A dual-phase bilayer oxygen permeable membrane with hierarchically porous structure fabricated by freeze-drying tape-casting method

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Abstract

A bilayer oxygen permeable membrane consisting of hierarchically porous $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}-(\text{La}_{0.8}\text{Sr}_{0.2})_{0.95}\text{MnO}_{3-\delta}$ (GDC-LSM) support and dense GDC-LSM film has been fabricated by a combined freeze-drying tape-casting and screen-printing method followed by co-sintering. Two dimensional (2D) SEM-BSE and reconstructed three dimensional (3D) XCT images indicated that the porous GDC-LSM support (870- μm -thick) contains graded straight pores with low tortuosity factor, promoting fast gas diffusion in the support, while the dense GDC-LSM film with a thickness of 30 μm provides a short path for the bulk transport of oxygen ions and electrons. However, the oxygen flux of the asymmetric GDC-LSM membrane is only 81% higher than that of the 900- μm -thick dense GDC-LSM symmetric membrane, indicating that the oxygen transport becomes limited by the surface oxygen exchange process for the GDC-LSM asymmetric membrane with a 30- μm -thick dense GDC-LSM film. When the permeate side surface is modified with $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}-\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (SDC-LSCF), the oxygen permeation flux of the GDC-LSM asymmetric membrane is significantly enhanced from 0.105 to 0.780 $\text{mL cm}^{-2} \text{ min}^{-1}$, while the activation energy is substantially decreased from 219.6 ± 8.7

to $138.1 \pm 3.3 \text{ kJ mol}^{-1}$, due to enhanced surface oxygen exchange kinetics. Furthermore, the coated asymmetric membrane shows 1100% higher oxygen flux than the coated symmetric membrane. When the sweep gas is switched from helium to CO_2 , although the adsorption of CO_2 on the permeate side surface leads to a slight decrease in oxygen permeation flux, a high oxygen permeation flux of $0.659 \text{ mL cm}^{-2} \text{ min}^{-1}$ can still be achieved, demonstrating that the coated GDC-LSM asymmetric membrane is promising for oxy-fuel combustion application.

Keywords: Oxygen Permeable Membrane, Hierarchical Oriented Pores, Freeze-Drying Tape-Casting, Surface Modification, Oxy-fuel Combustion

1. Introduction

One third of total CO₂ emissions in the US comes from the combustion of fossil fuels in power plants and needs to be harnessed by carbon capture and sequestration to reduce its impact in the environment[1]. Both the pre-combustion (O₂ separation from air) and post-combustion (CO₂ separation from exhaust gas) methods require capital- and energy-intensive gas separation units. In contrast, mixed ionic–electronic conducting (MIEC) oxygen permeable membrane (OPM) technology holds the promise to reduce oxygen production costs by ~30%[2], and thus offers a potentially cost-effective method for pure oxygen production process. An important method to utilize OPM in the combustion process of fossil fuels is the oxy-fuel process, in which the feed side of the membrane is exposed to pressurized air and the permeate side is swept by recycled CO₂. This process produces oxygen diluted with recycled CO₂ as an oxidant for the combustion of fossil fuels, resulting in an exhaust gas mainly consisting of CO₂ and H₂O, which is easy for CO₂ separation and capture without the need for the expensive post-combustion process[3-5]. Therefore, in the past two decades, the OPM-based oxy-fuel combustion technology has received increasing attention as a future energy conversion technology for CO₂ capture, storage and re-utilization[6-17]. Because the membranes need to be used in a CO₂-rich atmosphere, it's critical for the membranes to possess high chemical stability in CO₂-rich atmosphere.

