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Preparation and characterization of supported planar $Zr_{0.84}Y_{0.16}O_{1.92}$–$La_{0.8}Sr_{0.2}Cr_{0.5}Fe_{0.5}O_{3-\delta}$ composite membrane

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ABSTRACT

The $Zr_{0.84}Y_{0.16}O_{1.92}$ (YSZ)−$La_{0.8}Sr_{0.2}Cr_{0.5}Fe_{0.5}O_{3-\delta}$ (LSCrF) supported membrane was formed by a new variant of phase inversion tape casting method. A slurry composed of YSZ and LSCrF was co-tape cast with a slurry of graphite, and solidified into a green tape by immersion in the water bath. The as-formed green tape comprised a relatively dense layer at the top derived from the graphite slurry, a finger-like porous layer in the middle and a sponge-like layer at the bottom both derived from the YSZ–LSCrF slurry. After firing at 1420 °C in the air, the graphite layer was eliminated, and the other two layers were converted into ceramics. The resulting membrane consisted of a dense layer of thickness ~150 μm providing the oxygen separation function and a finger-like porous layer of thickness ~850 μm providing mechanical strength. Due to the use of graphite sacrificing layer, the finger-like pores in the support was fully opened up to the outer surface, allowing fast mass transport. The oxygen permeability of the membrane was measured by exposing its dense separation layer to the ambient air and the porous support to flowing CO at elevated temperatures. An oxygen permeation flux as large as 6.82×10^{-7} mol cm^{-2} s^{-1}, equivalent to 1.0 ml (STP) cm^{-2} min^{-1}, was obtained at 850 °C. And no significant changes to the microstructure and phase composition of the membrane were observed after the oxygen permeation test. The reasonably high oxygen permeability together with the satisfactory stability makes the supported planar YSZ–LSCrF composite suitable for practical applications.

1. Introduction

Dense membranes made of mixed oxygen ionic and electronic conductors are permeable to oxygen while imperious to nitrogen [1–6]. With these membranes, oxygen-consuming chemical processes such as partial oxidation of methane (POM) and air separation can be integrated into a single space, resulting in substantial economic and environmental benefits [7–11]. It is clear that oxygen permeation through the dense membranes involves transport of oxide ions and electrons in the bulk. In order to reduce the bulk transport resistance the membrane should be as thin as possible [1,2]. When the membrane becomes very thin, a porous mechanical support is needed [12–17]. To attain a good adherence between the membrane function layer and the mechanical support, they are preferred to be prepared from the same or similar materials [18–23]. Moreover, while providing the mechanical strength to the function layer, the support is required not to constitute a barrier to the transport of gaseous molecules.

The phase inversion tape casting method has been adopted for fabrication of planar supported ceramic membranes [24,25]. The as-prepared membranes consist of a dense function layer and a finger-like porous support (Fig. 1A). The finger-like pores are aligned along the thickness direction of the membrane, allowing fast gas phase transport. It is noted that a low porosity skin layer is present at top of the support, hindering gaseous molecules to transport into/out the finger-like pores in the support. In fact, in the study of hollow fiber oxygen separation membranes, the detrimental effect of the low porosity skin layer on the oxygen permeation has been noted, and the removal of it was found to result in a significant increase of the oxygen permeability of the hollow fiber membrane [21]. Therefore, similar improvement of the oxygen permeability is expected for the planar supported membrane if the low porosity skin layer is removed as well (Fig. 1B).

