High Performance of PIM-1/ZIF-8 Composite Membranes for O$_2$/N$_2$ Separation

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Supporting Information

ABSTRACT: This work reports the preparation, characterization, and O$_2$/N$_2$ separation properties of composite membranes based on the polymer of intrinsic microporosity (PIM-1) and the zeolitic imidazolate framework (ZIF-8). Especially, the composite membranes were prepared by growing ZIF-8 nanoparticles on one side of the PIM-1 membrane in methanol. Fourier transform infrared spectroscopy and thermo-gravimetric analysis indicated that there is no strong chemical interaction between ZIF-8 nanoparticles and PIM-1 chains. Scanning electron microscopy images showed that ZIF-8 nanoparticles adhere well to the PIM-1 membrane surface. The pure-gas permeation results confirmed that growth of ZIF-8 on the PIM-1 membrane can enhance the performance of O$_2$/N$_2$ separation. Particularly, the O$_2$/N$_2$ separation performance of the PIM-1/ZIF-8-7 composite membrane exceeds the Robeson upper bound line.

INTRODUCTION

In the past decades, membrane-based air separation to produce oxygen has been of special interest for chemists because of the versatile applications in furnace air enrichment, fuel cells, medical respiration, and so on.\textsuperscript{1−3} The polymer of intrinsic microporosity (PIM-1) is one of the most potential materials for air separation as it shows unusually high O$_2$ permeability and moderate O$_2$/N$_2$ selectivity.\textsuperscript{4,5} Nevertheless, PIM-1 membrane separation performance is still limited by the trade-off relationship between permeability and selectivity.\textsuperscript{6,7} Mixed matrix membranes (MMMs) afford the opportunity to break the performance limitation by adding the filler to PIM-1.\textsuperscript{8,9} With different metal−organic frameworks (MOFs) introduced into PIM-1, the corresponding MMMs have shown excellent gas separation performance.\textsuperscript{8−10} Particularly, the MMM based on PIM-1 and zeolitic imidazolate framework (ZIF-8), the O$_2$ and N$_2$ permeability were increased by 190 and 94%, respectively; meanwhile, the O$_2$/N$_2$ selectivity was increased by 50%.\textsuperscript{11} However, the poor compatibility between polymer substrates and MOF particles usually leads to nonuniform distribution of particles, especially for MMMs with high filler loading, and it may cause agglomeration and poor mechanical properties.\textsuperscript{12−14} Such a defective polymer−filler interface induces nonselective voids, which will affect gas separation performance.

Recently, a new strategy to improve the polymer−filler interface by growing MOF particles on membranes has been reported.\textsuperscript{15−17} Growing ZIF-8 particles on the surface of membranes has exhibited potential application in gas separation. Téllez et al. crystallized a thick continuous ZIF-8 membrane on highly porous flexible polysulfone, and the ZIF-8/polysulfone composite membrane showed a high H$_2$ separation performance.\textsuperscript{18} Wang et al. deposited an ultrathin ZIF-8 membrane on bromomethylated poly(2,6-dimethyl-1,4-phenylene oxide) (BPPO) after being modified with ethylene diamine, and the resulting ZIF-8/ED-modified BPPO composite membrane exhibited a significantly high H$_2$ permeability.\textsuperscript{19} Jansen and Budd et al. reported that growing ZIF-8 particles on the PIM-1 membrane in water could enhance O$_2$/N$_2$ selectivity. However, the O$_2$/N$_2$ separation performance could not exceed the Robeson upper bound line because of the low O$_2$ permeability.\textsuperscript{20}

In this work, we aimed to improve the performance of the composite membrane in O$_2$/N$_2$ separation. Because the methanol-treated PIM-1 membrane often results in a significant increase in permeability,\textsuperscript{21} we proposed using methanol as the solvent for the preparation of the PIM-1/ZIF-8 composite membrane will improve the O$_2$/N$_2$ separation performance. By growing ZIF-8 nanoparticles on one side of the PIM-1 membrane, a series of PIM-1/ZIF-8-X composite membranes were fabricated in methanol. Their structures, morphologies, and interactions of the composite membranes were characterized by Fourier transform infrared spectroscopy (FT-IR), thermo-gravimetric analysis (TGA), Brunauer−Emmett−Teller (BET) method, and scanning electron microscopy (SEM). O$_2$ and N$_2$ permeation properties of the resultant composite membranes were measured using a constant-volume/variable pressure method.