Current ceramic OPMs can be categorized into single-phase and dual-phase membranes. Most of the single-phase OPMs are cobalt-containing perovskite oxides, which possess very high oxygen permeability but insufficient long-term thermo-chemical stability and mechanical strength[8-12, 18-20]. In contrast, the dual-phase membranes consisting of an oxygen ionic conductor and an electronic conductor, exhibit significantly lower oxygen permeability, but improved thermo-chemical stability which is essential for the application in oxy-fuel combustion process[13-17, 21-23]. Although the chemical stability is intrinsic and difficult to change, the flux is determined by many external factors such as membrane

thickness, microstructure, and surface modification. Therefore, one viable strategy to enhance oxygen flux is to use stable composite membranes with relatively low permeability and then improve the performance through optimization of membrane thickness and/or microstructure. Oxygen ionic conductor of doped ceria exhibits acceptable oxygen ionic conductivity and good chemical stability at the elevated temperatures[24], while electronic conductor of strontium-substituted lanthanum manganite possesses high electronic conductivity and reasonable catalytic activity towards oxygen reduction ($O_2 \rightarrow 2O^{2-}$). Besides, these two materials have similar sintering temperatures, excellent thermo-chemical compatibility, and have been proven to be potential candidate for oxygen production and oxy-fuel combustion applications[15, 25-27]. Therefore, in this study, $Ce_{0.9}Gd_{0.1}O_{1.95}$ (GDC) and $(La_{0.8}Sr_{0.2})_{0.95}MnO_{3-\delta}$ (LSM) are chosen as the candidate materials to achieve highly stable oxygen permeable membranes for oxy-fuel combustion applications.

Oxygen permeation process involves surface oxygen exchange and bulk transport of oxygen ions and electrons in the membrane[28]. When the membrane is thick, the overall process is predominantly limited by the bulk diffusion and the oxygen permeation flux is inversely proportional to the thickness of the membrane according to the Wagner equation. In this case, reducing the thickness of the membrane will result in increased oxygen permeation flux, but this will also reduce its mechanical strength. To achieve both high flux and adequate mechanical strength, it is desirable to fabricate supported membranes with bilayer structure[12, 29-36]: a thin dense layer supported on a thick porous layer to facilitate the oxygen permeation and provide mechanical support, respectively. This strategy has achieved certain success in traditional bilayer membranes with sponge-like porous supports, showing flux improvement of three to four times[37, 38]. This level of improvement is still much lower than the expected value (~ 30 based on the Wagner equation for the thickness change from $900\text{ }\mu\text{m}$ to $30\text{ }\mu\text{m}$) because high tortuosity in the sponge-like porous support is not ideal for gas delivery. Although porosity can be increased by introducing pore formers as sacrificial phase[34], the tortuous microstructures of the supports still limit gas transport flux. In order to further improve oxygen permeation

fluxes to meet industrial application targets, a novel and cost-effective method to fabricate the membrane support with lower tortuosity factor is urgently needed. Recently, a freeze-drying tape-casting method, which combines tape-casting and freeze-drying process, has been developed as a unique technique to form membranes with oriented channels/pores, which have been applied in the fabrication of catalyst support structures, solid oxide fuel cells (SOFCs), and gas separation membranes[12, 29, 39-43]. Hierarchically porous support with low tortuosity factor facilitates gas delivery in the support, and is expected to significantly decrease the gas transport resistance in the bilayer membranes and thus dramatically enhance the membrane performance[12, 29]. It should be noted that surface oxygen exchange process becomes the rate-limiting step when the thickness of the dense layer is decreased to a certain value, and no significant increase in oxygen permeation flux will be achieved by further reducing the membrane thickness. On the other hand, surface oxygen exchange rate can be remarkably enhanced by introducing a catalyst layer onto the membrane surfaces with higher surface exchange coefficient (k_{chem})[21, 36 44, 45], such as $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ (SDC), $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ (LSC), and $\text{Ba}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.5}\text{Fe}_{0.5}\text{O}_{3-\delta}$ (BSCF).

In this study, freeze-drying tape-casting, screen-printing, and co-sintering are combined to fabricate supported GDC-LSM dual-phase asymmetric membranes with a thick hierarchically porous substrate and a thin dense functional layer. In comparison, symmetric GDC-LSM membranes with the same total thickness are also fabricated using a traditional dry-pressing method. The 2 dimensional (2D) and 3D microstructure of the membranes was examined using the scanning electron microscope (SEM) and X-ray computed tomography (XCT). The effects of microstructure and surface modification on the oxygen flux were systematically investigated. The asymmetric GDC-LSM membranes show dramatically enhanced oxygen flux compared with symmetric counterpart, offering a simple and economic solution for the development of high-performance oxygen permeable membranes for oxy-fuel combustion application.

