDADMACA) membrane. Furthermore, P(DADMACA-co-VAm) membrane exhibits superior CO₂ permeance and CO₂/gas selectivity for CO₂/N₂, CO₂/CH₄ and CO₂/H₂ mixed gas, respectively. Last, P(DADMACA-co-VAm) membrane displays favorable long-term stability and resistance to impurities. These results suggest that P(DADMACA-co-VAm) membrane has a great potential in CO₂ capture from flue gas, natural gas purification and synthesis gas purification.

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1. Introduction

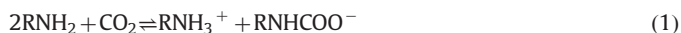
Over the several decades, membrane-based gas separation technology has received considerable attention in environmental remediation (e.g. CO₂ capture from flue gas) and clean energy supply (e.g., removal of CO₂ from natural gas and synthesis gas) because of its inherent advantages of energy efficiency, environmental compatibility and small footprint over traditional separation techniques such as absorption and cryogenic distillation [1–5]. Unfortunately, conventional polymeric materials for gas separation membranes are subject to a well-known trade-off between permeability and selectivity [6,7], which hampers them to meet the current requirements for further large-scale industrial applications

such as CO₂ capture from flue gas. The technical and economical demands highlight the urgent need for advanced membranes that could separate CO₂ from mixed gas more efficiently. Hence, a series of new membrane materials and membranes have been successfully developed [8–14]. In particular, facilitated transport membranes for CO₂ separation and CO₂-philic polymeric membranes currently exhibit superior separation performances over other types of membranes for CO₂ removal from different gas streams, because they are rich in reactive functional groups with CO₂ and CO₂-philic functional groups [15–18]. Many studies have demonstrated that the characteristics of these functional groups have a great influence on membrane performances [16,17].

Facilitated transport membranes for CO₂ separation could simultaneously improve permeability and selectivity owing to reversible reactions of functional groups, such as amino group [19–22], carbonate group [23–25] and carboxylate group [26,27] with the target gas-CO₂ based on nucleophilic addition mechanism. So far, the separation performances of many facilitated transport

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membrane materials have exceeded the Robeson upper bound (2008) for CO₂-related gas pairs [5,15,16,27,28]. The reactive functional groups in facilitated transport membranes are usually known as reactive carriers. Primary amino group is the most extensively used reactive carrier, and it shows high reaction rate constant with CO₂. The reversible reaction between primary amino group and CO₂ could be described by the zwitterion mechanism that converts CO₂ into carbamate ion shown in Eq. (1), and carbamate ion could be further hydrolyzed to bicarbonate ion in the presence of water [28]. Thus, the overall reaction is expressed in Eq. (2). Obviously, the CO₂ loading capacity of primary amino group could be enhanced with the assistance of water. Over the past years, a series of primary amino group-containing polymers, such as polyvinylamine (PVAm) [20,29], polyallylamine (PAAm) [30], and poly(amidoamine) (PAMAM) dendrimer [22], have been investigated as facilitated transport membrane materials. Among them, PVAm is an important representative, and the scale-up study of PVAm-based membranes for CO₂ capture from flue gas is in progress [31]. However, PVAm is a highly crystalline polymer because of regular polymer chains and strong hydrogen-bonding interactions among large amounts of polar primary amino groups, which goes against membrane performance improvement. To address this problem, several post modification methods, such as blending and crosslinking, have been adopted to suppress excessive crystallization [15,20,32], by which not only could improve the gas permeability but also benefit the facile interactions of primary amino groups with CO₂ molecules. It could be concluded that the relatively low crystallinity is favorable for high-performance membranes containing primary amino groups for CO₂ separation.



Carbonate group is another common reactive carrier, and it was first suggested to use in facilitated transport membranes for enhancing CO₂ transport by Ward [23]. Carbonate group shows a high CO₂ loading capacity of 1 mol CO₂ per mole as shown in Eq. (3). Unfortunately, the poor reaction kinetics of carbonate groups with CO₂ hinders large-scale practical applications, thereby a rate promoter is considered to be essential to increase the reaction rate. In the study of CO₂ absorbents, various amines have been attempted to blend into alkaline carbonate solutions for accelerating the absorption process, and the results demonstrated that the reaction could be obviously promoted even though a small amount of amine was added [33]. Similarly, it is expected that combining carbonate groups and amino groups into membranes might be a good choice for facilitated transport membranes for CO₂ separation, which may notably enhance the efficiency of carbonate groups.



