



New bio-inspired design for high-performance and highly robust $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ membranes for oxygen permeation

Tao Li^a, Tatiya Kamhangdatepon^b, Bo Wang^a, Unalome Wetwatana Hartley^b, Kang Li^{a,*}

^a Barrer Centre, Department of Chemical Engineering, Imperial College London, London, UK

^b Chemical Process Engineering, King Mongkut's University of Technology, North Bangkok, Bangkok, Thailand

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ABSTRACT

Ceramic-based oxygen permeation membranes (OPM) are considered to be promising for the separation of oxygen from air. However, state-of-art membrane designs are unable to deliver satisfactory performances in terms of permeation flux, mechanical/chemical stability and membrane surface area. In this study, a new bio-inspired design has been successfully introduced in the micro-monolithic membranes made of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) for oxygen separation. By carefully controlling the process parameters of the fabrication and utilizing the hydraulic pressure of internal coagulant, the geometry of channels in the micro-monolith has been converted from a circular shape to a triangle shape with rounded corners. This new bio-inspired, 'orange-like' architecture not only reduces the effective oxygen diffusional length down to approximately 50 μm , but also significantly increases the ratio of active region among the overall circumference up to 90%. This new bio-inspired micro-monolithic design displays an excellent oxygen permeation flux of 1.87 $\text{ml min}^{-1}\text{cm}^{-2}$ at 950 $^{\circ}\text{C}$, which is superior to the most reported values from LSCF material systems. In addition, such a design illustrates an excellent mechanical robustness that has long been a bottleneck for LSCF membranes. This work demonstrates a promising solution to tackle the long-existing trade-off between oxygen permeation performance and mechanical reliability.

1. Introduction

Air separation is an important separation process to produce pure oxygen or oxygen-enriched air which could be subsequently applied for a wide range of applications such as medical device, rocket propellant, oxy-fuel combustion and chemical synthesis [1–4]. The conventional approach for air separation is cryogenic distillation, which is well-matured and has been almost exclusively used for decades. However, this process is very costly due to the extremely low temperature requirement. On the other hand, several non-cryogenic processes have been explored in the past decades, among which dense ceramic oxygen permeable membranes (OPM) is one of the most promising alternatives. In principle, this chemical potential gradient-driven membrane process is energy efficient, despite requiring external heat to provide adequate operating temperatures (typically above 800 $^{\circ}\text{C}$) to facilitate ionic conduction. In addition, infinite selectivity can be theoretically realized since a defect-free, dense ceramic OPM is solely permeable towards oxygen [1,5].

So far, there has been a significant progress in OPM materials for spontaneous oxygen permeation, which can be classified into two main

categories depending on whether a separate electronic mediator is needed to preserve electroneutrality, namely single-phase membranes that exhibit mixed ionic/electronic conductivity (MIEC), and dual-phase composite membranes with percolating phases as both ionic and electronic conductors. The development of new OPM materials has received significant attention to fulfil several general criteria, including high oxygen permeation flux, good stability under different gaseous environments, proper mechanical strength and cost-effectiveness, which have been covered by some comprehensive reviews [6–9]. However, to compete with current cryogenic process, the geometry and morphology of the ceramic OPM need to be further designed and optimized.

Planar/disk-type is a geometry that receives probably the most attention mainly due to the mature manufacturing process, such as tape-casting. Air products has constructed a demonstration module based on tape-casted planar OPM, with a production rate of 5 tons/day [10,11]. However, like other ceramic devices, high-temperature sealing remained as one of the key engineering difficulties. Additionally, the external mechanical support, on which the thin OPM is typically deposited, could show different thermal expansion behaviour as the OPM

* Corresponding author.

E-mail address: Kang.Li@Imperial.ac.uk (K. Li).

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and lead to the accumulation of stresses, consequently resulting in delamination and catastrophic structural failure. On the contrary, tubular and the subsequently evolved micro-tubular (hollow fiber) design show the most important advantage of simplified sealing. It is also suggested to be the optimal design based on the calculation of a full-scale module [12]. Nevertheless, there is a long-existing trade-off between oxygen permeation flux and mechanical reliability associated with this design. According to the Wagner equation, OPM should be thin enough to minimize diffusional resistance and subsequently maximize permeation flux. Different from planar OPMs which is typically external-supported, the separation layer in the self-supporting tubular OPM also needs to provide mechanical robustness. Therefore, the reduction in thickness would inevitably jeopardize the mechanical strength. A new design featuring a good balance between high performance and good mechanical reliability is, therefore, in great need.

