ASIA-PACIFIC JOURNAL OF CHEMICAL ENGINEERING
Asia-Pac. J. Chem. Eng. (2016)
Published online in Wiley Online Library
(wileyonlinelibrary.com) DOI: 10.1002/apj.1972

Research article

Ceramic hollow fiber-supported PDMS composite membranes for oxygen enrichment from air

Changhong Pian, Jie Shen, Gongping Liu,† Zhengkun Liu and Wanqin Jin†*

State Key Laboratory of Materials-Oriented Chemical Engineering, Nanjing Tech University (former Nanjing University of Technology), Nanjing 210009, China

Received 3 November 2015; Revised 11 January 2016; Accepted 13 January 2016

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 104 GPU (1 GPU = 10^{-6} cm^3 standard temperature and pressure (STP)/cm^2 s cmHg) with O_2/N_2 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.

Keywords: oxygen enrichment; ceramic hollow fiber; polydimethylsiloxane; composite membrane

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.[1] 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.[2,3]

Many polymeric materials have been used to separate oxygen and nitrogen.[4–6] 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).[7] Polydimethylsiloxane (PDMS) membrane possesses high oxygen permeance because of the flexibility of the siloxane linkages (–SiO–).[8] Because of its high gas permeance and being readily available, PDMS has received considerable attention as one of the most important membrane materials for gas separation process in the past decades.[9–13] Gas separation membranes with higher permeance and selectivity result in lower capital cost and operating cost. Besides, the enhancement of selectivity will always improve the physical/thermodynamic performance of the membrane.[14] Thus, various studies focused on modification of PDMS in order to further increase the performance. Weinkauf *et al.* [15] reported that after radio-frequency (RF) plasma treatments on the surface of PDMS, the membrane showed an improvement of selectivity, but the O_2 permeance is only about 0.48 GPU. And the gas permeance of the prepared membrane dropped much during long-term operation. Zhang *et al.* [16] prepared PDMS membrane using cross-linking agent containing silicon–hydrogen bonds. At 30 °C and pressure difference of 0.05 MPa, although the membrane selectivity increased, the oxygen permeance decreased to 4.6 GPU. As mentioned previously, the optimal oxygen concentration is 25–40% for industrial application. A moderate O_2/N_2 ideal selectivity of PDMS membrane 2.0 can meet the concentration requirement of enriched-oxygen industrial application. In contrast, low permeation rates would require large membrane area, leading to high capital cost of commercial application.[17] Therefore, it is necessary to improve oxygen permeance of the PDMS membrane.

**Correspondence to:* Wanqin Jin, State Key Laboratory of Materials-Oriented Chemical Engineering, Nanjing Tech University, 5 Xinmofan Road, Nanjing 210009, China. E-mail: wqjin@njtech.edu.cn

†To whom all correspondence should be addressed.

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 min^{-1} for 2 h, 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

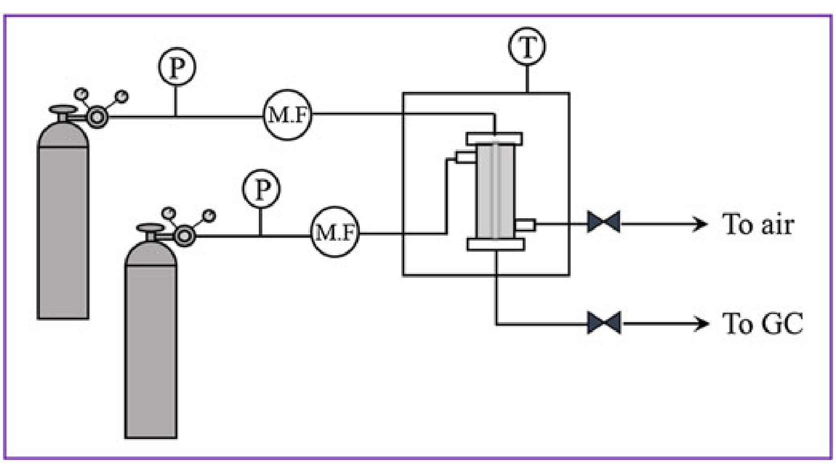

Figure 1. Schematic diagram of the apparatus for oxygen permeation measurement. GC, gas chromatography.

DOI: 10.1002/apj

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_{O2}) and nitrogen permeance (P_{N2}) can be calculated by using the following equations:

$$P = \frac{\Delta V/\Delta t}{\Delta PA} \quad (1)$$

where ΔV and Δt are the changes in volume for the permeated gas and in time, respectively. A is the effective membrane area. Besides that, ΔP 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:

$$\alpha_{O2/N2} = \frac{P_{O2}}{P_{N2}} \quad (2)$$

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.

