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Robust thin film composite PDMS/PAN hollow fiber membranes for water vapor removal from humid air and gases

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ABSTRACT

Water vapor in humid air and industrial gases needs to be removed for various applications such as air conditioning, foodstuffs storage, aviation and space flights. Membranes can remove water vapor from gas streams without involving phase change and regeneration. A robust and productive membrane is vital for water vapor removal but it is challenging to produce it. Here we present a defect-free thin film composite (TFC) polydimethylsiloxane (PDMS)/polyacrylonitrile (PAN) hollow fiber membrane with an ultrathin PDMS selective layer of about 260 nm. Different from previous works, the PAN substrate was spun at a high take-up speed of 60 m/min. It has an average of surface pore size of 5.6 nm and superior mechanical properties. After the optimal PDMS coating, the composite membrane shows a N_2 permeance of about 280 GPU, an O_2/N_2 selectivity of 2.2 and a water vapor permeance ranging from about 800 to 3700 GPU depending on operation conditions. In addition, the PDMS/PAN composite membrane has been tested for 48-hour outer door dehumidification and shown very stable and robust performance with a water vapor removal rate of 65% from the humid air. Besides, the PDMS/PAN composite membrane is not only able to efficiently dry the humid biogas but also upgrade its methane content simultaneously. Therefore, the newly developed TFC composite membrane has great potential for water vapor removal from humid air and various gas streams.

1. Introduction

Water vapor prevalently exists in many gas streams such as natural gas, flue gas and air. The removal of water vapor from specific gas streams is important for various applications, such as dehydration of natural gas, air conditioning, storage of foodstuffs, aviation and space flights [1–11]. Conventional methods for water vapor removal include condensation and adsorption. In the condensation method, water vapor is cooled down below the dew point and liquefied. In the adsorption process, water vapor is captured and adsorbed by adsorbents. Both methods are energy intensive and expensive. The former involves in cooling and phase change to condense vaporous water to liquid water, while the later requires regeneration steps of desiccants at high temperatures [1,9–13]. It may also suffer from the depletions of desiccants. Comparing to condensation and adsorption, membrane-based technologies offer an attractive alternative to remove water vapor because they do not need thermal regeneration and phase change [2,5,8–11,14–23]. Additionally, membrane-based technologies are compact, energy-efficient, easy to scale up, low initial investment, and simple in operation and maintenance [24–26]. Therefore, membrane-based dehumidification has received increasing attention recently because air conditioning nowadays accounts for about 50% of buildings' energy consumption and 20–40% of the total national energy use in developed countries [4,6,10,12,27].

During air conditioning, the cooling machine or chiller removes both the sensible heat (dry air enthalpy) and the latent heat (water vapor enthalpy) simultaneously. The latent heat accounts for the largest fraction of the total heat of the humid air, particularly for the air in hot and humid regions and periods [2,4,6,9,10,27]. Therefore, there is a need to remove the water vapor prior to conditioning the air through membrane-based dehumidifiers. Currently, most of the air/gas dehumidification membranes are made from polymers such as cellulosic polymers, polyamide, polyimide, polyacrylonitrile (PAN), polyethylene (PE), polypropylene (PP), polysulfone (PSf) and polydimethylsiloxane (PDMS) [9,12,14,16,28]. However, polymeric based membranes suffer from a tradeoff relationship between permeability and selectivity. A polymer with a high permeability usually exhibits a low selectivity and vice versa [28]. To overcome this tradeoff, inorganic-based membranes have also been developed and studied [17,19,29–34]. Unfortunately, it is difficult to fabricate large pieces of inorganic membranes for commercial gas separation applications because of poor reproducibility, processability, high cost and difficulties in scaling up [35,36]. To date,

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commercial gas and vapor separation membranes are dominant by polymeric hollow fiber membranes because they have a number of advantages such as good processability, self-supporting characteristics, a high ratio of surface area to volume and ease to scale up [36–39].

Due to the low H_2O vapor pressure in air, a desirable de-humidification membrane must have characteristics of high permeance in order to achieve a high water removal rate. To improve the permeance, it requires to minimize the dense-selective thickness of membranes to a submicron level (e.g., 0.1–1.0 μm) and to reduce the transport resistance of substrates [36,40–45]. However, it is technically challenging to produce such membranes having an ultrathin dense-selective layer without causing defects, particularly in large-scale membrane production [36]. Therefore, in order to make membranes more technically and economically viable to compete with conventional technologies, the configuration of thin film composite (TFC) hollow fiber membranes consisting of a porous substrate and a thin dense-selective layer is chosen for this study. A commercially available glassy polyacrylonitrile (PAN) and a rubbery polydimethylsiloxane (PDMS) are selected as the membrane materials because both PAN and PDMS have good chemical resistance and processability [46–48]. In addition, PAN and PDMS polymers are not expensive and have been widely used as membrane materials for liquid, gas and vapor separations [41,49–51]. Furthermore, PDMS has been known as the most gas permeable rubbery polymers due to its flexible siloxane linkages and an acceptable H_2O/N_2 selectivity (e.g., ~140) [13,52–54].

