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Oxygen permeation properties of supported planar $\text{Zr}_{0.84}\text{Y}_{0.16}\text{O}_{1.92}\text{-La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.5}\text{Fe}_{0.5}\text{O}_{3-\delta}$ composite membranes

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ABSTRACT

$\text{Zr}_{0.84}\text{Y}_{0.16}\text{O}_{1.92}$ (YSZ)- $\text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.5}\text{Fe}_{0.5}\text{O}_{3-\delta}$ (LSCrF) planar membranes consisting of an oxygen-permeable dense layer and a finger-like porous support were prepared using the phase inversion tape casting/sintering method. The thickness of the dense layer was varied in the range of 75–25 μm by adjusting the blade gap for the tape casting. The oxygen permeation flux through the membranes was measured at elevated temperatures with the dense layer side exposed to air and the porous support side swept with CO to remove the permeated oxygen. At 850 °C, oxygen permeation fluxes of 0.8, 0.9, 1.1 $\text{ml cm}^{-2} \text{min}^{-1}$ (STP) were observed for the membranes with a 75, 50, 25 μm thick dense layer, respectively. The oxygen permeation flux increased with decreasing the thickness of the dense layer appreciably, but the increment was much smaller than the extrapolated value assuming the linear dependence of the oxygen permeation flux on the reciprocal thickness, revealing that the overall oxygen permeation process was mainly controlled by the surface oxygen exchange step in the given thickness range. To enhance the surface oxygen exchange activity, the membrane was modified by applying a 10 μm thick porous YSZ-LSCrF layer on the dense layer side surface and depositing samarium doped ceria (SDC) nanoparticles on the inner surface of the porous support. The membranes with modified surfaces exhibited much increased oxygen permeation flux. An increased flux of 2.1 $\text{ml cm}^{-2} \text{min}^{-1}$ was obtained at 850 °C for the membranes with a 25 μm thick dense layer, which was almost twice as large as that for the un-modified membrane. The membrane with a thin dense separation layer and modified surfaces shows much increased oxygen permeation flux, promising for practical applications.

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1. Introduction

Dense ceramic membranes made from mixed oxygen ionic and electronic conductivity have attracted increasing attention [1–6]. With these membranes, chemical reactions such as partial oxidation of methane (POM) [7–11] or combustion of carbonaceous fuels [12–15] can be integrated with separation of oxygen from air. For successful applications, the membrane is required to possess a high oxygen permeation flux and chemical and mechanical stabilities under stringent operation conditions [16–18]. To increase the oxygen permeation flux of the membrane and the performance of the membrane reactor, the thickness of the membranes should be as thin as possible. When the membrane becomes very thin, it needs to be supported mechanically [19].

For a supported membrane, oxygen permeation consists of the transport of oxide ions and electrons in the bulk of the dense layer,

the oxygen exchange between the gas phase and the membrane surface, and the transport of gaseous molecules in the support [20,21]. The pores in the support are usually created by using pyrolyzable substances such as graphite or starch. The as-formed pores are randomly distributed, the resulting pore paths are tortuous, presenting a large resistance to the transport of the gaseous molecules and giving rise to a severe oxygen concentration polarization during oxygen permeation [20,22]. Recently, phase inversion technique has been developed for preparation of supported oxygen separation membranes [23–25]. Unlike the porous support prepared with the pyrolyzable pore former, the support prepared by the phase inversion method contains finger-like pores along the thickness direction, providing ideal channels for transport of gaseous molecules [24,26].

$\text{Zr}_{0.84}\text{Y}_{0.16}\text{O}_{1.92}$ (YSZ)- $\text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.5}\text{Fe}_{0.5}\text{O}_{3-\delta}$ (LSCrF) dual-phase composite membrane shows good stability under harsh reducing atmosphere at elevated temperatures [18]. The supported planar membrane prepared using the phase-inversion method exhibits a high oxygen permeation flux at elevated temperatures. An oxygen

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permeation flux of $1.0 \text{ ml cm}^{-2} \text{ min}^{-1}$ (STP) was observed at 850°C with one side of the membrane exposed to air and the other side to CO [27], and an even higher value of $2.5 \text{ ml cm}^{-2} \text{ min}^{-1}$ (STP) was attained in a packed bed POM membrane reactor configuration [28]. The membrane consisted of a relatively thick dense layer ($\sim 150 \mu\text{m}$), thus a further increase in oxygen permeation flux can be expected by reducing the thickness of the dense layer. For the membrane with a thinner dense layer, the surface oxygen exchange is likely to become the rate-limiting step. In that case, to enhance the surface step and hence the overall oxygen permeation process, the membrane surfaces should be modified by applying a porous layer or catalysts [29–32].

In the present work, supported YSZ-LSCrF dual-phase composite membranes with reduced thicknesses of dense layer were prepared by phase inversion tape casting, and the effects of thickness and surface modification on oxygen permeation were investigated.