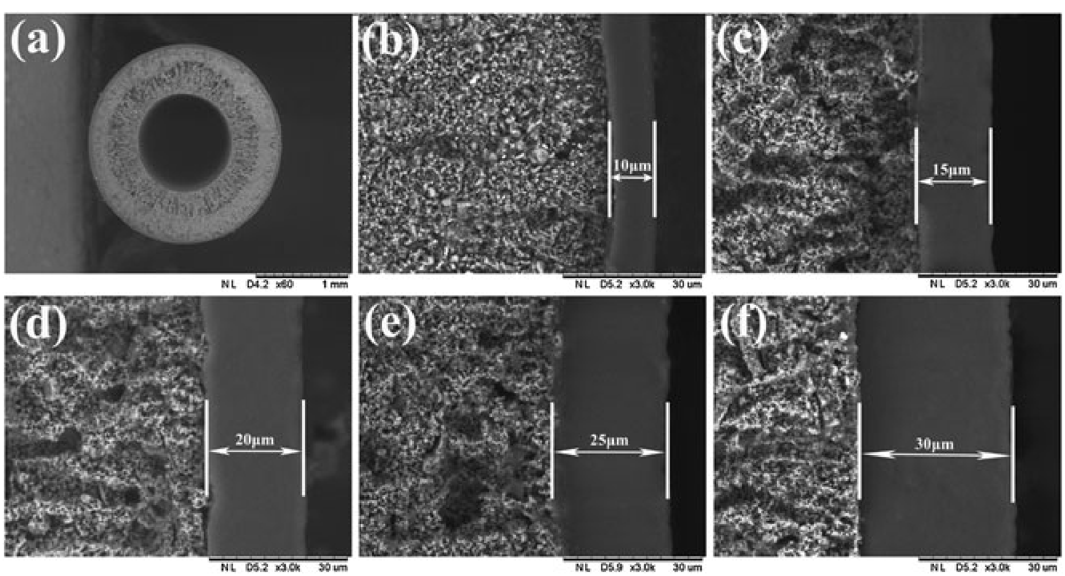

Figure 2. Scanning electron microscopy images of cross section of ceramic hollow fiber-supported PDMS composite membrane with different layer thickness.

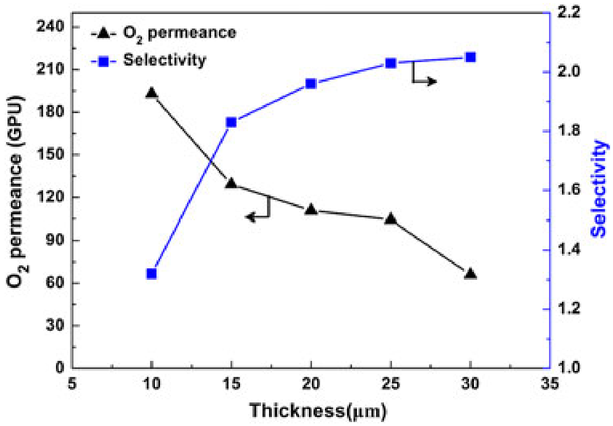

Figure 3. Effect of PDMS layer thickness on oxygen permeance and ideal selectivity for O_2/N_2 at room temperature and pressure difference of 0.1 MPa for pure gas.

Effect of feed temperature and pressure difference

Effects of temperature on permeation coefficient (P_{O2}, P_{N2}) and selectivity ($\alpha_{O2/N2}$) 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:

$$P = P_0 \exp\left(\frac{-E_J}{RT}\right) \tag{3}$$

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 (ΔP) on gas permeance (P_{O2}, P_{N2}) and selectivity ($\alpha_{O2/N2}$) 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

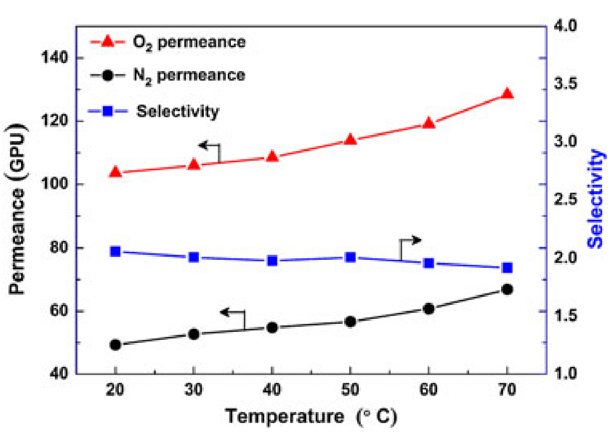

Figure 4. Effect of temperature on oxygen permeance, nitrogen permeance, and ideal selectivity for O_2/N_2 at pressure difference of 0.1 MPa for pure gas.

