ABSTRACT: Oxygen-enriched air has attracted increasing attention owing to its potential industrial application. In this work, ceramic hollow fiber-supported polydimethylsiloxane (PDMS) composite membranes were applied in separation of oxygen from air. The influence of PDMS layer thickness, pressure difference, temperature, and feed concentration on the oxygen-enriching performance was systematically investigated. The results indicated that the membrane (with the optimal PDMS layer thickness of 25 µm) achieved oxygen permeance of 10^4 GPU (1 GPU = 10^{-6} cm^3 standard temperature and pressure (STP)/cm^2 s cmHg) with O2/N2 ideal selectivity of 2.0 at room temperature and 0.1 MPa difference pressure. Over 10 days continuous operation, this enrichment performance kept stable, in which the oxygen concentration enriched from air can maintain about 30% by single-stage separation through the membrane. Our work demonstrated that the ceramic hollow fiber-supported PDMS composite membrane could be a competitive oxygen enrichment membrane for industry application.

INTRODUCTION

Oxygen-enriched air has been receiving increased attention, and its potential applications were expanded continuously in recent years, including combusting enhancement, fuel cell processes, emission control, and medical application. As we know, cryogenic distillation and pressure swing adsorption are the traditional methods to obtain oxygen-enriched air, which, however, are highly energy intensive. The membrane gas separation technology is attractive and alternative to conventional technologies for oxygen and nitrogen separation mainly because of its simplicity in operation, low cost, small size, and low energy consumption.

Many polymeric materials have been used to separate oxygen and nitrogen. In fact, air separation by polymer membranes has been considered as an economical and widespread alternative for oxygen molar fraction 25–40% and small-scale plants (10–23 ton/day). Polydimethylsiloxane (PDMS) membrane possesses high oxygen permeance because of the flexibility of the siloxane linkages (–SiO–). Because of its high gas permeance and being readily available,

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Our group has designed a type of organic/inorganic composite membrane with an active polymeric layer on a porous ceramic support by dip-coating method.\[9,18–21\] Owing to thin polymeric layer and low transport resistance, and high chemical and mechanical stability from ceramic support,\[20\] these membranes showed high separation performance in some fields, such as biofuels production,\[22\] solvent dehydration,\[19\] and CO\(_2\) capture.\[9\] Recently, we developed a new kind of hollow fiber organic/inorganic composite membrane.\[23\] Besides low transport resistance, many other advantages are found for hollow fiber membranes when compared with other configurations, such as high-packing density, cost-effectiveness, and a self-support structure. Our hollow fiber PDMS/ceramic composite membranes with high flux and selectivity showed great potential in pervaporation process.\[23,24\] Nevertheless, the oxygen enrichment properties of the ceramic hollow fiber-supported PDMS membrane are still unknown.

Therefore, this work aims to study the application of ceramic hollow fiber-supported PDMS membrane for oxygen enrichment process. By using the ceramic hollow fiber support, a high oxygen permeance of PDMS membrane is anticipated to be achieved. The effects of PDMS layer thickness, pressure difference, operating temperature, and oxygen concentration of the feed and long-term stability on the oxygen enrichment performance of the PDMS/ceramic hollow fiber membrane were systematically investigated.

**EXPERIMENTAL**

**Preparation and characterization of hollow fiber membranes**

The ceramic hollow fiber-supported PDMS composite membranes were prepared by conventional dip-coating method, which was described in our previous work.\[23\] Generally, a certain amount of PDMS polymer was dissolved in \(n\)-heptane, and after stirring at 300 \(r \text{ min}^{-1}\) for 2h, cross-linking agent Tetraethylorthosilicate (TEOS) and catalyst (dibutyltin dilaurate) were added. When the polymer solution obtained the appropriate viscosity, the ceramic hollow fibers were immersed in the coating precursor twice and each time for 60 s. After 24 h drying at room temperature and 12 h heat treatment at 120 °C, the composite membranes were successfully prepared. The membrane is with the effective area of 3.14 cm\(^2\). The cross-section morphology of the hollow fiber-supported membrane and the thickness of active layer were characterized by the scanning electron microscopy (TM3000, Hitachi, Japan).

**Gas separation measurement**

Pure gas permeation measurements were conducted via constant-pressure and variable-volume method to evaluate the gas separation performance of the composite membranes, and the gas permeation rate was measured by a bubble flow meter. Besides pure gas tests, binary gas tests were also carried out in this work for studying the effects of feed gas concentration and long-term operation. The process is described as follows: The oxygen enrichment performance of the hollow fiber membrane was measured by using a home-made apparatus shown in Fig. 1. Each value of gas permeance and O\(_2\)/N\(_2\) selectivity were repeated at least five times, and the measurement error was under 5%. Air as the feed gas entered from one side of the membrane, while He swept on the lumen side. After permeating through the PDMS hollow fiber membrane, O\(_2\) and N\(_2\) were carried by He and then entered gas chromatography (model GC-8A, Shimadzu, Japan). Before entering the membrane, the individual gas flow rates were controlled by mass flow controllers (model D07-19B; Beijing Jianzhong Machine Factory, China). The feed gas flow rate was 80 mL min\(^{-1}\), while the

![Figure 1. Schematic diagram of the apparatus for oxygen permeation measurement. GC, gas chromatography.](image-url)
sweep gas flow rate was 30 mL min$^{-1}$. Both sides of the membrane were kept at atmospheric pressure. The driving force was the partial pressure difference of oxygen across the membrane. The temperature surrounding the membrane was monitored by a programmable temperature controller. Finally, the composition of the permeate gas was analyzed with an on-line gas chromatograph equipped with a thermal conductivity detector.