2. Experimental

2.1 Fabrication of asymmetric GDC-LSM membranes

GDC and LSM powders (FuelCellMaterials Inc., USA) were mixed in a volume ratio of 6:4 by planetary ball mills in ethanol for 2 h and then dried at 80 °C overnight. Water-based GDC-LSM slurry was prepared with an ammonium polyacrylate dispersant (Darvan C-N, R.T. Vanderbilt Co., Inc., Norwalk, CT), a thickener (Vanzan, R.T. Vanderbilt Co., Inc., Norwalk, CT), and an acrylic latex emulsion binder system (Duramax HA-12, Rohm & Haas, Philadelphia, PA)[43]. The slurry was freeze-drying-tape-casted in an apparatus similar to that reported in Sofie's publication[40]. After being frozen for about 30 minutes, the GDC-LSM substrate was punched into pellets with a diameter of 20 mm. The pellets were frozen in a vacuum freeze dryer at -30 °C under 18 mTorr vacuum for one day. The pellets were first heated at 600 °C for 2 h to remove the polymer additives, and then heated at 1100 °C for 2 h in air to achieve sufficient mechanical strength for subsequent handling. GDC-LSM film was coated on the pre-sintered GDC-LSM pellets by a screen-printing method and then co-sintered at 1500 °C for 10 h with a heating and cooling rate of 2 °Cmin⁻¹. For comparison, GDC-LSM symmetric membranes were also prepared using the conventional dry-pressing method under a pressure of 250 MPa and sintered in the same condition.

To study the effect of surface modification on the oxygen permeation flux, Ce_{0.8}Sm_{0.2}O_{1.9} (SDC) and La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} (LSCF) powders synthesized by a Pechini method at the weight ratio of 1:1 were grounded with α -terpineol to form a surface-modifier ink, which was then printed onto the dense GDC-LSM film (permeate side) by a screen-printing method, followed by firing at 1050 °C for 2 h. The overall sample preparation process is schematically shown in Fig. 1. For simplification, the membranes prepared by the freeze-drying tape-casting method **without and with** SDC-LSCF surface modification layer are denoted as OPM-1 and OPM-2, respectively, while the membranes fabricated by the dry-pressing method **without and with** SDC-LSCF surface modification layer are named as OPM-3 and

OPM-4, respectively.

Fig. 1. Schematic diagram of the preparation processes of the GDC-LSM oxygen permeable membranes.

2.2 Characterization

The 2D microstructure of the GDC-LSM membranes was characterized using a SEM (Zeiss Ultra Plus FESEM, Germany) equipped with secondary electron (SE) and back-scattered electron (BSE) detectors, while the 3D microstructure of the GDC-LSM support was characterized using X-ray microscopy (MicroXCT 400, Xradia Inc., USA) and analyzed by an in-house Matlab code.

The oxygen permeation flux was studied in a home-built high-temperature oxygen permeation setup, as schematically shown in Fig. 2. A permeation cell was constructed by sealing the membranes to two Al_2O_3 tubes using two glass rings (Schott 8252, Germany) at 1000 °C for 1 h. The side wall of the membrane was covered with glass paste to avoid radial contribution to the oxygen permeation flux.

The effective area of the membranes for oxygen permeation was 0.78 cm^2 , while the thickness of all the four membranes were $900 \text{ }\mu\text{m}$. Oxygen permeation tests were performed at elevated temperatures ($875\text{-}950 \text{ }^\circ\text{C}$) by feeding ambient air (100 mLmin^{-1}) to the oxygen-rich chamber and by sweeping helium (He) or carbon dioxide (CO_2) on the permeate side. All the flow rates of inlet gases were controlled by digital mass flow controllers (Alicat Scientific Inc., USA). A gas chromatograph (GC, 7890A, Agilent Technologies Inc., USA) with a 13X molecular sieve column ($80\text{-}100 \text{ mesh } 1.5\text{m}\times 1/8''$, Agilent Technologies Inc., Netherlands) was employed to analyze the composition of the gas mixture. The oxygen permeation flux was calculated from the oxygen concentration and flow rate of the effluent, and corrected for the oxygen leakage by measuring the nitrogen concentration in the effluent.