2. Experimental

2.1. Membrane preparation

The $\text{Zr}_{0.84}\text{Y}_{0.16}\text{O}_{1.92}$ (YSZ)- $\text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.5}\text{Fe}_{0.5}\text{O}_{3-\delta}$ (LSCrF) membrane was prepared by phase inversion tape casting method. Two

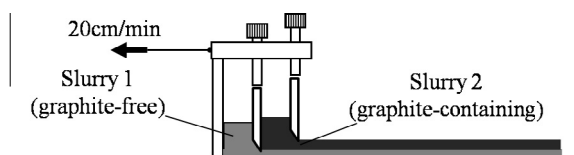


Fig. 1. Schematic illustration of phase inversion tape casting.

slurries were prepared. One slurry was composed of YSZ (43.7 wt%) (Fanmeiya), LSCrF (32.1 wt%), N-methyl-2-pyrrolidone (NMP) (20.2 wt%) (CP, Sinopharm Chemical Reagent Co.), polyethersulfone (PES) (3.68 wt%) (RadelA-100, Solvay Advanced Polymers) and polyvinylpyrrolidone (PVP) (0.6 wt%) (K30, Sinopharm Chemical Reagent Co.). The other slurry contained graphite, which was composed of YSZ (28.6 wt%) (Fanmeiya), LSCrF (21.0 wt%), graphite (12.5 wt%) (Shanshan Technology Co.), NMP (31.4 wt%) (CP, Sinopharm Chemical Reagent Co.), PES (5.2 wt%) (RadelA-100, Solvay Advanced Polymers) and PVP (1.3 wt%) (K30, Sinopharm Chemical Reagent Co.). The LSCrF powders were home-made using the solid state reaction method described in Ref. [18]. The two slurries were milled for 48 h and degassed for 0.5 h, and then co-tape cast onto a Mylar sheet using a device illustrated in Fig. 1, and then transferred into a water bath for solidification into a green tape via the phase inversion process. The as-formed green tapes comprised two layers: one being free of graphite and other containing graphite; the thickness of the graphite-free layer was varied by adjusting the blade gap. The green tapes were cut into a size of $6 \times 6 \text{ cm}^2$, and sintered at 1450°C for 10 h.

Surface modification was applied to the sintered YSZ-LSCrF membranes. A porous YSZ-LSCrF layer was coated on the surface of the dense layer side by screen printing a YSZ-LSCrF slurry followed by firing at 1150°C for 2 h. The slurry used was prepared by dispersing the YSZ and LSCrF powders (with a volume ratio of 60:40) in terpineol and ethyl cellulose. Nano-particles of samarium doped ceria ($\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{2-\delta}$, SDC) were deposited to the inner surfaces of the porous support by ion impregnation using an aqueous solution followed by firing at 750°C for 1 h. The solution was prepared from $\text{Ce}(\text{NO}_3)_3$ and $\text{Sm}(\text{NO}_3)_3$ (AR, Sinopharm Chemical Reagent Co.) in the stoichiometric molar ratio of SDC and with a total metal ion concentration of 0.3 M.

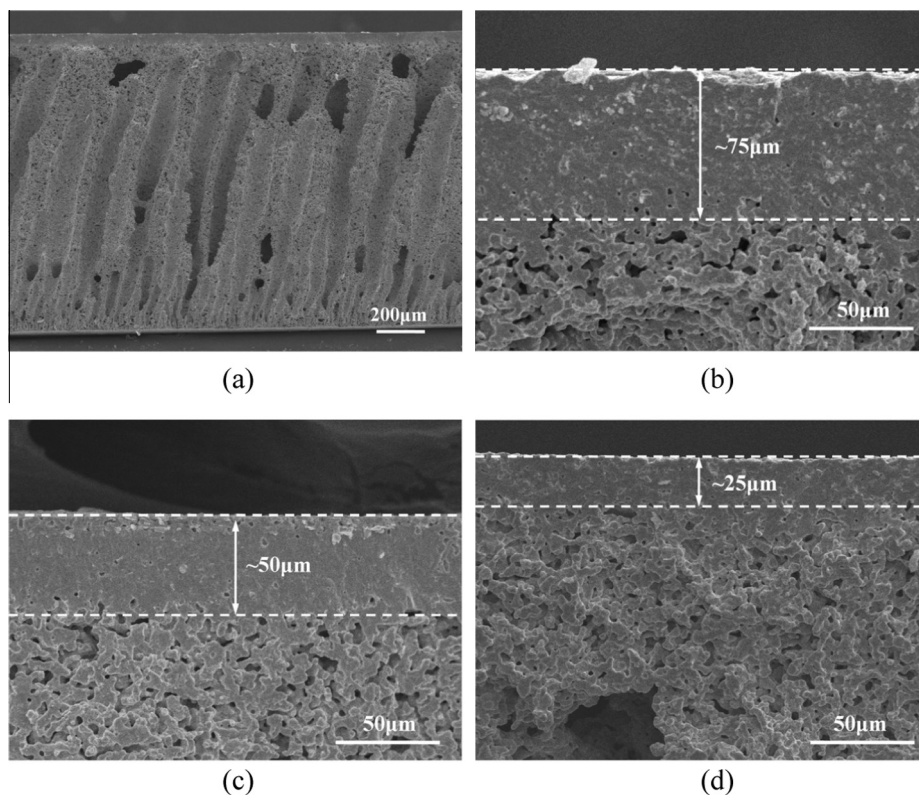


Fig. 2. SEM images of the sintered YSZ-LSCrF membranes. (a) Overall cross-sectional view; cross-sectional view of the dense layer of thickness (b) $75 \mu\text{m}$, (c) $50 \mu\text{m}$, (d) $25 \mu\text{m}$.

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