Recently, it is reported that yttria-stabilized zirconia (YSZ)–NiO composite anodes with open finger-like pores can be prepared by the modified phase inversion tape casting method using graphite as a scarifying layer [26]. The graphite layer co-formed with the YSZ–NiO layer is burned off at elevated temperatures in the air, thus opening-up the finger-like pores. In the present study, a

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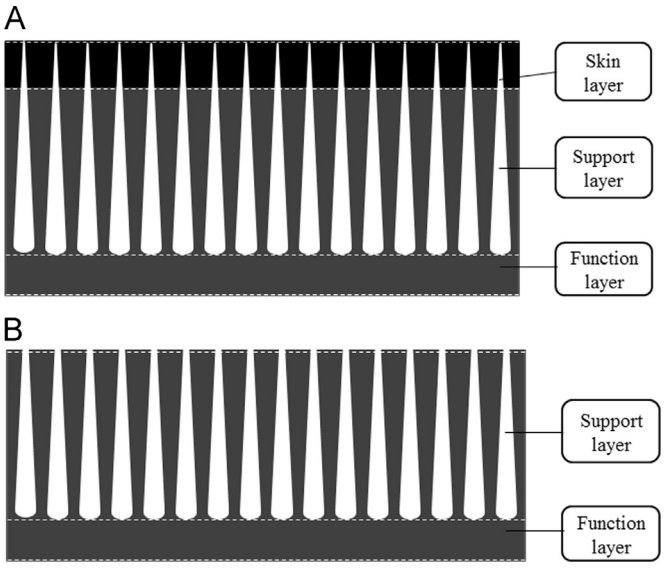

Fig. 1. Illustration of a supported membrane (A) with a low porosity skin layer, (B) without the skin layer.

similar approach was applied to the preparation of ceramic membranes. It has been reported that the hollow fiber composite membrane of $Zr_{0.84}Y_{0.16}O_{1.92}$ (YSZ)–$La_{0.8}Sr_{0.2}Cr_{0.5}Fe_{0.5}O_{3-\delta}$ (LSCrF) with a volume ratio of 60:40 exhibits excellent stability and satisfactory oxygen permeability under stringent conditions [27]. In the present study, the planar supported YSZ–LSCrF composite was prepared using the modified phase-inversion tape casting method, and its oxygen permeability and stability were investigated.

2. Experimental

2.1. Membrane preparation

Preparation of a green tape involved two slurries. One was composed of $Zr_{0.84}Y_{0.16}O_{1.92}$ (YSZ) (42.44 wt%) (FUCIDE), $La_{0.8}Sr_{0.2}Cr_{0.5}Fe_{0.5}O_{3-\delta}$ (LSCrF) (31.18 wt%), *N*-methyl-2-pyrrolidone (NMP) (22.09%) (CP, Sinopharm Chemical Reagent Co.), polyethersulfone (3.68%) (PES) (Radel A-100, Solvay Advanced Polymers) and polyvinylpyrrolidone (PVP) (0.61 wt%) (K30, Sinopharm Chemical Reagent Co); the LSCrF powder used here were prepared using the solid state reaction method described in Ref. [27]. The other consisted of graphite (28%) (Shanshan technology Co.), NMP (60 wt%) (CP, Sinopharm Chemical Reagent Co.), PES (10 wt%) (Radel A-100, Solvay Advanced Polymers) and PVP (2 wt%) (K30, Sinopharm Chemical Reagent Co.). The two slurries were milled for 48 h and degassed for 0.5 h, then co-cast on the Mylar sheet using the device illustrated in Fig. 2 with the blade gaps of 1.65 mm and 0.05 mm for the ceramic and graphite slurry, respectively. The cast was solidified to a green tape by immersion in a water bath for 12 h followed by drying at 80 °C for 24 h. For comparison, green tapes were also prepared from the YSZ–LSCrF slurry alone. All the green tapes were heated to 850 °C and stayed at that temperature for 4 h to burn off the polymers and graphite, and then sintered at 1420 °C for 10 h in air.

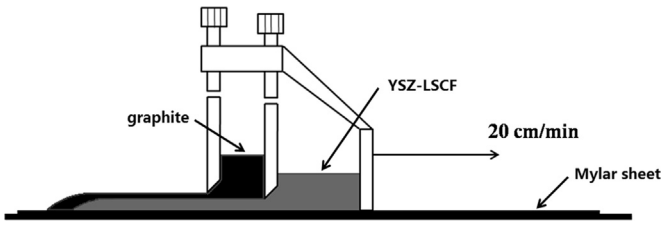

Fig. 2. Schematic illustration of phase inversion co-tape casting.