Recently, a new miniaturized honeycomb-like design has been demonstrated, exhibiting superior mechanical robustness and comparable oxygen permeation flux [13]. Such design suggests a feasible solution to overcome the long-existing trade-off. Herein, a new bio-inspired, micro-monolithic design has been developed, displaying an orange-shaped architecture and very well-controlled separation layer thickness. A phase inversion-assisted extrusion technique has been used, during which the composition of internal coagulant was carefully adjusted to evolve the channel geometry from circular to a teardrop shape. $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) was selected as a sample material since the widely available literatures about LSCF hollow fiber membranes would facilitate the comparison. The mechanical robustness and oxygen permeation performances were systematically investigated. Additionally, a benchmark has been proposed to estimate the equivalent thickness and effective surface area for such multi-channel geometry.

2. Experimental

2.1. Materials

Commercially available lanthanum strontium cobalt ferrite ($\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$, LSCF) powder was purchased from Fuel Cell Materials (USA) and used as supplied. Poly (methyl methacrylate) (Acrypet-PMMA, Mitsubishi Rayon Co. Ltd), N-Methyl-2-pyrrolidone (HPLC grade, VWR International) and Arlacel P135 (Uniquema, UK) were used as polymer binder, solvent and dispersant, respectively. A mixture of deionized (DI) water and ethanol (VWR International) was used as internal coagulant.

2.2. Fabrication of bio-inspired 6-channel LSCF micro-monolith

The 6-channel LSCF micro-monolith with an orange-like design was fabricated via a phase inversion-assisted extrusion process, details of which have been described elsewhere [13]. Fig. 1 depicts the schematic diagram of how the new design was inspired and proposed. For a conventional hollow fiber design, it has a typical annular geometry with two concentric circles. Given the outer diameter remains unchanged, the reduction in separation layer thickness is achieved via enlargement

of inner contour, which inevitably leads to compromising of mechanical strength. Therefore, additional structure needs to be introduced in the hollow lumen to function as the mechanical support. Inspired by the shape of an orange cross-section, the eventual design is by splitting the circular lumen into circular sectors (sextants or octants). Most importantly, the arc of each sector has a degree of curvature that is close to the outer circumference, whereas the regions in between the circular sectors and in the middle provides the required mechanical strength.

The spinning suspension was prepared by mixing the LSCF powder, polymer binder, solvent and additives, and then thoroughly milled for 4 days using a planetary miller to ensure proper homogeneity. A vacuum-assisted degassing step was undertaken prior to the extrusion to eliminate air bubbles trapped inside. During the spinning, a mixture of deionized (DI) water-ethanol ($\text{H}_2\text{O}/\text{ethanol} = 70/30$ by weight) was adopted as the internal coagulant instead of pure DI water that has been commonly used. After the micro-monolithic precursor was straightened and dried, a sintering step was undertaken at 1350°C for 6 h to obtain dense LSCF membranes.

2.3. Characterization

Field emission scanning electron microscope (FE-SEM, Gemini LEO 1525) was used to observe the morphology of 6-channel micro-monolith samples. The mechanical robustness was investigated by a three-point bending method using an Instron Testing System (Instron 5543) with a 1 kN load cell, during which the sample holder had a span of 30 mm.

The oxygen permeation flux of the sample was measured with 100 ml min^{-1} of argon as a sweep gas in the lumen side, while 100 ml min^{-1} of air is fed to the shell side at the atmospheric pressure. The oxygen concentration in the effluent gas from the lumen side was subsequently analysed using gas chromatography (GC, Varian 3900). The oxygen permeation flux was then calculated using the equation below:

$$J_{\text{O}_2} = \frac{V_{\text{Ar}} y_{\text{O}_2}}{A_o (100 - y_{\text{O}_2})} \quad (1)$$

Where J_{O_2} is the oxygen permeation flux ($\text{ml cm}^{-2} \text{ min}^{-1}$), V_{Ar} is the flow rate of the argon sweep gas (ml min^{-1}), A_o denotes the outer surface area (cm^2), y_{O_2} is the oxygen concentration detected by the GC.

3. Results and discussion

3.1. Morphology of 6-channel LSCF micro-monolith

Fig. 2 depicts the morphology of the 6-channel LSCF micro-monolith with a bio-inspired design, which has been successfully fabricated via a phase inversion-assisted extrusion technique. The outer diameter of sintered sample was $(1.95 \pm 0.03)\text{ mm}$ (Fig. 2 (a)), which is well within the accepted range for hollow fiber or micro-tubes. The theoretical outer surface area to volume ratio was calculated to be $1813.6\text{ m}^2\text{ m}^{-3}$ based on the assumption of closest hexagonal packing (Table 1). Such ratio compares well with most reported hollow fibers and is several folds higher than conventional flat and tubular membranes. In addition, an asymmetric micro-structure composed of micro-channels and spongy regions could be observed in Fig. 2(b) and (c), which was introduced during the phase inversion process as a result of interfacial instability, details of which have been discussed elsewhere [13,14], and well-preserved during sintering. Different from conventional ceramic monolith/honeycombs that have a regular channel geometry (e.g. circular, square or hexagonal), a triangle shape with rounded corners could be clearly observed in Fig. 2(a), which makes the cross section alike to an orange or grapefruit. After the sintering step at 1350°C , the outer surface of the membrane has been densified and

