Constructing asymmetric membranes *via* surface segregation for efficient carbon capture

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ABSTRACT

Novel asymmetric membranes consisting of polyethersulfone (PES) as the membrane matrix and poly (ethylene oxide) (PEO)-containing block-copolymer F68 as the versatile modifier are prepared *via* surface segregation. The membranes are then characterized by scanning electron microscope (SEM), Fourier transform infrared (FTIR) spectra, X-ray photoelectron spectroscopy (XPS), differential scanning calorimetry (DSC) and electronic tensile machine. The surface segregation of CO_2-philic EO groups greatly enhance CO_2 solubility in the membrane surface. Moreover, the increased PES chain mobility by the interaction between PES and F68 enhances the gas diffusivity in the bulk active layer. The membrane with 20 wt% F68 exhibits CO_2 permeance increment of 210% and CO_2/N_2 selectivity increment of 105%. Pressure, temperature and long term tests are conducted to get more integrated understanding of membrane performance. The strategy of constructing asymmetric membranes by surface segregation holds great promise for efficient carbon capture.

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1. Introduction

The escalating amount of CO_2 in atmosphere has become one of the most important environmental concerns nowadays [1–3]. Developing highly efficient and cost-effective CO_2 separation technologies are therefore urgently required. Among the diverse carbon capture materials, polymer-based membranes with advantages such as low cost and easy fabrication have found applications in several industrial processes [4,5]. To achieve high permeation flux, the active layer or the separation layer of the membrane should be fabricated as thin and robust as possible [6,7]. In this regard, thin film composite (TFC) membranes and integrally skinned asymmetric membranes are two types of ideal configurations. Asymmetric membranes are composed of dense active layer and porous support layer, where the active layer is mainly responsible for the gas separation performance. Compared with TFC membranes, asymmetric membranes are formed in one step, making them easy to scale up. Moreover, the active layer and support layer of asymmetric membranes are generally made from the same materials, therefore, no special attention should be paid on the interfacial compatibility to balance the active layer

thickness and mechanical stability [8–12]. At present, considerable research efforts have been devoted to investigating the structure-property relationship of TFC membranes [13–15], whereas much less efforts have been devoted to asymmetric membranes.

Solution–diffusion mechanism is the well-known gas transport mechanism for polymeric membranes: gas molecules are firstly absorbed on the upstream side (*i.e.* the surface) of the membranes, then diffuse through the bulk active layer and finally desorb on the downstream side [16]. Accordingly, high CO_2 permeance asymmetric membranes should be designed with the following characteristics: (i) The membrane surface should be sufficiently CO_2-philic to guarantee large sorption capacity for CO_2 molecules (high CO_2 solubility) [17]; (ii) The bulk active layer should possess favorable free volume properties to guarantee high diffusivity and diffusivity selectivity [18]. However, most of the research activities are focused on enhancing the surface affinity towards targeted gases by grafting, UV treatment or plasma treatment [17,19] or tuning the free volume properties of the bulk active layer by synthesizing new structured polymers [20–24], blending with the existing polymers [25,26] or preparing hybrid membranes [27,28]. Simultaneous enhancement of solubility on membranes surface and diffusivity of the bulk active layer for asymmetric membranes requires extensive and intensive exploitations.

Surface segregation has been proved a facile and effective method to improve surface properties of porous membranes, especially water treatment membranes [29–32]. In this method,

amphiphilic copolymer as the modifier together with the polymer as the membrane matrix is added to the membrane casting solution. During the subsequent nonsolvent induced phase separation process, hydrophilic segments of the copolymer tend to segregate to the nonsolvent phase to minimize the interfacial free energy, whereas the hydrophobic segments of the copolymer are entrapped in the membrane matrix [33]. This method should be well applicable for gas separation membranes. First, the segregated segments could be designed as CO_2-philic groups to enable high CO_2 solubility on the membrane surface. Second, free volume properties of the bulk active layer can be delicately manipulated by the rational design of hydrophobic segments. Moreover, the support structure can also be tuned by the incorporated modifier.

In the present study, for the first time, surface segregation method was utilized to prepare the integrally skinned asymmetric membranes for carbon capture. Commercial polyethersulfone (PES) was selected as the membrane matrix because of the low cost, superior mechanical and membrane forming characteristics, good permeability and selectivity [34]. A poly(ethylene oxide) (PEO)-poly(propylene oxide) (PPO)-PEO block copolymer Pluronic F68 (abbreviated as F68) was selected as the modifier because PEO could serve as the CO_2-philic segments [35], while the hydrophobic PPO could interact with PES for the robust anchorage of the modifier [36]. Compared with other Pluronic polymers, e.g. P123, F127 and F108, F68 has relatively lower molecular weight and non-crystalline PEO segments as well as higher PEO content, which may confer high capacity for CO_2 molecules [37]. Asymmetric membranes with different F68 content were prepared. Scanning electron microscope (SEM), Fourier transform infrared (FTIR) spectra, X-ray photoelectron spectroscopy (XPS), differential scanning calorimetry (DSC) and electronic tensile machine were utilized to probe the physical and chemical properties of membranes. The resulting membranes were applied to CO_2, N_2 and CH_4 single gas or mixed gas permeation experiments, the effect of pressure, temperature and long-term test on gas separation performances were investigated.