The surfaces of the sintered YSZ–LSCrF membrane were modified at both sides. To the porous side of the membrane, samarium doped ceria (SDC) nano-particles was deposited to the inner surface using the impregnation method. For impregnation, a solution was prepared from $Ce(NO_3)_3$ and $Sm(NO_3)_3$ (AR, Sinopharm Chemical Reagent Co.) in the appropriate molar ratio and with a total metal ion concentration of 0.2 M. The membrane was immersed in the solution followed by firing at 800 °C for 2 h, which was repeated three times to obtain sufficient SDC loading. To the dense side of the membrane, a thin porous layer of YSZ–LSCrF was coated as well by screen printing the YSZ–LSCrF slurry followed by firing at 1050 °C for 30 min in the air; the slurry used was prepared by dispersing the YSZ and LSCrF powder (with a volume ratio of 60:40) in terpineol and ethyl cellulose.

2.2. Characterization

The sintering behavior of the YSZ–LSCrF powder was examined by a dilatometer (DIL 402C Netzsch) using a powder compact sample with length 20 mm, width 5 mm and thickness 1 mm. The sample was prepared by mixing the appropriate amount of YSZ and LSCrF powder followed by a uniaxial pressing. The linear shrinkage of the sample was recorded while it was heated to 1500 °C at a rate of 5 °C/min. The thermal decomposition of a green tape formed by the phase-inversion method was analyzed using TGA (DTG-60H, Shimadzu) at a heating rate of 5 °C/min in the air.

The phase composition of the powder and sintered sample was analyzed by XRD (X'Pert Pro, Phillips, Netherlands), and the microstructure was examined by SEM (JSM-6390LA, JEOL, Japan). The density of the membranes was measured using the Archimedes method in mercury, from which the porosity was calculated using the formula $(1-\rho/\rho_{th})$x100% where ρ_{th} is the theoretical density of the YSZ–LSCrF composite. The oxygen permeability of the membrane was measured using a set-up as schematically shown in Fig. 3. The permeation cell was constructed by sealing a planar membrane to a stainless steel holder (Crofer 22 APU) [28,29]. The membrane had an effective area 14.4 cm^2 m, and its dense function layer side was exposed to the ambient air, while the porous support layer side to flowing helium or CO stream. The effluent from the cell was analyzed by an online gas chromatography (GC-14C,Shimadazu, Kyoto, Japan and GC9750, FuLi, China) equipped with a thermal conductivity detector and one column filled with 60–80 mesh GDX-502 for CO_2 detection and the other filled with 60–80 mesh 5 A molecular sieves for the other gases detection.

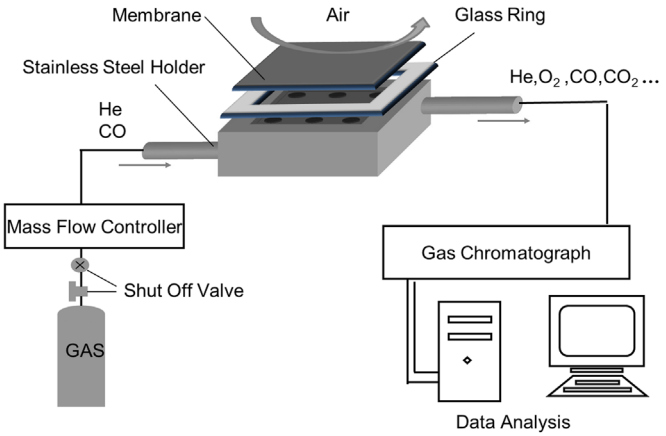

Fig. 3. Schematic diagram of the oxygen permeation measurement set-up.