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$Zr_{0.84}Y_{0.16}O_{1.92}$ –$La_{0.8}Sr_{0.2}Cr_{0.5}Fe_{0.5}O_{3-\delta}$ composite membrane for CO_2 decomposition

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ABSTRACT

$Zr_{0.84}Y_{0.16}O_{1.92}$ (YSZ)–$La_{0.8}Sr_{0.2}Cr_{0.5}Fe_{0.5}O_{3-\delta}$ (LSCF) disk composite membrane is investigated under CO_2/CO gradient at 800–900 °C. It reveals that the composite has excellent stability and appreciable oxygen permeability under the operation conditions. The oxygen permeation flux is 0.033 ml cm^{-2} min^{-1} for the disk membrane with a thickness of 0.5 mm at 900 °C. For all the samples with the thickness of 0.5, 1.0 and 1.5 mm, the oxygen permeation is controlled simultaneously by bulk oxygen diffusion and surface exchange, and the apparent activation energy decreased with the decreasing thickness . It is possibly explained as that the CO_2/CO atmosphere differently affects the chemical defects of the membranes with different thicknesses.

1. Introduction

Greenhouse gas emissions, carbon dioxide (CO_2) in particular, have become an increasing concern worldwide. Many researchers have contributed to the technologies of CO_2 capture and sequestration (CCS), developments of clear energy, and recycle of CO_2, in order to reduce the impact on the climate [1]. Although carbon dioxide decomposition into oxygen and carbon monoxide is conceptually simple (Eq. (1)), efficient decomposition is difficult due to the low equilibrium constant, $K_p = 7.8 \times 10^{-9}$ at 900 °C [2].

$$CO_2 = CO + \frac{1}{2}O_2 \quad (1)$$

However, the decomposition can be significantly improved when the produced oxygen is extracted by an oxygen permeable ceramic membrane with high oxygen permeability. In the membrane reactor, with CO_2 fed into one side of the membrane and a reducing matter (such as CO and CH_4) into the other side, CO_2 decomposes into CO and O_2 on the membrane surface, the oxygen permeates through the membrane and then is consumed by the reducing matter. Therefore, the decomposition can be maintained as the reducing matter is supplied continuously.

There are two main types of oxygen permeable ceramic membranes. One type is mixed oxygen-ion and electron conducting single-phase membranes. Among them, perovskites (Ln, A) (Co, B) $O_{3-\delta}$ (Ln = rare earth elements, A = Ca, Sr, Ba, B = transition metal elements) have been studied extensively for applications, such as in oxygen separation from air [3], partial oxidation of methane for production of syngas [4], and hydrogen production from water splitting [5]. Although the single-phase membranes usually show considerably high oxygen permeability, their stability remains problematic. It is generally unstable under a reducing atmosphere particularly for Co-containing single-phase membrane and very sensitive to CO_2 or CO for Ba-containing membrane [6,7]. Another type is the so-called dual-phase composite membranes which consist of an oxide ionic conductor for oxygen ions transport and an electronic conductor for electron transport [8]. With a composite membrane, the material selections would be extended and the problems with the single-phase membranes mentioned above would be resolved, nevertheless, the oxygen permeability of a composite membrane might be relatively low.

Our group has recently focused on the dual-phase composite membrane of Y_2O_3-stabilized ZrO_2 (YSZ) and perovskite-type $LaCrO_3$-based oxides targeting application in a system containing CO or CO_2 [9]. $LaCrO_3$-based materials generally show excellent chemical and mechanical stabilities over a wide range of oxygen partial and were extensively studied as the interconnect materials of solid oxide fuel cells (SOFCs). Moreover, $LaCrO_3$-based perovskites have also been studied for potential SOFC anode materials, e.g. $La_{1-x}Sr_xCr_{1-y}M_yO_3$ (M = Mn, Fe, Co, Ni) [10]. For a composite membrane, doped CeO_2 or doped bismuth oxide was reported as the ionic conductor. But in comparison of all the existing oxygen ionic conductors, YSZ has the best stability and is currently the most used in SOFCs.