Fig. 2. The schematic diagram of oxygen permeation test device.

3. Results and Discussion

3.1 Characterization of the dual-phase membranes

Fig. 3A-B show the cross-sectional SEM images of the sintered GDC-LSM support. Vertically oriented pores/channels run through the entire support layer from the bottom surface to the top surface. During the freeze-drying tape-casting process, the top surface shown in Fig. 3A was exposed to ambient air, while the bottom surface shown in Fig. 3A was placed on the Mylar polymer film in the casting bed with a low temperature of $-70\text{ }^{\circ}\text{C}$. Because of the low temperature, micron-sized ice crystals began to form from the bottom surface close to the Mylar film, and grew larger and larger toward the top surface, causing the ceramic phases to diverge. Therefore, both the bottom and top surfaces (Fig. 3C-D, respectively) show an acicular morphology of ice crystals/pores, a typical feature for freeze-drying tape-casting[12, 29, 39-43], and the pore/channel size (width) increases from the bottom surface with small pores to the top surface with macro-pores. After subsequent removal of ice crystals by sublimation during the freeze-drying process, a green support with continuously graded pores/channels was obtained. Many of these channels span the entire thickness of the tape precursor, resulting in a less tortuous microstructure.

Fig. 3. Morphology features of GDC-LSM support prepared using the freeze-drying tape-casting method. A-B) cross-sectional view, C) bottom view, and D) top view of

Fig. 3A.

Fig. 4. Reconstructed 3D microstructural images of porous GDC-LSM substrates reconstructed from A) the bottom surface with small pores and B) top surface with macro-pores, respectively. The blue and green regions within the 3D images represent solid and pore phases, respectively. C) Distribution of the local porosity along z -axis from the bottom surface to the top surface.

To further study the GDC-LSM support microstructure quantitatively, a 3D microstructure has been reconstructed by directly stacking the raw X-ray gray images

along the x -axis in sequence. The interval step between images is $4.53\mu\text{m}$, the same as the resolution of the images. Fig. 4A and 4B show the results of the GDC-LSM substrate reconstructed from the bottom surface with small pores and top surface with macro-pores, respectively. As shown in Fig. 4A-B, the solid phase (GDC-LSM) appears blue, whilst pores (gas transport channels) show up green, and the pore size is calculated to be from ~ 5 to $200\mu\text{m}$ with an average pore size of around $15.4\mu\text{m}$. The tortuosity factor is lower than 2.2, which is much smaller than that for those sponge-like porous substrates (with a tortuosity factor value of 4–10)[46], indicating that the freeze-drying tape-casting method can be used to prepare asymmetric membranes with the hierarchically oriented pores to achieve small tortuous gradient along the z -axis (thickness direction) shown in Fig. 4C and provide sufficient catalytic reaction sites (GDC, LSM and gas triple phase boundaries) for surface oxygen exchange near the dense functional layer, which is beneficial for decreasing the gas transport resistance in the support, and thus increasing the oxygen permeation flux of the supported membranes. Therefore, in this study, the GDC-LSM support prepared using the freeze-drying tape-casting method is adopted to fabricate GDC-LSM (support)/GDC-LSM (functional layer) bilayer membranes.