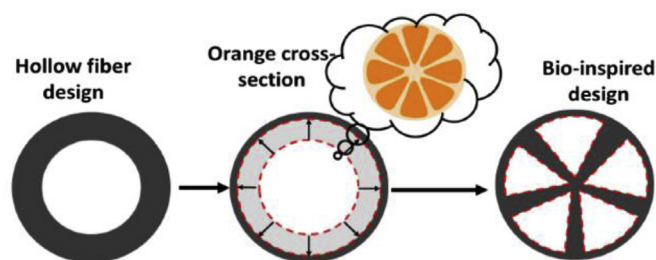


Fig. 1. Schematic diagram of the proposal of bio-inspired design.

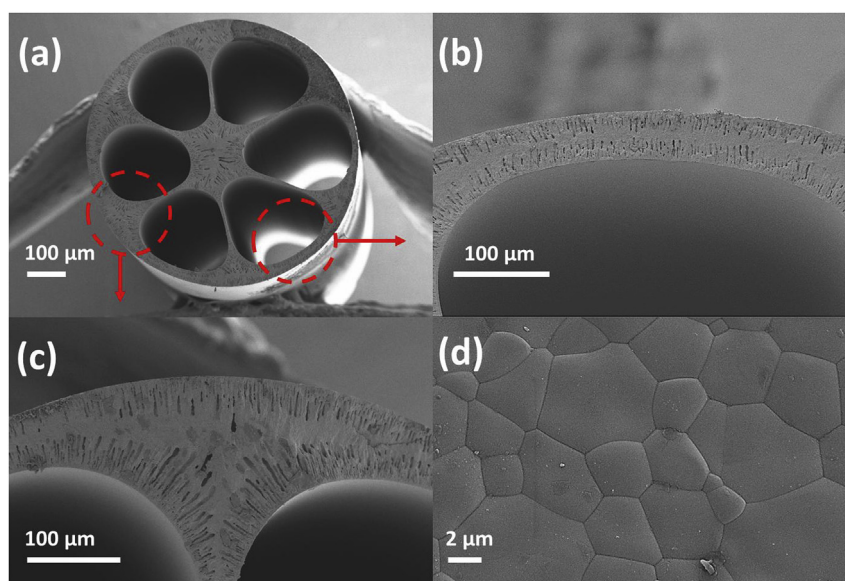


Fig. 2. SEM images of sintered LSCF micro-monolithic membrane with bio-inspired design: (a) whole view, (b) active region for oxygen permeation with a relatively uniform thickness, (c) cross section of the wall between the shell and two bores, (d) outer surface of membranes.

become defect-free (Fig. 2(d)), which could be well used for oxygen permeation test.

In the case of fabrication process for traditional hollow fibers as shown in Fig. 3(a), the hydraulic pressure from the internal coagulant (or bore fluid) is important. If it is not high enough (e.g. relatively slow extrusion rate), an irregular or deformed inner contour could be observed [15]. Therefore, it is critical for the internal coagulant to provide a hydraulic pressure that is sufficient to suppress the impact of shrinkage during the phase inversion, so as to maintain the regularity of the inner contour. As for the 6-channel design, 6 nozzles are arranged in a hexagonal configuration and multiple streams of internal coagulants were induced, as displayed in Fig. 3 (b). Therefore, in addition to preventing the buckling of inner contour, the hydraulic pressure could be further manipulated to modify the membrane geometry. For each individual stream, the hydraulic pressure at certain directions were offset by the pressure from the neighboring streams of internal coagulant, leading to a non-uniform expansion of lumen and the transformation from circular to a triangular shape. It is also noteworthy that the use of water-ethanol mixture in this work is extremely important to slow down the precipitation of the polymer binder and to provide sufficient time to establish the orange-shaped channel geometry.

As reported, one important feature of LSCF membranes with multi-channel architecture is the varying thickness of the separation layer. To estimate the effective oxygen diffusional path length for these non-uniform structures, an assumption was made that only the region of the sector, constrained by tangents subtending the center of the membrane (Fig. 4 (a)), facilitated oxygen diffusion, while the contribution from the remaining volume was negligible. The shaded area was subsequently normalized to an annulus of equivalent area with an identical outer radius (R) and central angle (θ). The calculated width of the annulus (d)

