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Robust CO_2 and H_2 resistant triple-layered (Ag-YSZ)/YSZ/($La_{0.8}Sr_{0.2}MnO_{3-\delta}$-YSZ) hollow fiber membranes with short-circuit for oxygen permeation

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ABSTRACT

Oxygen selective ceramic membranes have many important applications, not only for air separation but also as membrane reactors for cost-effective chemical synthesis. However, the prerequisite to realize these potentials is their stability in the presence of acid gases of CO_2 and reducing atmosphere containing H_2 and CH_4. This work seeks to validate the applicability of robust triple layer hollow fiber membranes consisting of (Ag+YSZ)/YSZ/$La_{0.8}Sr_{0.2}MnO_{3-\delta}$ (LSM)+YSZ to separate O_2 from air in the presence of these unavoidable gases for more advanced applications. To prepare the triple layer hollow fiber, the dual-layer fiber was firstly synthesized *via* a combined phase inversion and sintering method where the dense YSZ layer was present on top of the porous LSM-YSZ layer. We further deposited either porous Ag or its mixture with YSZ layer above the dense YSZ surface. The final fiber consists of three layers in sequence from outside surface to inside surface of Ag+YSZ/YSZ/LSM+YSZ. The dense central YSZ layer acts as the ionic conducting phase to prevent gas diffusion while the other two porous layers serve as the electronic conducting phase with catalytic effect to enhance the surface reaction kinetics. To overcome the electronic conductivity limitation of YSZ, silver (Ag) short circuit paste was additionally used to seal the membrane and electronically connect the outer and inner surfaces for electron shuttle for the two surface O_2 exchange reactions. Ag-YSZ coated fiber performed better than Ag coated fiber and showed increasing fluxes from 0.1 to 0.53 mL min^{-1} cm^{-2} upon increasing temperature from 700 to 900 °C. The O_2 fluxes remained constant irrespective of changing the sweep gas from pure He to its mixtures containing CO_2, H_2, or CH_4; mirroring the membrane robustness to tolerate these gases at high temperatures.

1. Introduction

The market for industrial oxygen production from air separation will expand in the near future to support the rapid development of clean energy technologies. By 2040, the electricity generation sector in the United States will consume around 2 million tons of oxygen per day which would account for 60% of the oxygen production [1]. This highlights the need for alternative oxygen production technology featuring less energy intensive and costly than the conventional cryogenic distillation and pressure swing adsorption processes. Oxygen-selective membrane technology is particularly attractive due to the potential saving of at least 30% oxygen production cost *via* oxyfuel or integrated gasification combined cycle (IGCC) combustion systems [2–7]. For these applications, the membrane materials have to meet several requirements. First, high oxygen permeation flux should meet industrial production specification [8]. Second, the membrane has long-term structure and sufficient chemical stability that allow steady operation at elevated temperature (above 800 °C) and in harsh atmosphere containing CH_4, CO, CO_2, H_2, H_2O or SO_2. Third, membrane possesses sufficient mechanical strength to withstand the thermally induced stress subjected to the membrane during thermal cycling for starting-up and shutting-down. Last, such materials should be inexpensive and available in abundant amount to enable large-scale production.

Ceramic materials remain the best candidate to fulfil these criteria [8–14]. Two classes of ceramic-based materials have attracted most interest, one of which is the single phase perovskite material exhibiting mixed (oxygen) ionic-electronic conductivity [15–18]. Perovskite mixed (oxygen) ionic-electronic conducting (MIEC) materials normally show high oxygen permeation fluxes but low stability and mechanical

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strength; leading to the deteriorated permeability due to phase decomposition and erosion in reducing and acidic gases and steam. The other class is dual-phase materials where the oxygen ionic conducting phase is combined with another electronic or MIEC phase as exemplified by gadolinium-doped ceria(GDC)/silver (Ag), samarium-doped ceria (SDC)/$La_{0.8}Sr_{0.2}MnO_{3-\delta}$ (LSM), yttria-stabilized zirconia (YSZ)/$La_{0.8}Sr_{0.2}MnO_{3-\delta}$, SDC/$PrBaCo_2O_{5+\delta}$, gadolinium-doped ceria (GDC)/$La_{0.6}Sr_{0.4}CoO_{3-\ddot{a}}$ [4,19–22]. Generally, these dual-phase materials have high stability which is offset by low oxygen flux due to the discrete ionic and electronic pathways or the presence of insulating components in phase boundaries formed by the unfavourable reactions between the phase constituents [23,24].

In terms of stability, single phase fluorite materials are superior to perovskite materials and they are stable in acidic and reducing gases [13,25–28]. Fluorite materials such as gadolinium-doped ceria (GDC) or samarium-doped ceria (SDC) are however also characterized by their dominant ionic conductivity. For oxygen production, these fluorite membranes need to be operated by oxygen pump mode with the aid of external electric power sources or alternatively, *via* a short-circuit mode [26]. Ceria-based materials nonetheless have drawbacks in terms of low mechanical strength and brittleness [29]. Yttria-stabilized zirconia (YSZ) which has been widely accepted as typical electrolyte material for solid oxide fuel cells, on the other hand, demonstrate higher mechanical strength relative to doped ceria in addition to high chemical and thermal stabilities [30–34]. In this context, this fluorite compound can be viewed as an attractive candidate for the oxygen ionic conducting phase.