RESULTS AND DISCUSSION

FT-IR, TGA, and BET. FT-IR spectra of ZIF-8, PIM-1 membrane, and PIM-1/ZIF-8-X composite membranes are shown in Figure 1. The FT-IR spectrum of the PIM-1 membrane was identical to that reported in the literature.\textsuperscript{22}
The absorption bands at 2860, 2930, and 2960 cm⁻¹ correspond to the stretching vibrations of −CH₃ groups. The absorption band at 2240 cm⁻¹ is assigned to the stretching vibrations of −CN groups. The absorption band at 1600 cm⁻¹ is attributed to the stretching vibrations of −C≡C− bonds.

Compared with the ZIF-8 and PIM-1 membrane, no new peak is found in PIM-1/ZIF-8-X composite membranes, indicating that there is no strong chemical interaction between ZIF-8 particles and PIM-1 chains.

Thermal properties of the PIM-1 membrane and PIM-1/ZIF-8-X composite membranes were evaluated by TGA. As shown in Figure 2, the PIM-1 membrane exhibited high thermal stability and a single-step decomposition at about 480 °C. Thermal analysis of PIM-1/ZIF-8-X composite membranes indicated that ZIF-8 particles have no effect on their thermal stability, thus, PIM-1/ZIF-8-X composite membranes demonstrated excellent thermal stability as the PIM-1 membrane. The TGA curves also showed that the amount of ZIF-8 grew on the PIM-1 membrane could be increased by the repeating growth cycle. Meanwhile, there was no obvious weight loss over the temperature range of 50–200 °C for all the membranes, indicating that no residual solvent was trapped in their pores, which will affect the permeation properties of the membranes.

As shown in the nitrogen adsorption–desorption isotherms (Supporting Information, Figure S3), both the PIM-1 membrane and the PIM-1/ZIF-8-X composite membrane exhibited type I isotherm, indicating most of the pores in these membranes are micropores. Small particles were observed on the PIM-1/ZIF-8-X composite membrane, corresponding to the nucleation stage of ZIF-8 crystallization. By repeating the growth cycle, a ZIF-8 nano-particle layer was eventually formed on the PIM-1 membrane. The particle size distributions of the PIM-1/ZIF-8-X composite membrane estimated from the SEM images are shown in Supporting Information Figure S4.

Morphologies of PIM-1/ZIF-8-X Composite Membranes. The SEM images of the PIM-1 membrane and PIM/ZIF-8-X composite membranes are displayed in Figure 4. The SEM images showed ZIF-8 nanoparticles adhere well to the PIM-1 membrane, which can be attributed to the attraction between the PIM-1 membrane and the ZIF-8 particles.
The cross section of the PIM-1/ZIF-8-7 composite membrane revealed that the ZIF-8 nano-particle layer is composed of intergrown crystals, which adhere to the surface of the PIM-1 membrane. The nanoparticle layer has a thickness of about 200 nm (Figure 5). No evident interface between the ZIF-8 nanoparticle layer and the PIM-1 membrane was observed, confirming that ZIF-8 adheres well on the PIM-1 membrane. Because only one side of the PIM-1 membrane was exposed to the ZIF-8 precursor solution, ZIF-8 nano-particles were selectively grown on one side of the PIM-1 membrane, resulting in a pizza-like composite membrane.