sector was then adopted as the effective diffusive path length, which is summarized in Table 1 and compared to references. To validate the calculation, oxygen permeation flux of the multi-channel samples was compared to reported LSCF hollow fibers with a similar cross-sectional thickness. For example, the 4-channel sample, whose equivalent thickness was calculated to be 240 μm , was reported to have an oxygen permeation flux of $0.51 \text{ ml min}^{-1} \text{ cm}^{-2}$ at 950°C [13]. In comparison, conventional LSCF hollow fibers with cross-sectional thicknesses of 220 μm and 270 μm were reported to have oxygen permeation flux of $0.54 \text{ ml min}^{-1} \text{ cm}^{-2}$ [18] and $0.4 \text{ ml min}^{-1} \text{ cm}^{-2}$ [19], respectively. It can be concluded that these oxygen permeation flux follows the general trend of being reversely proportional to the separation layer thickness, which helps to validate this method of estimating the equivalent thickness. In addition, it can be seen from the table that the bio-inspired design from this work provides an effective thickness of around 51.6 μm , which is markedly reduced compared to other reported values, up to 5 folds thinner. As shown in Fig. 2 (b), the majority of the active separation layer has a quite constant thickness, which is resulted from the combined effects of both prolonged precipitation time by using the H_2O -ethanol mixture as a weaker coagulant, as well as the pressure from the neighboring streams of non-solvent extruded.

3.2. Oxygen permeation through the 6-channel micro-monolithic membrane

The oxygen permeation test was conducted using an argon sweep gas of 100 ml min^{-1} and Fig. 5 displays the temperature dependence of oxygen permeation flux between 750 and 950°C , as compared to other sub-optimal micro-monolithic counterparts reported previously [13]. It can be seen from the figure that the bio-inspired design from careful manipulation of fabrication parameters shows a significantly improved

Table 1

Dimensions of different micro-monolithic samples and estimations of separation layer thickness and effective volumetric surface area.

Ref.	Types of Design	Outer diameter (mm)	Average channel diameter (mm)	Effective separation thickness (mm)	Volumetric surface area ($\text{m}^2 \text{ m}^{-3}$)	Active ratio (%)	Effective volumetric surface area ($\text{m}^2 \text{ m}^{-3}$)
[13]	3-channel	2.12	0.73	0.19	1711	49.5	847
	4-channel	2.41	0.81	0.24	1505	65.3	983
	7-channel	2.60	0.77	0.14	1395	69.3	967
[16]	4-channel	1.90	0.58	0.16	1909	55.3	1056
[17]	7-channel	2.40	0.60	0.26	1511	67.4	1018
This work	6-channel	1.95	N/A	0.05	1814	87.7	1591

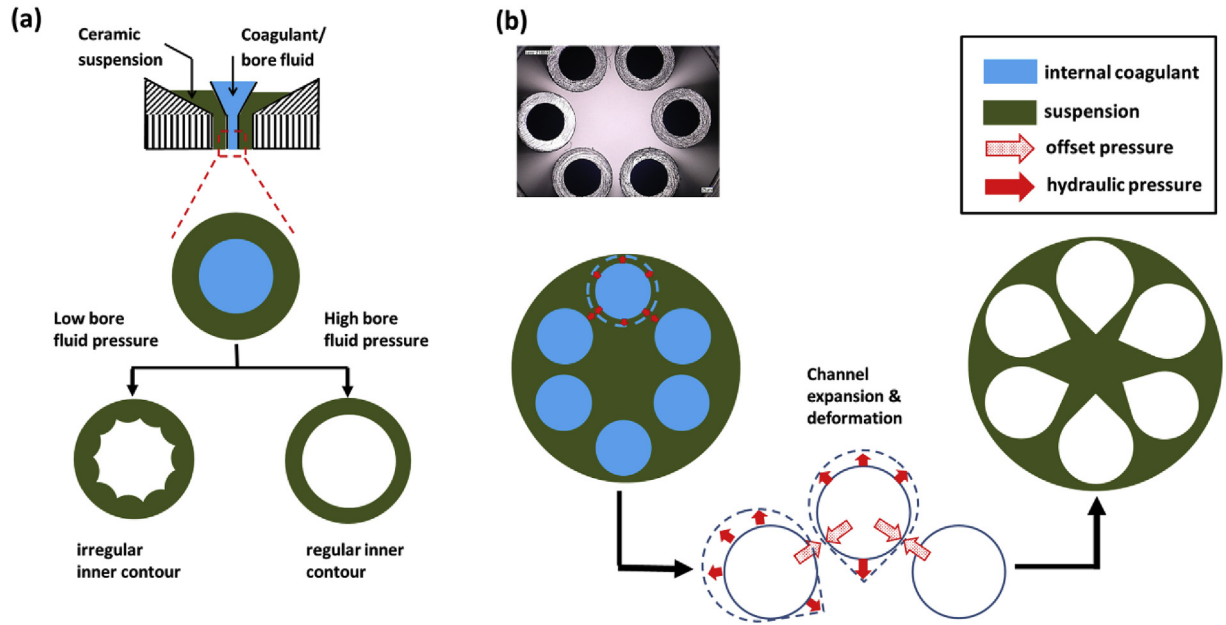


Fig. 3. Schematic diagram of: (a) normal and irregular inner contour in traditional hollow fiber membrane, (b) bio-inspired 6-channel micro-monolithic membrane with geometry control.

oxygen permeation flux, up to $1.87 \text{ ml min}^{-1} \text{ cm}^{-2}$ at 950°C , which is more than 3 times higher compared to other micro-monolithic counterparts. Such improvement is due to not only the reduced effective thickness, but also more efficient utilization of membrane circumference as active separation region.

