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Asymmetric dual-phase membranes prepared via tape-casting and co-lamination for oxygen permeation

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ABSTRACT

Asymmetric dual-phase membranes with a composition of 75 wt% $Ce_{0.85}Sm_{0.15}O_{2-\delta}$–25 wt% $Sm_{0.6}Sr_{0.4}Al_{0.3}Fe_{0.7}O_{3-\delta}$ (SDC–SSAF) were prepared by tape-casting and co-lamination technique. The membrane has a thin dense layer of ~40 μm and a porous support of ~460 μm. It demonstrated an oxygen permeation flux as high as 3.9 mL cm^{-2} min^{-1} at 950 °C. This high value is commercially attractive for pure oxygen production via asymmetric dual-phase membranes.

1. Introduction

Mixed ionic-electronic conducting (MIEC) membranes have attracted great attention due to their potential applications in pure oxygen production and as membrane reactors for natural gas conversion to syngas [1]. Recently, asymmetric membranes, consisting of a thin dense layer and a porous support showing high oxygen permeation fluxes, have attracted great attention. In previous researches, asymmetric membranes were prepared by various methods, such as tape-casting [2], dip coating [3], acid leaching [4] and phase inversion [5]. Among these methods, tape-casting is one of the promising methods for the preparation of asymmetric membranes in large scale. In this method, the slurry without any pore former is casted to form the dense separation layer and then the slurry containing pore formers is casted on the top of the dense layer.

During the past few years, researchers focused on the development of dual-phase membranes for oxygen separation and syngas generation in membrane reactors due to their high oxygen permeation fluxes and excellent stability under reducing or CO_2 atmosphere [6–8]. Among the dual-phase membranes, 75 wt% $Ce_{0.85}Sm_{0.15}O_{2-\delta}$–25 wt% $Sm_{0.6}Sr_{0.4}Al_{0.3}Fe_{0.7}O_{3-\delta}$ (SDC–SSAF) shows excellent performance in syngas generation and oxygen separation. The success of 1100 h syngas generation experiment in the SDC–SSAF membrane reactor verified the excellent stability of the membrane under both strongly oxidative and reducing conditions [6]. It is regarded that the oxygen permeation flux high up to 3.5 mL cm^{-2} min^{-1} is required to match current technological applications [9]. Herein, for the first time, we reported an asymmetric dual-phase membrane made of SDC–SSAF giving high oxygen permeation flux up to 3.9 mL cm^{-2} min^{-1} at 950 °C.

2. Experimental

Two slurries were separately prepared for dense layer and porous support, respectively. Oxides and carbonates were used as the starting ceramic powders. Certain amounts of starting ceramic powders, corn starch (only for the porous support), dispersant (triethanolamine) and solvent (ethanol and methyl ethyl ketone) were mixed and ball-milled for 10 h. Then proper amounts of plasticizer (dibutyl phthalate) and binder (PVB) were added into the above suspension and ball-milled for another 10 h to obtain slurries with good homogeneity and proper viscosity. After the 20 h ball-milling, the slurries were degassed for 10 min at 30 kPa before tape-casting. The distances between the blade and the carrier film were 200 and 300 μm for dense layer and support layer tapes, respectively. After tape-casting, the tapes were dried at 50 °C for 30 min. The green asymmetric membranes were obtained by stacking 8 pieces of porous support tapes and 1 piece of dense layer tape under a lamination pressure of ~100 MPa for 10 min. For comparison, SDC–SSAF membranes with symmetric structure were prepared by stacking 12 pieces of dense layer tapes.

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After co-lamination, the green tapes were shaped into disks and sintered at 1450 °C for 3 h with heating and cooling rates of 2 °C min^{-1}.

In the previous investigation, we found that a catalyst was needed to speed up the oxygen exchange rate on dual-phase membrane surfaces [7]. Thus, here the surface of dense layer side of the as-sintered asymmetric membrane was coated with $Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$ (SSC, prepared via a sol–gel method) (Fig. 1) active porous layer to improve oxygen exchange rates, and this membrane is named as cat-Asym. The SSC slurry was prepared by mixing SSC powder and terpineol at a weight ratio of 1:1. SSC nanoparticles formed on the porous support skeleton to improve the oxygen exchange rates were produced by dripping two drops of a solution containing 1 mol L^{-1} SSC nitrates solution into the porous support. This membrane is named as cat-Asym-cat. For comparison, the symmetric membrane with both sides coated by SSC active porous layer was prepared, and this membrane is named as cat-Sym-cat.

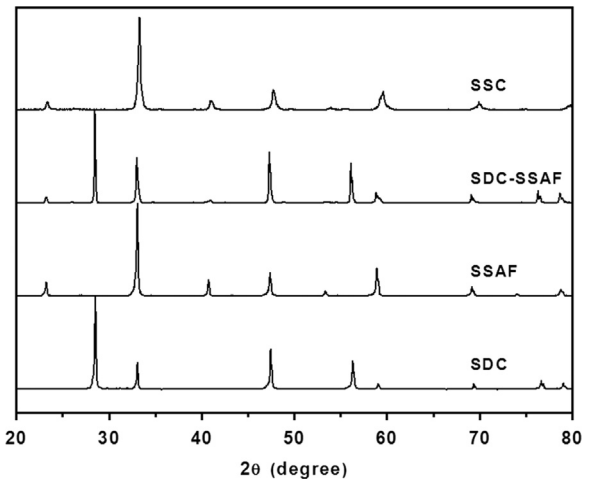

Fig. 1. XRD patterns of single-phase oxides and the as-sintered dual-phase membrane.