Gas Permeation Properties. The performance of the PIM-1 membrane and PIM-1/ZIF-8-X composite membranes in terms of pure-gas permeabilities of O2 and N2 are summarized in Table 1. Ultrahigh free-volume glassy polymer has weak size-sieving ability, and the selectivity is usually dominated by solubility selectivity. The PIM-1 membrane displays a high oxygen solubility coefficient, a medium solubility selectivity, and a very low diffusivity selectivity. The PIM-1 membrane prepared in this work has an O2 permeability of 1808 Barrer and a N2 permeability of 702 Barrer, which are similar to the value reported by Guiver.27 As shown in Table 2, the PIM-1/ZIF-8-2 composite membrane exhibited slight decrease in the solubility coefficient and diffusivity selectivity for both O2 and N2, probably attributing to the addition of a small number of nucleation state ZIF-8 particles. Because the PIM-1 membrane has a microporous structure, ZIF-8 nanoparticles may be grown into some of the pores, resulting in a decrease of free volume in PIM-1. However, the addition of the nucleation state of ZIF-8 particles reduced the pore size of the PIM-1/ZIF-8-2 composite membrane, which induced an increase in O2/N2 diffusivity selectivity, making the PIM-1/ZIF-8-2 composite membrane to be slightly increased in O2/N2 selectivity.
Compared with gas permeation properties of the PIM-1 membrane, PIM-1/ZIF-8-4 and PIM-1/ZIF-8-6 composite membranes showed increase in O₂/N₂ selectivity. However, PIM-1/ZIF-8-4 and PIM-1/ZIF-8-6 composite membranes exhibited decrease in O₂/N₂ diffusivity selectivity. These could be explained by the further addition of ZIF-8 particles, which blocked up more cavities of the PIM-1 membrane, leading to reduced selective voids, and decreased sorption sites for O₂ and N₂. Robeson et al. reported that the solubility selectivity of A/B gas pair decreases with increasing of free volume when the A gas is larger in size than the B gas. Therefore, it means that sorption sites are less available to larger gas molecules as the free volume decreases. Therefore, the solubility selectivity for O₂/N₂ increased as free volume decreased.

As shown in Table 2, N₂ solubility coefficients of PIM-1/ZIF-8-4 and PIM-1/ZIF-8-6 composite membranes were decreased; however, there was no significant decrease in O₂ solubility coefficients compared with that of the PIM-1 membrane. The kinetic diameters of O₂ and N₂ are 3.46 and 3.64 Å, respectively, which makes it very difficult to separate O₂ or N₂ from air by simple micropore-based sieving effects. Freeman reported that improving the solubility selectivity could perform beyond the Robeson upper-bound line. Therefore, the increases in O₂/N₂ selectivity of PIM-1/ZIF-8-4 and PIM-1/ZIF-8-6 composite membranes may be mainly attributed to the increases of solubility selectivity.

Regarding the PIM-1/ZIF-8-7 composite membrane, both diffusivity selectivity and solubility selectivity of O₂/N₂ were increased, resulting in an increase in the selectivity. The increases of diffusivity selectivity for O₂/N₂ may be attributed to the reduction in the average pore size, finally leading to a higher O₂/N₂ selectivity. The PIM-1/ZIF-8-7 composite membrane has an O₂/N₂ selectivity of 3.7 with an O₂ permeability of 1287 Barrer.

For all PIM-1/ZIF-8-X composite membranes, the diffusivity coefficients of O₂ and N₂ are almost similar to that of the PIM-1 membrane. The slight decreases in permeability of all PIM-1/ZIF-8-X composite membranes are mainly due to the reduction of free volume. Additional growth cycle could not always enhance selectivity of the composite membrane. Compared with the PIM-1/ZIF-8-7 composite membrane, the PIM-1/ZIF-8-8 composite membrane exhibited an obvious decrease in O₂/N₂ selectivity. The decrease of selectivity may be attributed to further growth of ZIF-8, which makes the composite membrane more size-selective.

Because the main objective of this work was to prepare high permeation membranes with enhanced selectivity, Figure 6 demonstrated the comparison between PIM-1/ZIF-8-X composite membranes and recently reported composite membranes. The O₂ permeabilities of PIM-1/ZIF-8-X composite membranes are much higher than those of in the relevant literature. Moreover, the O₂/N₂ separation performance of ZIF-8/PIM-1-7 successfully exceeded the Robeson upper bound line.

**CONCLUSIONS**

In this work, pizza-like composite membranes (PIM-1/ZIF-8-X) were prepared by growing ZIF-8 nano-particles on one side of the PIM-1 membrane. The resulting composite membranes have excellent thermal stability, large surface area, and microporous structures. Meanwhile, the ZIF-8 nanoparticles show good adhesion with the PIM-1 membrane. The composite membranes not only eliminate the polymer–filler interface voids but also exhibit high permeability for O₂. The gas permeation properties of the composite membranes indicate that a proper ZIF-8 growth time could improve the O₂/N₂ separation performance. The PIM-1/ZIF-8-7 composite membrane has an O₂/N₂ selectivity of 3.7, with an O₂ permeability of 1287 Barrer. The separation performance of the PIM-1/ZIF-8-7 composite membrane successfully exceeds the Robeson upper bound line, indicating that the PIM-1/ZIF-8-7 composite membrane has excellent separation performance.
Fabrication of the PIM-1 Membrane. The PIM-1 membrane was prepared by casting 2 wt % PIM-1/chloroform solution onto a flat-bottomed glass Petri dish. The solvent was then allowed to evaporate slowly in order to form the membrane. The membrane was left for 2 days to complete solvent evaporation. Thereafter, the membrane was transferred to a vacuum oven and dried at 70 °C for 48 h to remove any residual solvent.