If the resistance from gas phase mass transfer is considered negligible, there are two major steps for the oxygen transporting process through the LSCF membrane, including the surface exchange in both feed side (oxygen-rich) and permeate side (oxygen-lean), and the bulk diffusion of oxygen ions through the membrane. The oxygen permeation flux could be calculated based on Wagner equation [7,20]:

$$j_{\text{O}_2} = \frac{RT}{(4 \cdot F)^2} \sigma_{\text{amb}} \frac{1}{(L + 2L_c)} \ln \left(\frac{p'_{\text{O}_2}}{p''_{\text{O}_2}} \right) \quad (2)$$

Here, L denotes the membrane thickness, p'_{O_2} and p''_{O_2} represent the oxygen partial pressure at upstream and downstream side, respectively. σ_{amb} is the ambipolar conductivity, which is a material property and calculated based on the material's ionic conductivity (σ_i) and electronic conductivity (σ_e), as shown in the equation below:

$$\sigma_{\text{amb}} = \frac{\sigma_i \cdot \sigma_e}{\sigma_i + \sigma_e} \quad (3)$$

L_c is the critical thickness, which represents the relative importance of

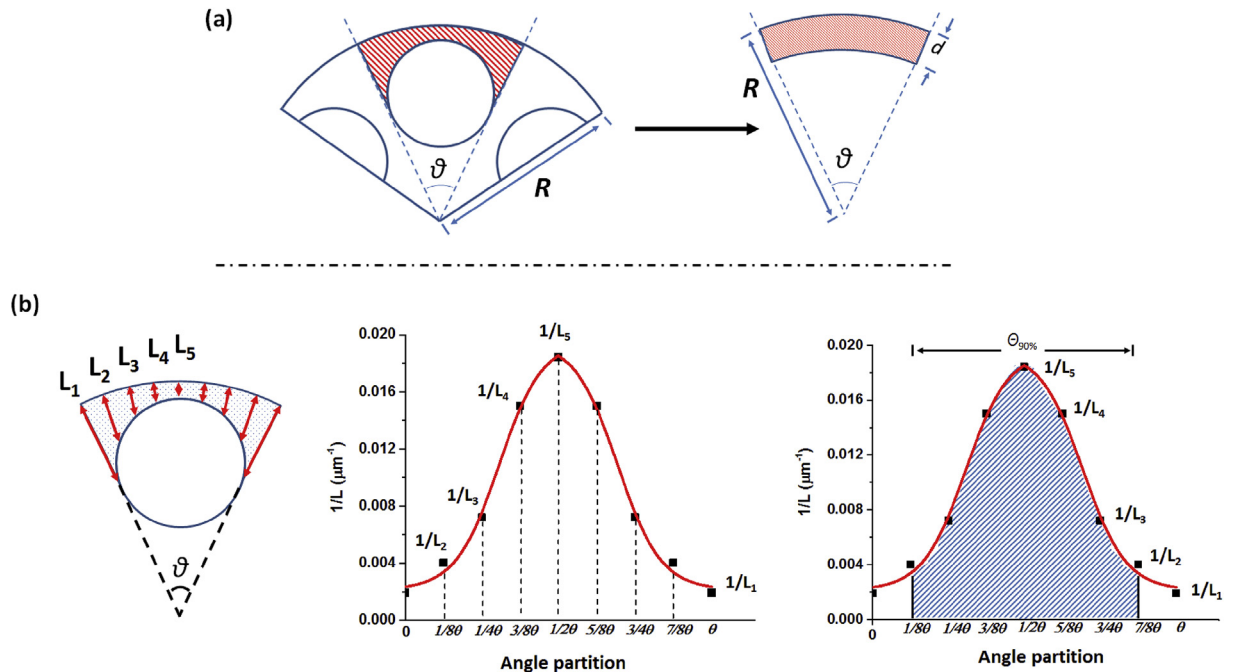


Fig. 4. Schematic diagrams of: (a) estimation of the effective diffusible pathway length of 6-channel micro-monolithic membrane, with the shaded sections of equivalent area; (b) estimation of effective separation region.