Fig. 5 shows the microstructure of the asymmetric and symmetric GDC-LSM membranes (OPM-1 and OPM-3, respectively). Fig. 5A-a show the cross-section of the sintered membranes along the thickness direction. The thickness of both membranes is about $900\mu\text{m}$. OPM-1 membrane has an asymmetric bilayer structure (Fig. 5A). The thickness of the porous top layer is $\sim 870\mu\text{m}$, while the dense bottom layer is $\sim 30\mu\text{m}$. The top porous support of OPM-1 contains large oriented pores which penetrate through the entire support with a porosity of 41.6% calculated from the XCT raw images (Fig. 4C) and the reconstructed 3D images in Fig. 4A-B, and the bottom layer (GDC-LSM film) is almost free of pores (Fig. 5B), demonstrating that the combined freeze-drying tape-casting and screen-printing method is an efficient way to prepare this bilayer asymmetric membrane with thin dense film. In contrast, the OPM-3 membrane possesses a dense symmetric structure (Fig. 5a) with a relative density higher than 95% (measured by the Archimedes method in water), which is

also confirmed by SEM-BSE images of the membrane surface (Fig. 5b-c). Therefore, OPM-3 membrane is dense enough for oxygen permeation measurement. In the BSE images of the dense functional layer of the sintered membranes as shown in Fig. 5C (OPM-1) and Fig. 5c (OPM-3), GDC and LSM phases appear bright and gray, respectively, while pores are dark. The grain sizes of GDC and LSM phases are found to vary from 1-4 μm and 1-3 μm , respectively.

Fig. 5. SEM-BSE images of the GDC-LSM membranes sintered at 1500 $^{\circ}\text{C}$ for 10 h. A-C) OPM-1, a-c) OPM-3, A-a) cross-sectional SEM images, B-b) SEM images and C-c) BSE images of surface of dense layer.

In this study, to further enhance the oxygen permeation flux, a porous SDC-LSCF layer, serving as surface oxygen exchange catalyst, was printed onto the permeate side surface of OPM-1 and OPM-3 via the screen-printing method to obtain modified membranes (denoted as OPM-2 and OPM-4, respectively). Fig. 6 shows the typical cross-sectional SEM-BSE images of the modified membranes, and ~20- μm -thick SDC-LSCF layer was successfully coated onto the sintered GDC-LSM membranes.

Fig. 6. Cross-sectional SEM-BSE images of the modified GDC-LSM membranes. A-a) SEM, B-b) BSE, A-B) OPM-2, a-b) OPM-4.

3.2 Oxygen permeation properties of the dual-phase membranes

Fig. 7A shows the Arrhenius plots of the oxygen permeation flux of the four GDC-LSM membranes between 875 and 950 °C under air/He gradient with air and He flow rate of 100 mL/min and 30 mL/min, respectively. In all cases, the oxygen permeation flux increases with increasing operating temperature as expected due to the increase of oxygen ionic conductivity as well as surface oxygen exchange activity with increasing operating temperature[28]. The flux follows the order of OPM-2>>OPM-1>OPM-4~OPM-3. The oxygen flux and activation energies of coated/uncoated symmetric membranes are very close, indicating that the oxygen permeation process of the symmetric membranes is not limited by the surface exchange process but by the bulk diffusion of oxygen ions. For the asymmetric membranes, the application of surface catalyst layer leads to 642% higher oxygen flux at 950 °C (0.780 and $0.105 \text{ cm}^3 \text{ cm}^{-2} \text{ min}^{-1}$, respectively) and 37.1% lower activation energy for oxygen permeation (from 219.6 ± 8.7 to $138.1 \pm 3.3 \text{ kJ/mol}$). These significant changes in oxygen flux demonstrate that the rate-limiting step may be different with and without surface modification. Considering that the surface catalyst mainly accelerates the surface oxygen exchange process, apparently the rate-limiting step in uncoated asymmetric membranes is the surface oxygen exchange process.

