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Gas transport property of polyallylamine–poly(vinyl alcohol)/polysulfone composite membranes

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Abstract

Polyallylamine (PAAm) was synthesized by free radical polymerization and characterized by Fourier transform infrared resonance (FT-IR) spectroscopy, hydrogen nuclear magnetic resonance (^{1}H NMR) spectroscopy and differential scanning calorimetry (DSC). The composite membranes were prepared by using PAAm–poly(vinyl alcohol) (PVA) blend polymer as the separation layer and polysulfone (PSF) ultrafiltration membranes as the support layer. The surface and cross-section morphology of the membrane was inspected by environmental scanning electron microscopy (ESEM). The gas transport property of the membranes, including gas permeance, flux and selectivity, were investigated by using pure CO_2, N_2, CH_4 gases and CO_2/N_2 gas mixture (20 vol% CO_2 and 80 vol% N_2) and CO_2/CH_4 gas mixture (10 vol% CO_2 and 90 vol% CH_4). The plots of gas permeance or flux versus feed gas pressure imply that CO_2 permeation through the membranes follows facilitated transport mechanism whereas N_2 and CH_4 permeation follows solution–diffusion mechanism. Effect of PAAm content in the separation layer on gas transport property was investigated by measuring the membranes with 0–50 wt% PAAm content. With increasing PAAm content, gas permeance increases initially, reaches a maximum, and then decreases gradually. For CO_2/N_2 gas mixture, the membranes with 10 wt% PAAm content show the highest CO_2 permeance of about 1.80×10^{-5} cm^3 (STP) cm^{-2} s^{-1} KPa^{-1} and CO_2/N_2 selectivity of 80 at 0.1 MPa feed gas pressure. For CO_2/CH_4 gas mixture, the membranes with 20 wt% PAAm content display the highest CO_2 permeance of about 1.95×10^{-5} cm^3 (STP) cm^{-2} s^{-1} KPa^{-1} and CO_2/CH_4 selectivity of 58 at 0.1 MPa feed gas pressure. In order to explore the possible reason of gas permeance varying with PAAm content, the crystallinity of PVA and PAAm–PVA blend polymers was measured by X-ray diffraction (XRD) spectra. The experimental results show an inverse relationship between crystallinity and gas permeance, *e.g.*, a minimum crystallinity and a maximum CO_2 permeance are obtained at 20 wt% PAAm content, indicating that the possibility of increasing CO_2 permeance with PAAm content due to the increase of carrier concentration could be weakened by the increase of crystallinity.

Keywords: Polyallylamine; Composite membrane; Gas transport property; Facilitated transport

1. Introduction

The use of polymer membranes to selectively remove carbon dioxide from gas mixtures attracts great interest to wide variety of applications, such as upgrading natural gas, recovering landfill gas, enhancing oil recovery, mitigating global warming, and removing CO_2 from breathing air in a spacecraft or confined space [1,2]. Traditional polymer membranes used for CO_2 removal are made from a single polymer, such as cellulose acetate, cellulose triacetate or polyimide. These membranes have a major difficulty associated with the trade-off relationship between permeability and selectivity suggested by Robeson [3], which indicates that a high permeation rate and high selectivity are hardly obtained simultaneously. Fortunately, the upper bound relationship between permeability and selectivity might be elevated by facilitated transport membranes (FTMs), because they have both a high permeability and a high selectivity through the reversible reactions between reactive carriers and the targeted gas—carbon dioxide [4,5].

There are two main types of reactive carriers: the mobile carrier, which moves freely across the membrane, and the fixed carrier, which only has very limit mobility around its equilibrium position. In mobile carriers containing membranes, the mobile carriers react with a specific component on the feed side form-

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ing the carrier–solute complexes; these complexes move across the membrane and release the specific component on the downstream side. In fixed carriers containing membranes, the specific component reacts at one carrier site and then hops to the next carrier site along the direction of the content driving force via the "Tarzan" mechanism suggested by Cussler [6,7].

According to the abovementioned two types of carriers, CO_2 facilitated transport membranes are classified into immobilized liquid membranes (ILMs) or supported liquid membrane (SLMs), ion-exchange membranes, and fixed-site carrier membranes [8]. For immobilized liquid membranes, although this type of membrane shows a remarkably high selectivity, membrane instability is recognized as a serious problem. The instability is possibly caused by carrier solution evaporation especially at a high temperature or carrier solution being forced to permeate through the porous support under a high transmembrane pressure (carrier washout), and carrier degradation led by the irreversible reaction with impurities in the feed gas stream [9]. For ion-exchange membranes, instability problem is alleviated because ionic carriers were retained inside membranes by the attractive electrostatic force. However, the electrostatic force between carrier and ion-exchange membrane cannot prevent the carrier leakage perfectly since the carrier might be lost especially in the presence of other ions [10,11].