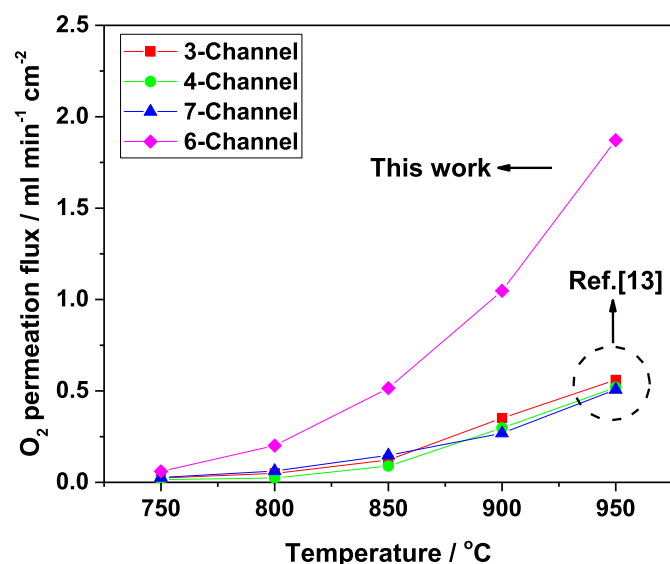


Fig. 5. Oxygen permeation flux of 6-channel micro-monolithic membrane and data of multi-channel counterparts from literature [13].

surface exchange and bulk diffusion and is defined as $L_c = \frac{D}{K}$ [21]. K and D denote the coefficients of surface exchange and bulk diffusion, respectively. As reported before, for LSCF material system, K increases much faster than D when the temperature increases due to their varied activation energy [22], leading to dramatically decreased critical thickness L_c . Thus, bulk diffusion becomes the rate-limiting step and Equation (2) could be simplified as:

$$j_{O_2} = \frac{RT}{(4F)^2} \sigma_{amb} \frac{1}{L} \ln \left(\frac{p'_{O_2}}{p_{O_2}} \right) \quad (4)$$

When the ratio of active circumference was estimated, an assumption was made that the membrane was operated at high enough temperature that the bulk diffusion becomes the rate-limiting step. According to Equation (4), the permeation flux is linear to the reciprocal membrane thickness L^{-1} . Similar to the estimation of effective membrane thickness, the defined active region is illustrated in Fig. 4 (b). The angle of the total shaded area (θ) was measured using Image software prior to the estimation. A simplified profile of flux distribution has been generated by dividing the shaded area into 8 sectors with identical angle partition. The thickness at various spots (L_1 to L_5) have been measured. According to Equation (4), the oxygen permeation flux is reversely proportional to the thickness, so the profile of oxygen flux of the shaded area could be generated based on the reciprocal of thickness ($1/L$) and a subsequent fitting step using the Maxwell-Boltzmann function. The estimation of the effective separation region is based on angle. The angle of the area that contributes to 90% of the oxygen flux (θ_{90}) is defined as active and the calculated results have been shown in Table 1. It can be seen that the ratios of effective area for sub-optimal micro-monolithic designs ranged between 49.5% and 69.3%, which indicates that approximately 30–50% of the surface area remains idle. This is mainly due to the difference in curvature of inner lumen and outer circumference, which leads to rapidly increasing thickness of the separation layer and consequently increased bulk diffusion resistance. While this ratio of active surface for the bio-inspired design has been improved to almost 90%, which shows an improvement of 28.5%–81.8% when compared to other micro-monolithic designs. The estimated active ratios have been used to further calibrate the theoretical surface area per volume, as shown in Table 1. It could be observed from the table that such novel bio-inspired design provides an effective volumetric surface area of $1591 \text{ m}^2 \text{ m}^{-3}$, showing an increment up to 87.8% compared to other micro-monolithic counterparts ranged

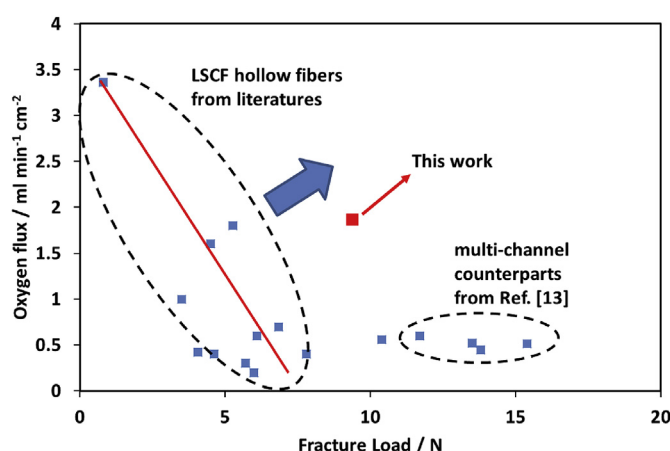


Fig. 6. Comparisons of oxygen permeation flux and mechanical strength with other references [19,23–31]. (Some fracture load not provided in the literature but calculated using relevant data, all fracture load data was normalized into 30 mm span. Most oxygen flux data were collected at 950 °C and with 100 ml min^{-1} of sweep gas flow rate).

between 847 and $1056 \text{ m}^2 \text{ m}^{-3}$, which is another key feature that facilitates oxygen permeation.