According to the variable-volume method of Stern et al.,$^{[25]}$ oxygen permeance ($P_{O_2}$) and nitrogen permeance ($P_{N_2}$) can be calculated by using the following equations:

\[
P = \frac{\Delta V}{\Delta t \Delta P A}
\]

(1)

where $\Delta V$ and $\Delta t$ are the changes in volume for the permeated gas and in time, respectively. $A$ is the effective membrane area. Besides that, $\Delta P$ is the gas pressure difference across the membrane. Permeance is frequently expressed in GPU.

The selectivity is defined as the ratio of permeance of two gases in the membranes:

\[
\alpha_{O_2/N_2} = \frac{P_{O_2}}{P_{N_2}}
\]

(2)

RESULTS AND DISCUSSION

Effect of PDMS thickness

Typical scanning electron microscopy images of the ceramic hollow fiber-supported PDMS composite membrane with different layer thicknesses are shown in Fig. 2. It can be clearly observed that there are two kinds of structures in hollow fiber membrane (Fig. 2a). One is the sponge-like structure in the middle of the hollow fiber wall, and the other is the finger-like structure located at the inner and outer walls of the support. PDMS separation layer was coated on the outer surface of ceramic hollow fiber, without interfacial voids between PDMS layer and ceramic support. The thickness of the PDMS separation layer is closely related to polymer solution viscosity and coating times for dip coating, which were investigated in our previous work$^{[26]}$.

The effect of membrane thickness on the permeance and selectivity was studied by varying the thickness of the PDMS layer, and the results are shown in Fig. 3. In general, there is a trade-off relationship between permeance and selectivity with different thicknesses of active layer. It presents a drop in oxygen permeance with the increases of the thickness of PDMS layer. The selectivity increases rapidly with the membrane thickness as the layer thickness is less than 25 µm. To further increase membrane thickness, the ideal selectivity nearly remains unchanged. The reasonable explanation is that the mass transfer resistance increases with the thickness of the membrane, leading to the drop of oxygen permeance. In addition, some defects will be existing within the thin polymeric layer; thus, the selectivity is low when the membrane thickness is thin.$^{[23,27]}$ What’s more, specific energy consumption does not increase with the layer thickness increase.$^{[2]}$ So, the 25 µm may be thought of as the optimum value. However, when the film thickness reaches a certain value, the film can be regarded as dense membrane without defects. As a result, the ideal selectivity for $O_2/N_2$ increased to approximately 2.0, which is close to the intrinsic selectivity of PDMS material.
Effect of feed temperature and pressure difference

Effects of temperature on permeation coefficient \( P_{O_2}, P_{N_2} \) and selectivity \( \alpha_{O_2/N_2} \) of the ceramic hollow fiber-supported PDMS composite membrane were investigated under different temperatures from 20 to 70 °C at the pressure difference of 0.1 MPa. As shown in Fig. 4, both oxygen and nitrogen permeance increase with the testing temperature. It is attributed to the improved polymer chain mobility and then larger available free volume of PDMS membrane for gas diffusion at higher temperature. It is interesting to find that the ideal selectivity for \( O_2/N_2 \) can keep at about 2.0, exhibiting a good stability under high temperature. Usually, the membrane showed an ‘inverse’ permeance/selectivity behavior by increasing feed temperature.\(^{[28]}\) The simultaneous positive responses of permeance and selectivity to temperature in this work are attributed to the confinement effect from the rigid ceramic substrate that constrains the excessive swelling of PDMS separation layer. This phenomenon is in agreement with our previous studies on ceramic-supported polymer composite membranes for pervaporation.\(^{[18,23]}\) The interesting finding is favorable for practical application of ceramic hollow fiber-supported PDMS composite membrane, because the \( O_2 \) permeance can be easily improved by elevating operation temperature while maintaining a high \( O_2/N_2 \) ideal selectivity.

Generally speaking, the temperature dependence of the permeance (both oxygen and nitrogen) follows the Arrhenius expression:

\[
P = P_0 \exp\left(-\frac{E_J}{RT}\right)
\]  

where \( P_0 \) is constant, \( E_J \) is the activation energy for permeation, \( R \) is the gas constant, and \( T \) is the operation temperature in Kelvin. Figure 5 shows the Arrhenius plot of oxygen and nitrogen permeance vs temperature. The calculated average activity energies of oxygen and nitrogen permeation through PDMS composite hollow fiber are 3.48 and 4.71 kJ mol\(^{-1}\), respectively.