Further evidence can be found in the comparison between uncoated membranes. Asymmetric OPM-1 only shows 81% higher flux than that of symmetric OPM-3 at 950 °C, which is far lower than the theoretical value (3000%) predicted by the Wagner equation (the flux is inversely proportional to the thickness of the dense layer). This insignificant gain in flux by reducing the thickness also suggests that the overall oxygen permeation process in the uncoated asymmetric membrane is limited by the slow surface oxygen exchange process. Therefore, the use of surface oxygen exchange catalyst dramatically enhanced the oxygen permeation flux of the asymmetric membrane. The flux of OPM-2 is 1100% higher than that of OPM-3 and OPM-4. This level of improvement is much larger than those (~3-400 %) achieved in bilayer membrane with sponge-like support. It should also be pointed out that SDC-LSCF coated onto the ~30-μm-thick GDC-LSM layer will result in remarkable increase in the length of three-phase-boundary and the percolation probability of each phase in GDC-LSM dual-phase asymmetric membrane[47], and thus considerable enhancement in ambipolar conductivity ($\sigma_{amb} = \frac{\sigma_{ion} * \sigma_{e-}}{\sigma_{ion} + \sigma_{e-}}$) and oxygen permeation flux. Therefore, to further improve the oxygen permeation flux of GDC-LSM dual-phase asymmetric membranes, future work should be focused on surface modification rather than further reduction of the membrane thickness.

To further explore the performance of the membranes for use in oxygen permeation, the dependence of oxygen permeation flux on helium flow rate is also investigated. Fig. 7B shows that the oxygen permeation flux increases with increasing helium flow rate. When the flow rate of helium is increased from 10 to 50 mL min⁻¹, the oxygen permeation flux of the membranes OPM-1, OPM-2, OPM-3, and OPM-4 increased from 0.095, 0.557, 0.053, and 0.057 to 0.110, 0.875, 0.063, and 0.068 cm³ cm⁻² min⁻¹, respectively, which can be attributed to the reduced oxygen partial pressure at the permeate side of the membranes and thus the increased driving force for oxygen permeation. However, a much higher flux increase rate of 57% is observed for the modified asymmetric membrane than that (10~20%) of other membranes, suggesting that the surrounding oxygen partial pressure has a great influence on the surface exchange process of

the membrane, especially for the asymmetric membrane surface-modified by the oxygen exchange catalyst.

Fig. 7. A) Arrhenius plots of the oxygen flux through GDC-LSM membranes and B) He sweep flux dependence of oxygen permeation flux at 950 $^{\circ}\text{C}$. (●) OPM-1, (□) OPM-2, (★) OPM-3, and (△) OPM-4.

Chemical stability in CO_2 -rich atmosphere is critical for an oxygen permeable membrane to be used for oxy-fuel combustion process. Therefore, the oxygen permeation properties of the GDC-LSM asymmetric membranes under air/ CO_2 gradient are also evaluated to examine their applicability in the oxy-fuel combustion process. Fig 8A shows the Arrhenius plots of their oxygen permeation flux of the GDC-LSM asymmetric membranes under air/He or air/ CO_2 gradient with a sweep gas flow rate of 30 mL min^{-1} . As expected, the oxygen permeation flux increases with increasing temperature. For the uncoated GDC-LSM asymmetric membrane (OPM-1), oxygen permeation flux under air/helium and air/ CO_2 gradient is similar ($\sim 0.104 \text{ cm}^3$

$\text{cm}^{-2} \text{ min}^{-1}$ at 950°C), suggesting that GDC-LSM asymmetric dual-phase membrane has adequate stability for application in oxy-fuel combustion process. However, the oxygen permeation flux of coated GDC-LSM asymmetric membrane (OPM-2) decreases from 0.780 to $0.659 \text{ cm}^3 \text{ cm}^{-2} \text{ min}^{-1}$ at 950°C when helium is switched to pure CO_2 (Fig. 8A). Similar level of oxygen flux decrease has also been observed by other groups[12, 15, 19]. The slight decrease in oxygen permeation flux may be attributed to the competitive CO_2 adsorption with O_2 desorption for reaction sites on the membrane surface since some active O_2 desorption sites have been covered by adsorbed CO_2 , leading to a decrease in the surface oxygen exchange rate. The apparent activation energy under air/ CO_2 gradient decreases from 219.7 ± 7.9 (OPM-1) to $147.7 \pm 1.9 \text{ kJ mol}^{-1}$ (OPM-2) after surface modification, but its value is still larger than that ($138.1 \pm 3.3 \text{ kJ mol}^{-1}$) under air/He gradient, indicating that the surface exchange process can be significantly enhanced by surface modification but CO_2 adversely affects the surface oxygen exchange process.