3.3. Mechanical robustness of the 6-channel micro-monolithic membrane

The mechanical property was investigated using a 3-point bending method. With a span of 30 mm for the sample holder, the measured fracture load was $(9.1 \pm 0.3) \text{ N}$, which is slightly lower than those micro-monolithic counterparts that range between 10.4 and 15.4 N [13], but still a few folds higher than reported values for conventional micro-tubular counterparts.

For self-support LSCF hollow fiber membranes, there has been a long-existing trade-off relationship between oxygen permeation flux and mechanical robustness. As mentioned earlier, such trade-off is resulted from that the dense separation layer also acts as the major mechanical support. Such trade-off could be observed from Fig. 6, which summarizes the fracture load results and oxygen permeation flux (at 950 °C) from several literatures regarding LSCF hollow fiber membranes. Although the conditions for the permeation test weren't identical, it clearly illustrates the general trendline describing such trade-off effect. The results of the previous micro-monolithic designs [13] have also been highlighted, which indicates an effective approach to enhance the mechanical property while maintaining comparable oxygen permeation flux. Further optimization in architecture reported in this work has been highlighted in red and proven effective as its position is on the preferable direction towards top right corner, which represents the achievement of both decent oxygen separation performance and mechanical reliability.

4. Conclusions

In this study, a new bio-inspired design has been demonstrated for high-performance LSCF oxygen permeation membranes. The geometry of the channels was successfully manipulated via careful control of fabrication parameters, which has been converted from the conventional circular or square shape to the teardrop shape. Such modification in channel geometry not only helped to reduce the effective oxygen diffusive pathway length down to approximately $50 \mu\text{m}$, but also significantly enhanced the ratio of active circumference from 50% to almost 90%, resulting in high oxygen permeation performances up to $1.87 \text{ ml min}^{-1} \text{ cm}^{-2}$ at 950 °C and superior effective volumetric surface area of $1591 \text{ m}^2 \text{ m}^{-3}$. In addition, excellent mechanical robustness was obtained, which is several folds higher than conventional hollow fiber

membranes. Such bio-inspired design has shown to be a promising strategy to tackle the long-existing trade-off and achieve both decent oxygen permeation performance and mechanical reliability via a simple approach.

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Appendix A. Supplementary data