Quaternary ammonium group is a highly CO₂-philic functional group, and various quaternary ammonium compounds have been widely used for fabrication of absorbents, adsorbents and membranes for CO₂ capture [34–36]. For example, two kinds of quaternary ammonium compounds in the form of blends of Pebax[®] 1657 exhibit outstanding solubility selectivity of CO₂ over N₂ under humid conditions. Moreover, polyelectrolyte membranes containing quaternary ammonium groups show the extremely high CO₂/gas selectivity along with a very low CO₂ permeance for CO₂ separation [37]. In addition, these polyelectrolyte membranes have been used for removing other acid gases such as H₂S from gas mixtures, and the transport of H₂S by reversible reaction was analogous to that for CO₂. However, there are several reasons that impede the fabrication of high permeance membranes based on strong polyelectrolytes. On one hand, the charged groups on

flexible polyelectrolyte chains often result in high polymer cohesion energy and a concomitant of low free volume, which has a detrimental effect on gas permeability. On the other hand, it is difficult to form a defect-free thin active layer upon porous supports that is suitable for gas separation [38,39]. Therefore, the cooperation of quaternary ammonium group-containing compounds with materials possessing good film-forming property is an alternative approach to developing quaternary ammonium group-containing thin film composite membranes for CO₂ separation.

Herein, a novel strategy for improving gas separation performance is suggested via the combination of primary amino groups, carbonate groups and quaternary ammonium groups into the membrane. Following this strategy, not only could circumvent the aforementioned limitations of single functional group used but also achieve the synergistic effects of multiple functional groups. Primary amino groups and carbonate groups as reactive carriers are responsible for CO₂ transport based on facilitated transport mechanism. Meanwhile, primary amino groups could dramatically accelerate the reaction between carbonate groups and CO₂ as a rate promoter [33]. Furthermore, quaternary ammonium groups play the following multiple roles in enhancing the efficiency of reactive carriers: (1) Act as the water reservoir to render the membrane hydrated that benefits the aforementioned reversible reactions. On one hand, the mobility of reactive carriers bounded to polymer chains could be increased in water-swollen membranes, which results in the facile interactions of reactive carriers with CO₂ [20]. On the other hand, facilitated transport mechanism is related to CO₂ diffusion together with water by forming a more mobile complex of HCO₃⁻ under humid conditions [22,40], enhancing CO₂ loading capacity of primary amino group. (2) Act as the polar group to improve CO₂ solubility coefficient and solubility selectivity of CO₂ over other gases [36], achieving CO₂ enrichment in the membrane that could increase the rate of forward reactions that transform CO₂ to HCO₃⁻. (3) Transport rate of HCO₃⁻ could increase because it is able to permeate through the membrane with lower energy barrier in the presence of polyelectrolyte (quaternary ammonium salts) [41], which could also promote the forward reactions.

In the present work, multiple functional groups containing composite membranes for CO₂ separation were developed. Firstly, N-vinylformamide (NVF) and diallyldimethylammonium chloride (DADMAC) were selected for the synthesis of poly(diallyldimethylammonium carbonate-co-vinylamine) (P(DADMACA-co-VAm)) random copolymer. Then P(DADMACA-co-VAm)/polysulfone (PSf) composite membranes, denoted as P(DADMACA-co-VAm) membrane, were prepared via the solution casting method using PSf ultrafiltration flat sheet membranes as porous supports. The chemical compositions of the as-synthesized membrane materials were investigated by attenuated total reflectance infrared (ATR-FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS). The thermal properties of the as-synthesized membrane materials were investigated by differential scanning calorimetry (DSC). The structure properties of membranes were investigated by wide angle X-ray diffraction (WAXD), field emission scanning electron microscopy (FESEM) and atomic force microscopy (AFM). In order to demonstrate the synergistic effects of multiple functional groups, the gas separation property of P(DADMACA-co-VAm) membrane was compared with polyvinylamine (PVAm) membrane and poly(diallyldimethylammonium carbonate) (PDADMACA) membrane using CO₂/N₂ (15/85 by volume) mixed gas. After that, the separation performances of P(DADMACA-co-VAm) membrane were further investigated for CO₂/CH₄ (10/90 by volume) and CO₂/H₂ (40/60 by volume) mixed gas, and the effects of slow gas (N₂, CH₄ and H₂) on CO₂ transport in the membrane were studied. Moreover, the recovery and purity of the products achieved for CO₂ capture from flue gas and fuel gas

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