Fig. 8. A) Temperature dependence and B) sweep flux dependence of the average flux through asymmetric GDC-LSM membrane. (▼△) OPM-1, (●□) OPM-2, solid and empty symbols denote the oxygen permeation flux under air/CO₂ and air/He gradient, respectively.

Fig. 8B shows the effect of the sweep gas flow rate on the oxygen permeation flux at 950 °C. Due to the reduced oxygen partial pressure at the permeate side and thus increased driving force for oxygen permeation, the oxygen permeation flux increases with increasing flow rate of CO₂, which is consistent with the results under air/He gradient in Fig. 7B. For the membranes OPM-1 and OPM-2, the oxygen permeation flux increases from 0.093 and 0.524 to 0.107 and 0.759 cm³ cm⁻² min⁻¹, respectively, when the flow rate of CO₂ increases from 10 to 50 mL min⁻¹.

The GDC-LSM dual-phase asymmetric membrane prepared by the freeze-drying tape-casting method consists of a thick hierarchically porous GDC-LSM support and a thin dense GDC-LSM functional layer, which is beneficial for bulk mass transport of oxygen ions and electrons. Moreover, the surface-modified asymmetric membrane possesses a porous support structure and surface modification layer, thus imposing less resistance to surface oxygen exchange. The combination of these two factors provides an explanation to the much larger flux of SDC-LSCF coated asymmetric OPM-2 than that of conventional symmetric membrane OPM-3 and OPM-4. The oxygen permeation flux is comparable to that of a 1.0-mm-thick asymmetric cobalt-containing GDC-LSCF membrane[48] and the 0.2-mm-thick SDC-LSM hollow fiber[15] prepared using the phase-inversion method, indicating that the combined freeze-drying-tape-casting and screen-printing method is an effective way to fabricate high-performance oxygen permeable membranes. It should be noted that the oxygen permeation flux through the asymmetric GDC-LSM dual-phase membrane is almost an order of magnitude lower than that of asymmetric LSCF membrane prepared by the same method[12, 60] (as listed in Table 1), but it is expected when taking into account the difference in the oxygen ion and electron transport properties between these two membranes. In the future, cobalt-containing or iron-containing dual-phase oxygen permeable membranes with higher oxygen permeation flux and

acceptable thermo-chemical stability, as listed in Table 1, will be made into asymmetric geometry to achieve higher flux to meet the requirement of pure oxygen production and oxy-fuel combustion application.

Table 1 Oxygen permeation flux (J_{O_2} , $\text{cm}^3 \text{ cm}^{-2} \text{ min}^{-1}$) of some reported oxygen-permeable membranes with He/ CO_2 as the sweep gas.