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References

- [1] J. Sunarso, S. Baumann, J.M. Serra, W.A. Meulenberg, S. Liu, Y.S. Lin, J.C. Diniz da Costa, Mixed ionic–electronic conducting (MIEC) ceramic-based membranes for oxygen separation, *J. Membr. Sci.* 320 (2008) 13–41.
- [2] R.W. Baker, Future directions of membrane gas separation technology, *Ind. Eng. Chem. Res.* 41 (2002) 1393–1411.
- [3] Peter Vang Hendriksen, Peter Halvor Larsen, Mogens Mogensen, F.W. Poulsen, K. Wiik, Prospects and problems of dense oxygen permeable membranes, *Catal. Today* 56 (2000) 283–295.
- [4] T. Burdyny, H. Struchtrup, Hybrid membrane/cryogenic separation of oxygen from air for use in the oxy-fuel process, *Energy* 35 (2010) 1884–1897.
- [5] R.J. Allam, Improved oxygen production technologies, *Energy Proced.* 1 (2009) 461–470.
- [6] J. Sunarso, S.S. Hashim, N. Zhu, W. Zhou, Perovskite oxides applications in high temperature oxygen separation, solid oxide fuel cell and membrane reactor: a review, *Prog. Energy Combust. Sci.* 61 (2017) 57–77.
- [7] Y. Wei, W. Yang, J. Caro, H. Wang, Dense ceramic oxygen permeable membranes and catalytic membrane reactors, *Chem. Eng. J.* 220 (2013) 185–203.
- [8] A. Chronos, R.V. Vovk, I.L. Goulatis, L.I. Goulatis, Oxygen transport in perovskite and related oxides: a brief review, *J. Alloys Compd.* 494 (2010) 190–195.
- [9] S.M. Hashim, A.R. Mohamed, S. Bhatia, Current status of ceramic-based membranes for oxygen separation from air, *Adv. Colloid Interface Sci.* 160 (2010) 88–100.
- [10] M.F. Carolan, V.E. Stein, P. Armstrong, Development of planar ceramic membranes for tonnage oxygen production in advanced energy applications, *Jülicher Werkstoffkolloquium – Gas Separation Membranes for Zero-Emission Fossil Power Plants*, Jülich, 2009.
- [11] Paul N. Dyer, Robin E. Richards, Steven L. Russek, D.M. Taylor, Ion transport membrane technology for oxygen separation and syngas production, *Solid State Ionics* 134 (2000) 21–33.
- [12] Jaap F. Vente, Wim. G. Haije, Ruud IJpelaar, F.T. Rusing, On the full-scale module design of an air separation unit using mixed ionic electronic conducting membranes, *J. Membr. Sci.* 278 (2006) 66–71.
- [13] Y. Chi, T. Li, B. Wang, Z. Wu, K. Li, Morphology, performance and stability of multi-bore capillary $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ oxygen transport membranes, *J. Membr. Sci.* 529 (2017) 224–233.
- [14] M. Lee, B. Wang, Z. Wu, K. Li, Formation of micro-channels in ceramic membranes – spatial structure, simulation, and potential use in water treatment, *J. Membr. Sci.* 483 (2015) 1–14.
- [15] Y. Santoso, T. Chung, K. Wang, M. Weber, The investigation of irregular inner skin morphology of hollow fiber membranes at high-speed spinning and the solutions to overcome it, *J. Membr. Sci.* 282 (2006) 383–392.
- [16] J. Zhu, G. Zhang, G. Liu, Z. Liu, W. Jin, N. Xu, Perovskite hollow fibers with precisely controlled cation stoichiometry via one-step thermal processing, *Adv. Mater.* 29 (2017).
- [17] J. Zhu, T. Wang, Z. Song, Z. Liu, G. Zhang, W. Jin, Enhancing oxygen permeation via multiple types of oxygen transport paths in hepta-bore perovskite hollow fibers, *AIChE J.* 63 (2017) 4273–4277.
- [18] X. Tan, Y. Liu, K. Li, Preparation of LSCF ceramic hollow-fiber membranes for oxygen production by a phase-inversion sintering technique, *Ind. Eng. Chem. Res.* 44 (2005) 61–66.
- [19] X. Tan, Z. Wang, K. Li, Effects of sintering on the properties of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ perovskite hollow fiber membranes, *Ind. Eng. Chem. Res.* 49 (2010) 2895–2901.
- [20] C. Wagner, Equations for transport in solid oxides and sulfides of transition metals, *Prog. Solid State Chem.* 10 (1975) 3–16.
- [21] H.J.M. Bouwmeester, H. Kruidhof, A.J. Burggraaf, Importance of the surface exchange kinetics as rate limiting step in oxygen permeation through mixed-conducting oxides, *Solid State Ionics* 72 (1994) 185–194.
- [22] Sherman J. Xu, W.J. Thomson, Oxygen permeation rates through ion-conducting perovskite membranes, *Chem. Eng. Sci.* 54 (1999) 3839–3850.
- [23] X. Tan, Y. Liu, K. Li, Preparation of LSCF ceramic hollow-fiber membranes for oxygen production by a phase-inversion sintering technique, *Ind. Eng. Chem. Res.* 44 (2005) 61–66.
- [24] Z. Wang, N. Yang, B. Meng, X. Tan, K. Li, Preparation and oxygen permeation properties of highly asymmetric $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ perovskite hollow-fiber membranes, *Ind. Eng. Chem. Res.* 48 (2009) 510–516.
- [25] C. Yacou, J. Sunarso, C.X.C. Lin, S. Smart, S. Liu, J.C. Diniz da Costa, Palladium surface modified $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ hollow fibres for oxygen separation, *J. Membr. Sci.* 380 (2011) 223–231.
- [26] H. Liu, X. Tan, Z. Pang, J.C. Diniz da Costa, G.Q. Lu, S. Liu, Novel dual structured mixed conducting ceramic hollow fibre membranes, *Separ. Purif. Technol.* 63 (2008) 243–247.
- [27] B. Zydorczak, K. Li, X. Tan, Mixed conducting membranes - macrostructure related oxygen permeation flux, *AIChE J.* 56 (2010) 3084–3090.
- [28] A. Thursfield, I.S. Metcalfe, Methane oxidation in a mixed ionic–electronic conducting ceramic hollow fibre reactor module, *J. Solid State Electrochem.* 10 (2006) 604–616.
- [29] H. Pan, L. Li, X. Deng, B. Meng, X. Tan, K. Li, Improvement of oxygen permeation in perovskite hollow fibre membranes by the enhanced surface exchange kinetics, *J. Membr. Sci.* 428 (2013) 198–204.
- [30] B. Zydorczak, Z. Wu, K. Li, Fabrication of ultrathin $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ hollow fibre membranes for oxygen permeation, *Chem. Eng. Sci.* 64 (2009) 4383–4388.
- [31] X. Tan, Z. Wang, H. Liu, S. Liu, Enhancement of oxygen permeation through $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ hollow fibre membranes by surface modifications, *J. Membr. Sci.* 324 (2008) 128–135.