To design robust and defect-free TFC hollow fiber membranes for the removal of water vapor from air and gases, this work focuses on the following three parts: (1) developing a highly porous and strong hollow fiber membrane substrate in a productive way; (2) fabricating a defect-free TFC membrane with an ultrathin dense-selective layer while minimizing the polymer intrusion by applying a solution coating method; and (3) testing the performance of the composite membrane using synthetic humid air and biogas, and real outdoor air as feeds under various conditions such as RH and flow rate of the feed gas, applied vacuum pressure and flow rate of sweep gas. This study may offer insightful knowledge for producing practical membranes for applications such as air and gas dehumidification.

2. Experiments and methods

2.1. Materials

The Sylgard®184 silicone elastomer kit was bought from Dow Corning (Singapore) Pte Ltd. Polyacrylonitrile (PAN) was provided by Chung Yuan Christian University, Taiwan, with the help of Prof. Chein-Chieh Hu. Cyclohexane (analytical reagent grade, ≥99.99%) was purchased from Fisher Chemical. *N*-methyl-2-pyrrolidone (NMP, ≥99.5%), polyethylene glycol (PEG) and polyethylene oxide (PEO) were bought from Merck. Deionized (DI) water was generated by a water purification system (Millipore, Elix). Gases including oxygen (O_2, ≥99.9995%), nitrogen (N_2, ≥99.9995%), helium (He, ≥99.9995%), CH_4/CO_2 mixed gas ($CH_4/CO_2 = 50/50$ vol%) and pure air used in this study were supplied by Singapore Oxygen Air Liquide Pte. Ltd. (SOXAL). Pure air mainly consisted of N_2 and O_2 (i.e., $O_2 = 21 \pm 1\%$, $H_2O < 3$ ppm, $C_nH_m < 5$ ppm).

2.2. Preparation of hollow fiber substrates

The PAN hollow fiber substrates were fabricated via a dry-wet spinning process. The spinning conditions were tabulated in Table 1. The as-spun hollow fiber substrates were soaked in fresh tap water for three days to remove the residual solvent, freeze-dried in a freeze dryer (CHRIST, Beta 2–8 LDplus) for 48 h, and then stored for further investigations. The details about hollow fiber membrane spinning operations could be found elsewhere [55,56].

Table 1
Conditions and parameters for spinning PAN hollow fiber membranes.

Conditions/parameters	
Air gap	5 cm
Take up speed	**60.0 m/min**
External coagulant	Tap water
Coagulant bath temperature	25 ± 2 °C
Dope and bore fluid temperature	25 ± 2 °C
Bore fluid flow rate	**16.0 ml/min**
Bore fluid composition	H_2O/NMP = 10/90 (wt%)
Polymer dope flow rate	**30.0 ml/min**
Polymer dope composition	PAN/NMP = 20/80 (wt%)

2.3. Synthesis of crosslinked PDMS

The preparation of partially crosslinked PDMS is described as follows: 10 g of the base (a component of the Sylgard®184 silicone elastomer kit) and 1.0 g of the cross-linker (another component of the elastomer kit) were dispensed into a plastic beaker (50 ml) and mixed for 3 min at room temperature (~25 °C). Then the beaker containing the homogeneous mixture was immerged into a 75 ± 1 °C water bath and mixed manually until the mixture became very viscous (close to gelation). Subsequently, the beaker contained the viscous crosslinked PDMS was removed from the water bath, then PDMS was dissolved with cyclohexane and a 5 wt% PDMS stock solution was prepared. The stock PDMS solution was kept stirring with the aid of a magnetic stirrer (2Mag-Magnetic eMotion, MIX 15 eco) at room temperature overnight. Then the PDMS solution was subjected to further studies and characterizations.

2.4. Fabrication of PDMS/PAN composite membranes

To fabricate a PDMS/PAN composite membrane, the PAN substrate was dipped into the PDMS solution for a few seconds (e.g. 5 s), then taken out and dried in air at room temperature for at least 2 days. The dry composite membrane was subjected to gas permeation tests and other characterizations. The details of the membrane module fabrication and the dip coating methods could be found elsewhere [56].

2.5. Pure gas permeation tests for PAN substrates and the composite membranes

Pure gas permeation tests were carried out at room temperature (25 ± 2 °C) using a permeation cell system as described in the previous work [56]. A transmembrane pressure of 5.0 ± 0.1 psi (1 bar = 14.7 psi) was used to measure the gas permeance of the hollow fiber substrates. A transmembrane pressure of 2 bar (29.4 ± 0.4 psi) was applied to measure the gas permeance of the coated/composite membranes. The effective membrane length was 15 cm. The gas permeate flow rate was determined using a universal gas flowmeter (Agilent, ADM1000) which has a measurement range of 0.5–1000 ml/min. For each experimental condition, at least three membrane modules were produced for gas permeation tests. Unless stated otherwise, the average results were reported in this work.

The pure gas permeance (J) can be calculated according to the following equation:

$$J = \frac{P}{L} = \frac{Q}{A\Delta P} = \frac{Q}{n\pi D L_m \Delta P} \tag{1}$$

where $Q$is the gas permeate flow rate (cm^3/min), $n$is the number of fiber(s) in each module, D is the outer diameter of hollow fiber membranes (cm), $L_m$is the effective length of hollow fibers on the module (cm) and ΔP is the pressure difference across the membrane (cmHg). The unit of permeance can be expressed as GPU (1 GPU = 1×10^{-6} cm^3 (STP)/cm^2 s cmHg).