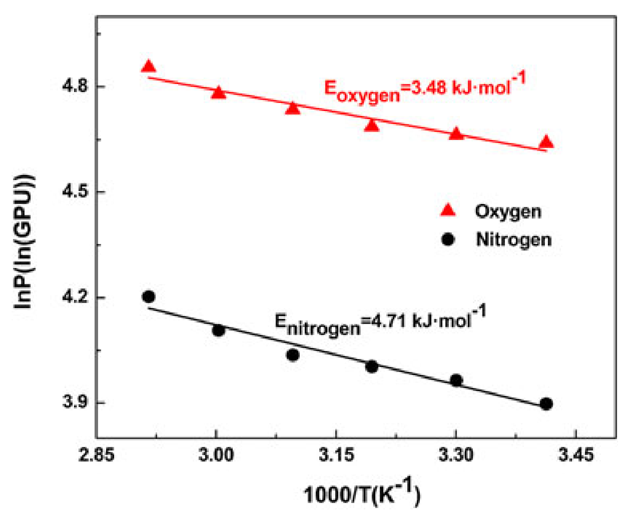

Figure 5. Arrhenius plots of both oxygen and nitrogen permeance for ceramic hollow fiber-supported PDMS composite membrane at pressure difference of 0.1 MPa.

DOI: 10.1002/apj

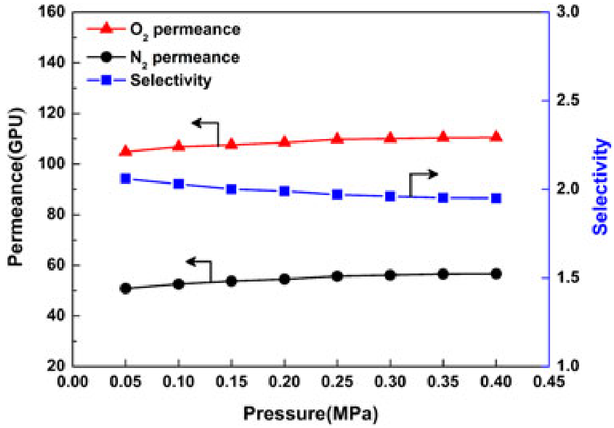

Figure 6. Effect of pressure difference on oxygen permeance, nitrogen permeance, and ideal selectivity for O_2/N_2 at room temperature for pure gas.

demonstrated it through investigating the permeance of PDMS to H_2, O_2, N_2, CO_2, CH_4, C_2H_6, C_3H_8, CF_4, C_2F_6, and C_3F_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 O_2 concentration in feed, the 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.

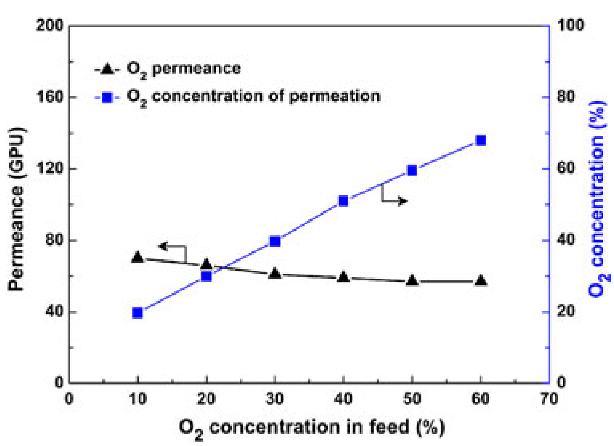

Figure 7. Effect of feed gas concentration on oxygen enrichment performance at room temperature for binary mixed gas (F_{He} = 30 mL min^{-1}).