One of the most practical membrane configurations in industry is hollow fiber since it enables very high oxygen fluxes (given its very thin transport layer) and maximizes surface area to volume ratio allowing packing of hundreds of fibers in a single module [7,35]. The asymmetric structure of the hollow fiber leads to the thin separation layer which further reduces the bulk diffusion resistance. Moreover, surface modification can additionally be performed to further improve the oxygen fluxes of the original fiber [36–39]. Previously, our research group demonstrated a novel short-circuit membrane concept to realize the oxygen permeation through these robust ion conducting membranes like SDC or GDC by depositing the electronic conducting phase on both membrane surfaces but without the application of external power source; a short-circuit *via* the sealant was provided for electron shuttle between the two membrane surfaces to promote the surface oxygen exchange reactions [26]. Our previous work on this short-circuit membrane concept was based on disk-shaped membrane as it is easily prepared *via* coating method to deposit the porous electronic conducting phase on both membrane surfaces. Now with the advancement of ceramic hollow fiber synthesis technique, the dual or triple-layer ceramic hollow fiber can be prepared; based on which, this novel membrane concept can be adopted to hollow fiber geometry.

In this work, the short-circuited triple-layered ((Ag+YSZ)/YSZ/(LSM+YSZ)) ceramic hollow fiber membrane was developed. The robustness of such membrane for oxygen permeation in acidic or reducing gas atmosphere has been proven by using a series of sweep gases containing CO_2, H_2, or CH_4. To prepare such membrane, dual-layer LSM+YSZ/YSZ hollow fiber was firstly synthesized by the combined phase inversion (co-spinning) and sintering method in one step as shown in Fig. 1(a). Secondly, another porous electron conductor layer of Ag or Ag+YSZ (50:50 w/w) was coated on the outside surface of the dense YSZ layer as shown in Fig. 1(b). The central densified YSZ layer has been utilized as the oxygen ion conductor (marked by violet color in Fig. 1(a)) while the inside porous LSM-YSZ layer and outside Ag or Ag-YSZ serve not only for the electron conduction but also for catalyst to improve the oxygen surface exchange reactions. The application of LSM (Ag) and YSZ composite coating is to strengthen the surface kinetics enhancement contributed by the extra triple phase boundaries (TPB) area, thus optimizing the oxygen permeation [40–42].

2. Experimental section

The materials employed are listed in the experimental section of supplementary Information (SI). To prepare the triple-layer hollow fibers, dual-layer LSM+YSZ/YSZ hollow fibers were firstly prepared by using the co-spinning and sintering method based on the phase-inversion route as detailed elsewhere [40,43]. To fabricate the dual-layer hollow fibers, two separate suspensions (or dopes) of YSZ and LSM-YSZ were prepared with compositions shown in Table S1. The spinning conditions or parameters were also shown in Table S1. The presence of graphite particles in the dope to prepare the hollow fiber is to make the inner layer in a more porous structure favorable for surface reactions. More detailed information on the dual layer hollow fiber preparation by wet spinning through a triple-orifice spinneret (Fig. S1) can be referred from the SI. The precursors were sintered at 1400 °C to obtain the dense membrane. The ethanol diluted Ag paste or the ethanol diluted Ag-YSZ (50:50 w/w) mixture was uniformly brushed on the dense outer surface of YSZ/LSM+YSZ dual-layer hollow fibers followed by calcination at 700 °C to remove the organic components and create the surface kinetics enhancement layer. Short circuiting of the resultant hollow fiber was performed by coating the cross-section of the membrane end by Ag sealant. The hollow fiber was then fixed within the home-made oxygen permeation cell in Fig. S2. Air with the flow rate of 100 mL min^{-1} was used as feed gas in shell side while He or CO_2 with a varying flow rate was used as sweep gas in the lumen side. When the reducing gases such as H_2 or CH_4 is used as a sweep gas, the sweep gas is flown over the shell side while the feed gas (air) is flown over the lumen side (reversing the original feed and permeate side configuration). An online gas chromatography (GC6890N, Agilent) with a thermal conductivity detector was utilized to analyze the composition of the permeate gas collected on the sweep side outlet. The oxygen permeability, i.e., $J_{O2}$was calculated using Eq. (1). This equation should be modified when H_2 or CH_4 was used as sweep gas to account for their reactions with the permeated oxygen (assuming no deposition of carbon or coking). The amount of the oxygen consumed in these reactions can be approximated from the amount of the reaction products.

$$J_{O2} = (x_{O_2} - x_{N_2}/4.02) \times \frac{F_{out}}{A_m} \quad (1)$$

Where F_{out} is the flow rate of the permeate stream, mL min^{-1}; x_{O2} and x_{N2} are the volume fractions of oxygen and nitrogen in the tail gas, respectively; A_m is the effective membrane area for permeation, cm^2.

3. Results and discussion

3.1. Morphologies of dual-layer YSZ/LSM-YSZ hollow fibers

The morphologies of the dual-layer YSZ/LSM+YSZ hollow fibers before and after sintering at 1400 °C are shown in Fig. 2(a) and (b), respectively. De-ionized and tap water were used as the respective internal and external coagulants. Hollow fiber precursor (prior to sintering) features asymmetric cross-section structure. The inner circumference layer of fiber precursor contains macroporous structure with finger-like pores whereas its outer circumference layer is comprised of sponge-like denser microporous structure. After sintering, dense YSZ layer with an average thickness of 27 μm formed on top of 210-μm thick LSM-YSZ porous layer. The dense layer serves for the ionic conduction only thus preventing any gas molecular diffusion through fiber. The porous inner circumference layer (Fig. 2(b3)), on the other hand, provides three-fold functions, i.e., as gas diffusion channels, as a mechanical support for the dense layer, and as surface reaction catalyst. The last role, in particular, is attained *via* increasing the amount of triple phase boundaries (i.e., contact points between oxygen gas, oxygen ions and electrons) that leads to the enhanced rate of O_2 reduction to O^{2-} (and the opposite reaction). This effect is