In fixed-site carrier membranes, when carriers are bonded to fundamental polymer chains by covalent bond, washout and evaporation of carrier are effectively prevented. However, it is obvious that the diffusivity and thus permeability of a fixed-site carrier membrane are lower than that of a mobile carrier membrane [12]. Hence, the fixed-site carrier membranes should be favorable when stability of membranes is emphasized.

In our previous reports [13–21], a series of fixed-site carrier composite membranes whose separation layer is composed of amine containing polymers, such as poly(*N*-vinyl-γ-sodium aminobutyrate), poly(*N*-vinyl-γ-sodium aminobutyrate-*co*-sodium acrylate), polyvinylamine (PVAm), pentaerythrityl tetraethylenediamine (PETEDA) dendrimer were prepared and characterized, indicating that they effectively promote CO_2 permeation by facilitated transport effect. Like them, polyallylamine (PAAm) might be a promising material for preparing facilitated transport membranes because it also contains primary amino group in pendant chain, which could also react reversibly with CO_2 [22,23]. Yamaguchi et al. [24] impregnated cross-linked PAAm into a porous membrane filter and compared its CO_2 transport properties with a Nafion 117 ion-exchange membrane using mono protonated ethylenediamine as carrier. In addition, they established a simulation model to demonstrate that carrier and complex diffusivity passing through the cross-linked PAAm membrane is much slower than that of ion-exchange membranes, which explains different facilitated transport effects of them. To obtain high purity H_2 by separating CO_2 from the synthesis gas for enhancing the water gas shift reaction, Zou and Winston Ho [25] prepared CO_2-selective membranes containing both mobile and fixed carriers by blending PAAm, amino acid salt, potassium hydroxide and formaldehyde with poly(vinyl alcohol) (PVA) as the separation layer. The gas transport properties of the membranes, including CO_2, H_2 flux and permeability, CO_2/H_2, CO_2/N_2 and CO_2/CO selectivity, were investigated using two gas mixtures with various composition of CO_2, H_2, N_2 and CO. The effects of feed pressure (up to about 3.039×10^2 KPa (3 atm)), water content and temperature (up to about 180 °C) on permselectivity were also studied. They confirmed that CO_2 permeates through the membranes following the facilitated transport mechanism and water plays an important role in the facilitated transport. However, because both mobile and fixed carriers contained in the membrane contribute to gas transport properties, the effects of PAAm and PAAm content were not studied individually in this paper. Furthermore, for membranes containing PAAm, no report could be found about their permselectivity of CO_2/N_2 and CO_2/CH_4 gas mixtures, which are main components of flue gas and natural gas, respectively.

As mentioned above, although PAAm shows a CO_2 selective permeation property, rather a few gas separation membranes containing PAAm have been prepared and researched. The main reason is that PAAm contains a high density of primary amino groups regularly spaced along its polymeric hydrocarbon backbone, so PAAm is very brittle in the dry state and it lacks processability and has difficulty in forming film, fiber, and hydrogel. In addition, when an anionic polymer is added into a PAAm solution, PAAm precipitates and coagulates, making production of blend polymer containing PAAm with other polymers quite difficult [26]. Thus, applications of PAAm, especially in gas separation membranes, are limited for these drawbacks. Considering PAAm exhibits low processability as mentioned above, we have tried to prepare a composite membrane for removing CO_2 from natural gas, field gas and flue gas by using PAAm–PVA blend polymer as the separation layer because PVA is a very well known membrane material with good mechanical property. It is expected that the entanglement of the PAAm with PVA chains reduces the brittleness of pure PAAm polymer. Furthermore, since both PAAm and PVA are highly hydrophilic polymer, the water can be efficiently retained in the membrane, which might bring about better separation performance because water contained in the membranes could not only increase CO_2 solubility and diffusibility but also enhance facilitated transport effect by participating in the reversible reaction of CO_2 and amine carriers [20,21,27]. Thus, compared with dry membranes, a higher gas permeance and selectivity can be obtained by a water containing membrane. Matsuyama et al. [27] discovered that CO_2 permeance of a membrane in wet state is at least one order of magnitude larger than that of the membrane in dry state, and CO_2/N_2 selectivity of the wet membrane is about 2-fold of the dry membrane. Although flue gas is nearly dry, natural gas and field gas usually contain water, which will benefit hydrophilic polymeric membrane-based CO_2 separation, especially for amine group containing membranes.

In this work, PAAm was synthesized by free radical polymerization and characterized by Fourier transform infrared resonance (FT-IR) spectroscopy, hydrogen nuclear magnetic resonance (^{1}H NMR) spectroscopy and differential scanning