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

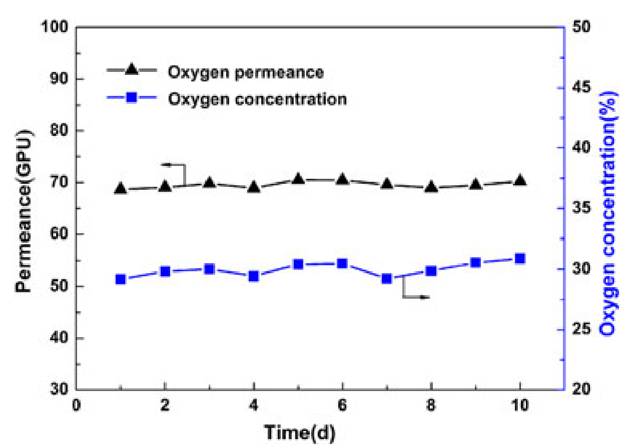

Figure 8. Long-term stability of the PDMS membrane at room temperature for binary mixed gas.

Table 1. Gas separation performance of different membranes.

Membrane	Temperature (°C)	Pressure difference (MPa)	Ideal selectivity	Permeance (GPU)	References
PDMS/tetraethoxysilicone	30	0.05	3.45	4.6	[16]
PDMS/Polyethersulfone (PES)	25	0.2	1.7	63	[30]
Fluorine-filled PDMS	25	0.05	3.47	6.0	[31]
Silicone-coated PES	50	0.05	5.1	13.1	[32]
Dual-layer PES	25	0.68	6.96	4.79	[33]
PDMS	35	0.1	2.0	22.9	[29]
PDMS/hollow fiber	25	0.1	2.0	104	This work

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,[23] 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 O_2 permeance of 104 GPU and O_2/N_2 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.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (nos. 21490585 and 21476107), Innovative Research Team Program by the Ministry of Education of China (no. IRT13070), Natural Science Foundation of Jiangsu Province (no. BK20140930), and the Project of Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD).

REFERENCES

[1] Zhu Y, Legg S, Laird C. Optimal design of cryogenic air separation columns under uncertainty. *Comput. Chem. Eng.* 2010; **34**: 1377–1384.
[2] Meriläinen A, Seppälä A, Kauranen P. Minimizing specific energy consumption of oxygen enrichment in polymeric hollow fiber membrane modules. *Appl. Energ.* 2012; **94**: 285–294.
[3] Baker R. Future directions of membrane gas separation technology. *Ind. Eng. Chem. Res.* 2002; **41**: 1393–1411.
[4] Madaeni S, Esmaeili M, Attar Nosrati S, Barzin J. Preparation and characterization of PES and PA composite membranes for air separation at low pressures. *Int. Polym. Proc.* 2013; **28**: 281–290.
[5] Tsai C, Ruaan R, Hu C, Lee K. Interfacially polymerized layers for oxygen enrichment: a method to overcome Robeson's upper-bound limit. *ACS. Appl. Ppl. Mater. Inter.* 2013; **5**: 5563–5568.
[6] Huang M, Li X, Ji X, Qiu W, Gu L. Actual air separation across multilayer composite membranes. *J. Appl. Polym. Sci.* 2000; **77**: 2396–2403.
[7] Belaissaoui B, Le Moullec Y, Hagi H, Favre E. Energy efficiency of oxygen enriched air production technologies: cryogeny vs membranes. *Sep. Purif. Technol.* 2014; **125**: 142–150.
[8] Rao H, Liu F, Zhang Z. Oxygen-enriching properties of silicone rubber crosslinked membrane containing cobalt. *J. Membr. Sci.* 2007; **296**: 15–20.
[9] Liu S, Liu G, Wei W, Xiangli F, Jin W. Ceramic supported PDMS and PEGDA composite membranes for CO_2 separation. *Chin. J. Chem. Eng.* 2013; **21**: 348–356.
[10] Salih A, Yi C, Peng H, Yang B, Yin L, Wang W. Interfacially polymerized polyetheramine thin film composite membranes with PDMS inter-layer for CO_2 separation. *J. Membr. Sci.* 2014; **472**: 110–118.
[11] Saedi S, Madaeni S, Shamsabadi A. PDMS coated asymmetric PES membrane for natural gas sweetening: effect of preparation and operating parameters on performance. *Can. J Chem. Eng.* 2014; **92**: 892–904.
[12] Chen H, Thong Z, Li P, Chung T. High performance composite hollow fiber membranes for CO_2/H_2 and CO_2/N_2 separation. *Int. J. Hydrogen. Energ.* 2014; **39**: 5043–5053.
[13] Campo M, Magalhães F, Mendes A. Separation of nitrogen from air by carbon molecular sieve membranes. *J. Membr. Sci.* 2010; **350**: 139–147.
[14] Seppälä A. Irreversibility in a gas separation medium. *Chem Phys.* 2010; **367**: 99–109.