Fabrication of PIM-1/ZIF-8 Composite Membranes. The PIM-1 membrane was cut into a circular piece (approximately 2.8 cm in diameter, 70 μm thickness). It was fixed on the bottom, in a vial containing a mixture of two solutions, 2-methylimidazole (1.65 g, 20.1 mmol) in methanol (30 mL) and Zn(NO3)2·6H2O (0.75 g, 2.37 mmol) in methanol (30 mL). The ZIF-8 growth solution was stirred (500 rpm) at ambient temperature. After 12 h, the membrane was removed from the vial and washed three times with methanol to increase the amount of ZIF-8 crystallized on the PIM-1 membrane, the above growing process was repeated with freshly mixed solution of 2-methylimidazole and Zn(NO3)2·6H2O. The desired membrane (PIM-1/ZIF-8-X, X means growth cycle) was dried under vacuum at 70 °C for 24 h.

Characterization Techniques. 1H NMR spectra were recorded on a Bruker AV400 spectrometer, and chemical shifts were reported in ppm relative to a tetramethylsilane standard. The chemical bonds were investigated using a FT-IR spectrometer (Nicolet Magna-IR 750) at a scanning range from 4000 to 400 cm⁻¹. The thermal degradation of the PIM-1 membrane and PIM-1/ZIF-8-X composite membranes were monitored by using a TA instrument with a 2050 thermogravimetric analyzer. The analyses were carried out with a rate of 10 °C/min at temperatures ranging from 50 to 800 °C, N2 was used as the purge gas and its flow rate was controlled at 50 mL/min. The BET surface area of membranes was measured with a Micro ASAP 2460 and the samples were degassed by heating at 120 °C. The surface morphologies of membrane samples were observed by a field emission SEM (Gemini SEM-500, Germany). Cross sections of membrane samples were fractured in liquid nitrogen and coated with platinum via sputtering before analysis.

Gas Permeation Measurements. The pure-gas permeabilities of O2 and N2 were measured by using a constant-volume/variable-pressure method at 35 °C. The membranes were degassed under vacuum at 80 °C overnight to remove dissolved gases and moisture. The results reported here are the average of three measurements. After degassing the whole apparatus, the membrane was mounted in a permeation cell. Then, permeate gas was introduced on the upstream side (with ZIF-8 nano-particles), and the permeate pressure on the downstream side (without ZIF-8 nano-particles) was monitored by using a MKS-Baratron pressure transducer.

Pure-gas permeability is determined by

\[
P = \frac{22414}{A} \times \frac{V}{RT} \times \frac{L}{p} \times \frac{dp}{dt}
\]

where \(P\) is the permeability (Barrer) (1 Barrer = 10⁻¹⁰ cm³(STP)/cm²·s·cmHg), \(A\) is the effective membrane area (cm²), \(V\) is the downstream volume (cm³), \(R\) is the universal gas constant (8236.56 cm³·cmHg/mol K), \(T\) is the absolute temperature (K), \(L\) is the membrane thickness (cm), \(p\) is the upstream pressure (cmHg), and \(dp/dt\) is the permeation rate (cmHg/s).

The ideal selectivity for the O2/N2 gas pair is determined by

\[
\alpha_{O2/N2} = \frac{P_O}{P_N}
\]

The diffusion coefficient \(D\) (cm²/s) is obtained by

\[
D = \frac{L^2}{\theta}
\]

where \(L\) is the membrane thickness (cm) and \(\theta\) is the time lag of the permeability measurement (s).

The solubility coefficient \(S\) [cm³(STP)/(cm³ cmHg)] is calculated by

\[
S = \frac{P}{D}
\]
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