X-ray diffraction (XRD, Rigaku D/Max-RB) and scanning electron microscopy (SEM, Quanta 200 FEG) were used to characterize the crystalline structure and morphology of the membranes. The membranes were sealed by silver rings and their effective areas of the membranes were controlled around 1.0 cm^2. Oxygen permeation measurements were carried out under an air/He gradient. Dried air and high purity helium were fed to the porous support side and dense layer side, respectively. The concentrations of oxygen and nitrogen in the effluents were analyzed by an online gas chromatograph (Agilent 6890). The leakage due to the imperfect sealing was less than 1% in all permeation tests.

3. Results and discussion

Fig. 1 shows the XRD patterns of the single-phase oxides SDC, SSAF and dual-phase membrane SDC–SSAF. It can be seen from the diffraction peaks of the as-sintered dual-phase membrane that the membrane consists of a fluorite phase (SDC) and a perovskite phase (SSAF), and no any other impurities. The surface of the asymmetric membrane is dense without any cracks (Fig. 2a). The asymmetric membrane has a total thickness of ~500 μm and a dense layer thickness of ~40 μm (Fig. 2b and c). Porous support

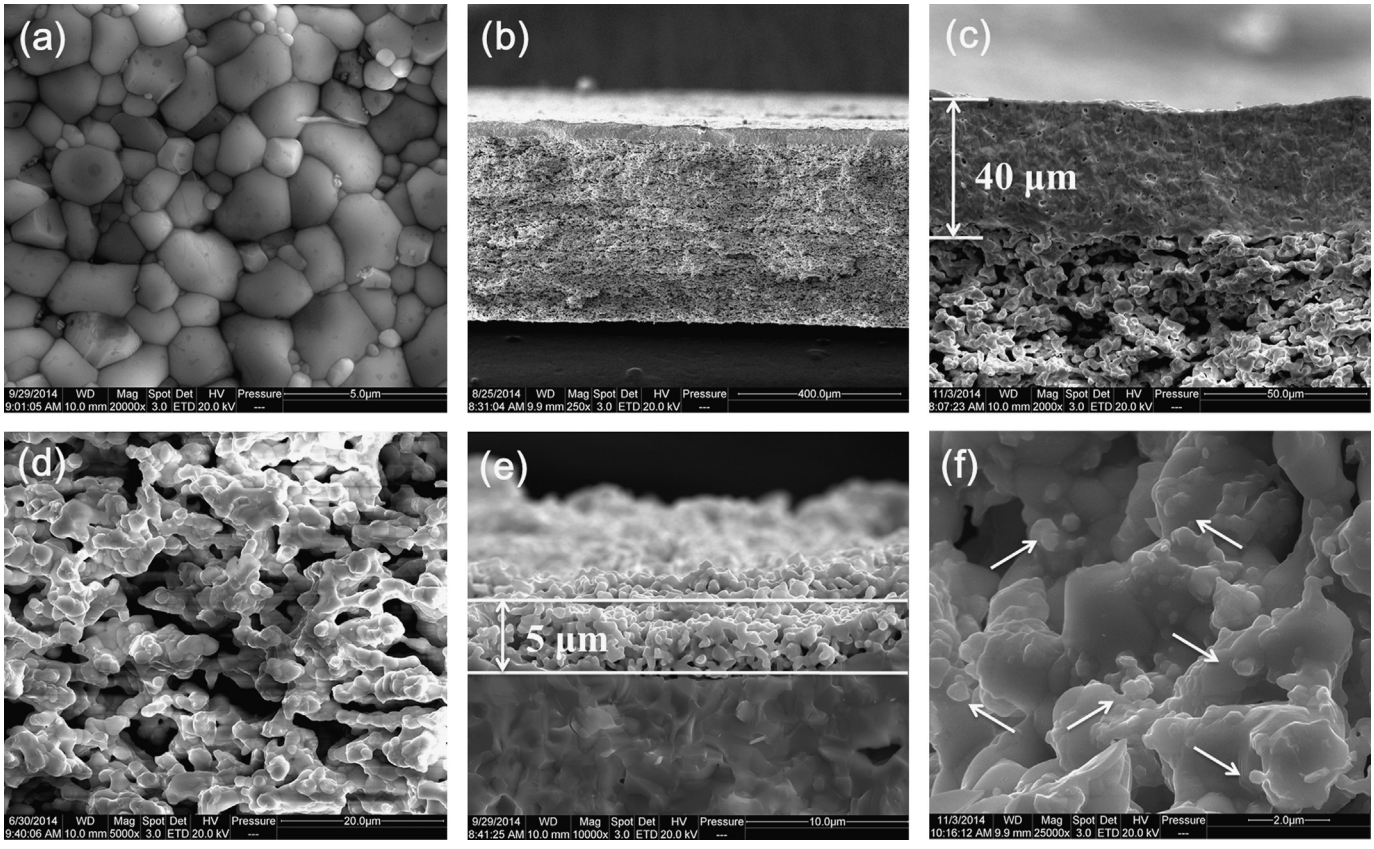

Fig. 2. SEM images of asymmetric membranes prepared via tape-casting and co-lamination. (a) Top-view of the dense layer, (b) cross-view of the asymmetric membrane, (c) cross-view of the dense layer of the asymmetric membrane, (d) cross-view of the porous support, (e) SSC catalyst layer on the surface of the dense layer side, and (f) SSC catalyst particles impregnated into the porous support and some of the particles marked by arrows.