Membrane Composition	Type	Method (^a)	Thickness (mm)	T (°C)	J_{O_2}		Ref.
					air/He	air/ CO_2	
$\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{2-\delta}\text{-NiFe}_2\text{O}_4$	Disk	1	0.5	950	0.18	0.16	[13]
$\text{Ce}_{0.9}\text{Pr}_{0.1}\text{O}_{2-\delta}\text{-Pr}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$	Disk	1	0.6	950	0.27	0.18	[49]
$\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}\text{-Gd}_{0.8}\text{Sr}_{0.2}\text{FeO}_3$	Disk	1	0.5	950	0.80		[50]
SDC- $\text{La}_{0.9}\text{Sr}_{0.1}\text{FeO}_{3-\delta}$	Disk	1	1.1	950	0.214	0.214	[14]
$\text{Nd}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}\text{-Ce}_{0.9}\text{Nd}_{0.1}\text{O}_{2-\delta}$	Disk	1	0.6	950	0.26	0.21	[17]
SDC- $\text{PrBaCo}_2\text{O}_{3-\delta}$	Disk	1	0.6	925	0.32		[51]
$\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}\text{-CoFe}_2\text{O}_4$	Disk	1	1.0	900	0.07		[52]
$\text{Ce}_{0.8}\text{Gd}_{0.15}\text{Cu}_{0.05}\text{O}_{2-\delta}\text{-SrFeO}_{3-\delta}$	Disk	1	0.5	900	0.84		[53]
LSCF	Disk	1	1.0	900	0.20		[54]
LSCF	Disk	1	0.8	950	0.81		[12]
				900	0.53		
$\text{Ce}_{0.85}\text{Gd}_{0.1}\text{Cu}_{0.05}\text{O}_{2-\delta}\text{-La}_{0.6}\text{Ca}_{0.4}\text{FeO}_{3-\delta}$	Disk	1	0.5	950	0.87	0.70	[55]
$\text{Al}_{0.02}\text{Gd}_{0.02}\text{Zn}_{0.96}\text{O}_{1.02}\text{-Gd}_{0.1}\text{Ce}_{0.9}\text{O}_{1.95-\delta}$	Disk	1	1.1	940		0.19	[56]
$\text{Sm}_{0.5}\text{Sr}_{0.5}\text{Cu}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}\text{-Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$	Disk	1	0.6	1000		1.12	[57]
$\text{Sm}_{0.3}\text{Sr}_{0.7}\text{Cu}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}\text{-Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$	Disk	1	0.6	1000		1.15	[57]
$\text{Ce}_{0.9}\text{Pr}_{0.1}\text{O}_{2-\delta}\text{-Pr}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.5}\text{Co}_{0.5}\text{O}_{3-\delta}$	Disk	1	0.5	1000	1.08	1.01	[58]
$\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{2-\delta}\text{-Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$	Disk	1	0.5	975		0.67	[59]
GDC-LSM (OPM-4)	Disk	1	0.9	950	0.058	0.058	This work
				900	0.022		
SDC- $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-\delta}$	hollow fiber	2	0.3	950	0.430	0.403	[15]
$\text{Zr}_{0.84}\text{Y}_{0.16}\text{O}_{1.92}\text{-La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-\delta}$	Disk	2	1.0	900	0.255		[34]
GDC-LSCF	Disk	2	0.9	900	0.450		[48]
LSCF	Disk	3	1.0	950	5.6		[12]
				900	4		
LSCF	Disk	3	1.0	1000		7.2	[60]
GDC-LSM (OPM-1)	Disk	3	0.9	950	0.105	0.104	This work
				900	0.039	0.039	
GDC-LSM (OPM-2)	Disk	3	0.9	950	0.780	0.659	This work
				900	0.444	0.349	

(^a) Method 1: dry-pressing, 2: phase-inversion, 3: freeze-drying-tape-casting;

Conclusions

A high-performance GDC-LSM dual-phase asymmetric membrane with novel hierarchically porous GDC-LSM support and SDC-LSCF surface modification layer has been successfully prepared by a combination of freeze-drying tape-casting and screen-printing methods. The surface coated asymmetric membrane with the unique straight open pores exhibits 1100% higher oxygen permeation flux than the corresponding symmetric membrane with the same total thickness, and much higher than that can be achieved by the conventional asymmetric membranes with

sponge-like porous support. The presence of hierarchically oriented pores exposed to air can facilitate gas transport in the support while the surface modification layer on the permeate side can accelerate surface oxygen exchange process and thus significantly enhancing the overall oxygen permeation flux. The novel hierarchically porous support layer obtained from the freeze-drying tape-casting shows unique advantage in the development of high-performance dual-phase oxygen permeable membrane for oxygen production and oxy-fuel combustion application.

Acknowledgements

We're grateful to the financial support from the U.S. National Science Foundation (Grand Number: DMR-1210792). The authors also greatly acknowledge the financial support by the National Natural Science Foundation of China (Grand Number: 51502207) and the Fundamental Research Funds for the Central University (Grand Number: 2042015kf0043 and 2042016kf0022).

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Graphical Abstract