[15] Houston K, Weinkauf D, Stewart F. Gas transport characteristics of plasma treated poly (dimethylsiloxane) and polyphosphazene membrane materials. *J. Membr. Sci.* 2002; **205**: 103–112.
[16] Rao H, Liu F, Zhang Z. Preparation and oxygen/nitrogen permeability of PDMS crosslinked membrane and PDMS/tetraethoxysilicone hybrid membrane. *J. Membr. Sci.* 2007; **303**: 132–139.
[17] Bisio G, Bosio A, Rubatto G. Thermodynamics applied to oxygen enrichment of combustion air. *Energ. Convers. Manage.* 2002; **43**: 2589–2600.
[18] Xiangli F, Chen Y, Jin W, Xu N. Polydimethylsiloxane (PDMS)/ceramic composite membrane with high flux for pervaporation of ethanol-water mixtures. *Ind. Eng. Chem. Res.* 2007; **46**: 2224–2230.
[19] Zhu Y, Xia S, Liu G, Jin W. Preparation of ceramic-supported poly(vinyl alcohol)-chitosan composite membranes and their applications in pervaporation dehydration of organic/water mixtures. *J. Membr. Sci.* 2010; **349**: 341–348.
[20] Liu G, Xiangli F, Wei W, Liu S, Jin W. Improved performance of PDMS/ceramic composite pervaporation membranes by ZSM-5 homogeneously dispersed in PDMS via a surface graft/coating approach. *Chem. Eng. J.* 2011; **174**: 495–503.
[21] Xia S, Dong X, Zhu Y, Wei W, Xiangli F, Jin W. Dehydration of ethyl acetate-water mixtures using PVA/ceramic composite pervaporation membrane. *Sep. Purif. Technol.* 2011; **77**: 53–59.
[22] Liu G, Wei W, Wu H, Dong X, Jiang M, Jin W. Pervaporation performance of PDMS/ceramic composite membrane in acetone butanol ethanol (ABE) fermentation-PV coupled process. *J. Membr. Sci.* 2011; **373**: 121–129.
[23] Dong Z, Liu G, Liu S, Liu Z, Jin W. High performance ceramic hollow fiber supported PDMS composite pervaporation membrane for bio-butanol recovery. *J. Membr. Sci.* 2014; **450**: 38–47.
[24] Liu D, Liu G, Meng L, Dong Z, Huang K, Jin W. Hollow fiber modules with ceramic-supported PDMS composite membranes for pervaporation recovery of bio-butanol. *Sep. Purif. Technol.* 2015; **146**: 24–32.
[25] Stern S, Sinclair T, Gareis P. An improved permeability apparatus of the variable-volume type. *Mod. Plast.* 1964; **42**: 154–158.
[26] Wei W, Xia S, Liu G, Gu X, Jin W, Xu N. Interfacial adhesion between polymer separation layer and ceramic support for composite membrane. *AICHE. J.* 2010; **56**: 1584–1592.
[27] Qin F, Li S, Qin P, Karim M, Tan T. A PDMS membrane with high pervaporation performance for the separation of furfural and its potential in industrial application. *Green Chem.* 2014; **16**: 1262–1273.
[28] Madaeni S, Enayati E, Vatanpour V. Separation of nitrogen and oxygen gases by polymeric membrane embedded with magnetic nano-particle. *Polym. Adv. Technol.* 2011; **22**: 2556–2563.
[29] Stern S, Shah V, Hardy B. Structure-permeability relationships in silicone polymers. *J. Polym. Sci. Pol. Chem.* 1987; **25**: 1263–1298.
[30] Merkel T, Bondar V, Nagai K, Freeman B, Pinnau I. Gas sorption, diffusion, and permeation in poly(dimethylsiloxane). *J. Poloym. Sci. Pol. Chem.* 2000; **38**: 415–434.
[31] Zhang Z, Huang J, Lin Y, Rao H. Oxygen-enriching properties of a new hybrid membrane cross-linked from PDMS and fluorine-containing silicone resin. *Polym. Eng. Sci.* 2013; **53** : 2328–2335.
[32] Kesting R, Fritzsche A, Murphy M, Handermann A, Cruse C, Malon R. Process for forming asymmetric gas separation membranes having graded density skins. *US Pat.* 1989; **4**: 871–494.
[33] Li Y, Chung T, Xiao Y. Superior gas separation performance of dual-layer hollow fiber membranes with an ultrathin dense-selective layer. *J. Membr. Sci.* 2008; **325**: 23–27.