2. Experimental

2.1. Materials

PES (6020 P, Mw=29000) was purchased from BASF Co. (Ludwigshafen, Germany). Pluronic F68 (Mw=8400, HO(CH_2-CH_2-O)$_{75}$-(CH(CH_3)-CH_2-O)$_{30}$-(CH_2-CH_2-O)$_{75}$H) was obtained from Sigma-Aldrich. PES and F68 were first dried in a vacuum oven at 60 °C for 24 h before use. N,N-dimethylformamide (DMF), ethanol, and tetrahydrofuran (THF) were purchased from Tianjin Guangfu Fine Chemical Engineering Institute. De-ionized water was used through the whole experiments.

2.2. Preparation of the membranes

Asymmetric membranes were prepared by the following procedure. First, the membrane casting solutions were prepared by vigorous stirring of PES and specific amount of F68 block copolymer in DMF and THF mixture solvent (mass ratio DMF/THF=12/5) at 60 °C for 5 h. The PES concentration was fixed as 25 wt% of the total mass of PES plus solvent. The weight ratios of F68 to PES were 0, 5, 10, 20 and 30 wt%, respectively. After left over night to remove the bubbles, the solutions were cast on a glass substrate by using a steel knife. Then, after 10 s evaporation, the substrate together with the casting solution was immersed into a coagulation bath. The coagulation bath was water or ethanol. After peeling off from the substrates, the pristine membranes were washed with deionized water to remove the residual solvent, and then the

membranes were immersed in water for 1 day. Subsequently, the asymmetric membranes were dried at atmosphere (25 ± 2 °C, 40 RH%) for 1 day before use. The resultant asymmetric membranes are donated as PES-F68 (X), where X refers to the wt% of F68 to PES in the casting solutions.

The dense membranes were prepared by conventional solution casting method to investigate the effect of F68. The dense membranes containing the same casting composition with asymmetric membranes were firstly dissolved at 60 °C for 5 h. After releasing the bubbles, the solutions were cast on a glass substrate in an oven at 60 °C for 24 h. Subsequently, the dense membranes were further dried in a vacuum oven at 60 °C for 48 h to remove the residual solvent. Similar as the asymmetric membranes, the dense membranes are designated as PES-F68 (X)d, where d refers to dense membranes.

2.3. Membrane characterization

Cross section morphology of asymmetric membranes and dense membranes was observed by a field emission scanning electron microscope (SEM) (Nanosem 430) at 10 kv. The membranes were cryogenically fractured in liquid nitrogen and then sputtered with a thin layer of gold prior to analysis. The membrane cross-sectional morphologies were further observed by atomic force microscopy (AFM, Multimode 3, Bruker Co.) at a scan size of 5 μm × 5 μm. The surface roughness was determined in terms of the root mean square (Rq) of the height data. The Fourier transform infrared (FTIR) spectra of the membranes surface were obtained by a BRUKER Vertex 70 FTIR spectrometer in the range of 4000–400 cm^{-1}. The surface composition of asymmetric membranes was analyzed by a PHI-1600 XPS with Mg Ka as the radiation source. The takeoff angle of the photoelectron was set as 90°, corresponding to the measured depths of about 10 nm. The glass transition temperatures (T_g) of asymmetric membranes were detected by a Netzsch DSC (204, F1) calorimeter under nitrogen protection. The measurements were performed from −25 to 350 °C at the scan rate of 10 °C/min. Mechanical properties of asymmetric membranes were obtained by using an electronic tensile machine (Yangzhou Zhongke WDW-02). Each sample was cut into 1.0 cm × 3.5 cm and tested with an elongation rate of 50 mm min^{-1} at room temperature.

2.4. Gas permeation experiments

Gas permeation performances of asymmetric membranes were tested at room temperature and 2 bar by using conventional constant pressure/variable volume technique [38]. Single gases of CO_2, N_2 and CH_4 or CO_2/CH_4 (50/50 vol.%), CO_2/N_2 (50/50 vol.%) gas mixtures were applied as the feed gas, while N_2 (for CO_2, CH_4 and CO_2/CH_4 feed gas) or CH_4 (for N_2 and CO_2/N_2 feed gas) was used as the sweep gas. The composition of the permeate side was measured by using an Agilent 6820 gas chromatography equipped with a thermal conductive detector (TCD). After reaching the steady state (about 1 h), gas permeance (P/l, GPU, 1 GPU=1×10^{-6} cm^3(STP)/cm^2 s cmHg) of the membranes was calculated from the average value of three tests, by using the equation: $(P/l)_i = Q_i/\Delta p_i A$, where Q_i represents the gas volumetric flow rate of "i" (cm^3/ s)(STP), Δp_i is partial pressure difference across the membrane (cmHg), A represents the effective membrane area (12.56 cm^2 in this study). The gas selectivity ($\alpha_{i/j}$) was calculated by: $\alpha_{i/j} = (P/l)_i/(P/l)_j$.

Gas permeability of dense membranes prepared by solution casting method was also tested for comparison and assistant elucidation. The dense membranes were tested by a constant volume/variable pressure apparatus described in our previous paper [38] to obtain the permeability (P), diffusivity (D) and solubility (S) data