Figure 6 shows the effects of pressure difference \( \Delta P \) on gas permeance \( P_{O_2}, P_{N_2} \) and selectivity \( \alpha_{O_2/N_2} \) of the ceramic hollow fiber-supported PDMS composite membrane. It could be seen that the permeance and selectivity curves almost exhibit horizontal lines. Pressure difference does not influence oxygen permeance and nitrogen permeance of polymeric membrane according to the general solution–diffusion mechanism. This phenomenon agrees with what Stern et al. had carried out. He proved it by studying the modified PDMS membranes.\(^{[29]}\) Merkel et al. also
demonstrated it through investigating the permeance of PDMS to \( \text{H}_2, \text{O}_2, \text{N}_2, \text{CO}_2, \text{CH}_4, \text{C}_2\text{H}_6, \text{C}_3\text{H}_8, \text{CF}_4, \text{C}_2\text{F}_6 \), and \( \text{C}_3\text{F}_8 \) with detailed theoretical calculation.[30]

In this work, by varying the pressure difference from 0.05 to 0.4 MPa at room temperature, the oxygen permeance and oxygen/nitrogen ideal selectivity keep at 104 GPU and 2.0, respectively.

**Effect of feed concentration**

The effect of feed gas concentration on ceramic hollow fiber-supported PDMS composite membrane was investigated at room temperature with the pressure difference of 0.1 MPa, and the results are shown in Fig. 7. The feed concentration was controlled by adjusting the oxygen and nitrogen ratio with mass flow controllers. The total flow rate of mixed gas was kept at 80 mL min\(^{-1}\) and helium flow rate of 30 mL min\(^{-1}\) on the lumen side. It is found that the concentration of oxygen in the permeation increases linearly with the oxygen concentration in feed increasing from 10% to 60%. With the increase of \( \text{O}_2 \) concentration in feed, the \( \text{O}_2 \) concentration is linearly increased, while the permeance of oxygen did not change significantly. We separated oxygen from air feed by the PDMS membrane to obtain 30% oxygen in the permeation by single stage. Based on the relationship between oxygen feed concentration and separation performance, it can also easily help us design the oxygen enrichment process to obtain preferred higher oxygen concentration by performing more than one stages.

**Long-term stability**

The long-term stability is an important criterion for PDMS membrane in the process of practical oxygen enrichment. Therefore, we studied the effect of operation time on oxygen enrichment from air. Figure 8 presents the result of continuous operation of ceramic hollow fiber-supported PDMS composite membrane at room temperature, and the pressure difference was kept at 0.1 MPa. It is found that there are little changes in oxygen permeance and selectivity over a long period of over 10 days operation without interruption. Furthermore, after the long-term stability process, the membrane still showed oxygen permeance of 104 GPU and selectivity of 2.0 for pure gas. After single stage of membrane separation under room temperature and low feed pressure, the oxygen concentration in the air can be easily enriched to over 30%, which also meets the energy-saving requirement for industrial application.

**Oxygen enrichment performance compared with literatures**

Many research groups focus on separating oxygen from air with membrane technology. The detailed comparisons of gas separation performance using PDMS membrane are listed in Table 1. It could be found that the ceramic hollow fiber-supported

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**Figure 6.** Effect of pressure difference on oxygen permeance, nitrogen permeance, and ideal selectivity for \( \text{O}_2/\text{N}_2 \) at room temperature for pure gas.

**Figure 7.** Effect of feed gas concentration on oxygen enrichment performance at room temperature for binary mixed gas (\( f_{\text{He}} = 30 \text{ mL min}^{-1} \)).

**Figure 8.** Long-term stability of the PDMS membrane at room temperature for binary mixed gas.
A ceramic hollow fiber-supported PDMS composite membrane can be considered to own higher gas permeance, while the ideal selectivity keeps relatively good. It is mainly due to the low transport resistance of the ceramic hollow fiber substrate and optimal interfacial morphology of composite membrane, which prevents more PDMS penetrating to the defect-free PDMS separation layer. In order to satisfy the need of practical application, the development of membrane with high permeance is of great significance.

CONCLUSION

Ceramic hollow fiber-supported PDMS composite membrane was successfully applied to enrich oxygen from air. An optimized PDMS thickness of 25 μm was proven to achieve good oxygen permeance and selectivity. Several factors were found to play key roles in the oxygen enrichment process such as feed temperature and oxygen concentration. The membrane performed a high and stable oxygen enrichment performance during 10 days of continuous operation. The pure gas separation showed average O2 permeance of 104 GPU and O2/N2 ideal selectivity of 2.0. Moreover, the concentration of 30% oxygen can be obtained with air in the feed by single-stage separation through the PDMS membrane. Our work demonstrated that the hollow fiber ceramic-supported PDMS composite membranes can be expected as a promising candidate for oxygen enrichment process.

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