It is previously reported by our group [11], $Zr_{0.84}Y_{0.16}O_{1.92}$ (YSZ)–$La_{0.8}Sr_{0.2}Cr_{0.5}Fe_{0.5}O_{3-\delta}$ (LSCF) composite membrane shows appreciable oxygen permeability and excellent stability under air/CO gradient. In this work, YSZ–LSCF composite membrane is investigated under CO_2/CO gradient at 800–900 °C.

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2. Experimental

LSCF powder was synthesized by solid state reactions [11]. LSCF and commercial YSZ (d_{50}=0.8 μm, Fanmeiya, Anhui, China) were mixed in a volume ratio of LSCF: YSZ=40:60 by ball-milling with ethanol as medium. Disk-shaped membranes were prepared by uniaxial pressing at 168 MPa, and sintered at 1400 °C for 10 h. The as-prepared disks with a diameter of 12.0 mm were polished to the thickness of 0.5, 1.0 and 1.5 mm and ultrasonically cleaned in ethanol.

Oxygen permeation of the as-prepared membranes was examined under CO_2/CO gradient at 800–900 °C using a home-made apparatus with an online gas chromatography (GC9750, FuLi, China) equipped with a thermal conductivity detector and two columns, one filled with GDX-502 for detection of CO_2 and CO and the other filled with 5 Å molecular sieves for detection of the other concerned gases; one side of the membrane was exposed to pure CO_2 (or air) with a flow rate of 30 ml min^{-1} and the other side was swept by pure CO (or He) with a flow rate of 25 ml min^{-1}. Phase composition of the pre- and post-tested samples was analyzed by X-ray diffraction (XRD) with Cu-Kα radiation (TTR-III, Rigaku, Japan), Microstructure was examined by scanning electron microscopy (SEM; JSM-6390LA, JEOL, Japan). Relative density was measured by the Archimedes method.

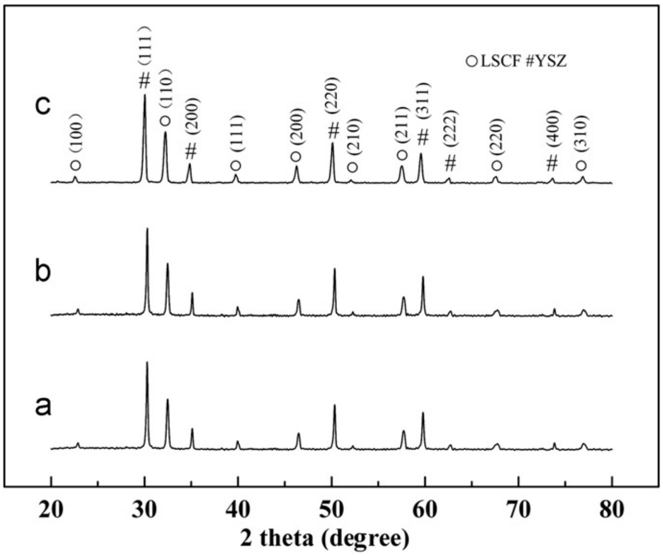

Fig. 1. XRD patterns of disk YSZ–LSCF composite membranes, the pre-tested membrane (a), CO side surface (b) and CO_2 side surface (c) of the post-tested membrane, (○) LSCF, (#) YSZ.

3. Results and discussions

Fig. 1 shows XRD patterns of the pre- and post-tested YSZ–LSCF composite membranes. There are only the diffraction peaks of cubic YSZ and perovskite-type LSCF. It reveals that the composite is stable during the preparation process and under the operation conditions. In contrast, the single-phase membranes mentioned above are usually very sensitive to CO_2 or CO [6,7].

Fig. 2 shows the SEM images of the pre- (Fig. 2a) and post-tested YSZ–LSCF membranes (Fig. 2b–d). The membrane possesses a symmetric structure. The relative density of all the samples is higher than 95% by the Archimedes method. For the post-tested membrane (testing time more than 100 h), no change is observed on the CO_2 side (Fig. 2b, the top side), but slight corrosion is observed on the CO side (Fig. 2b, the bottom side). However, the corrosion has not caused any obvious change for the

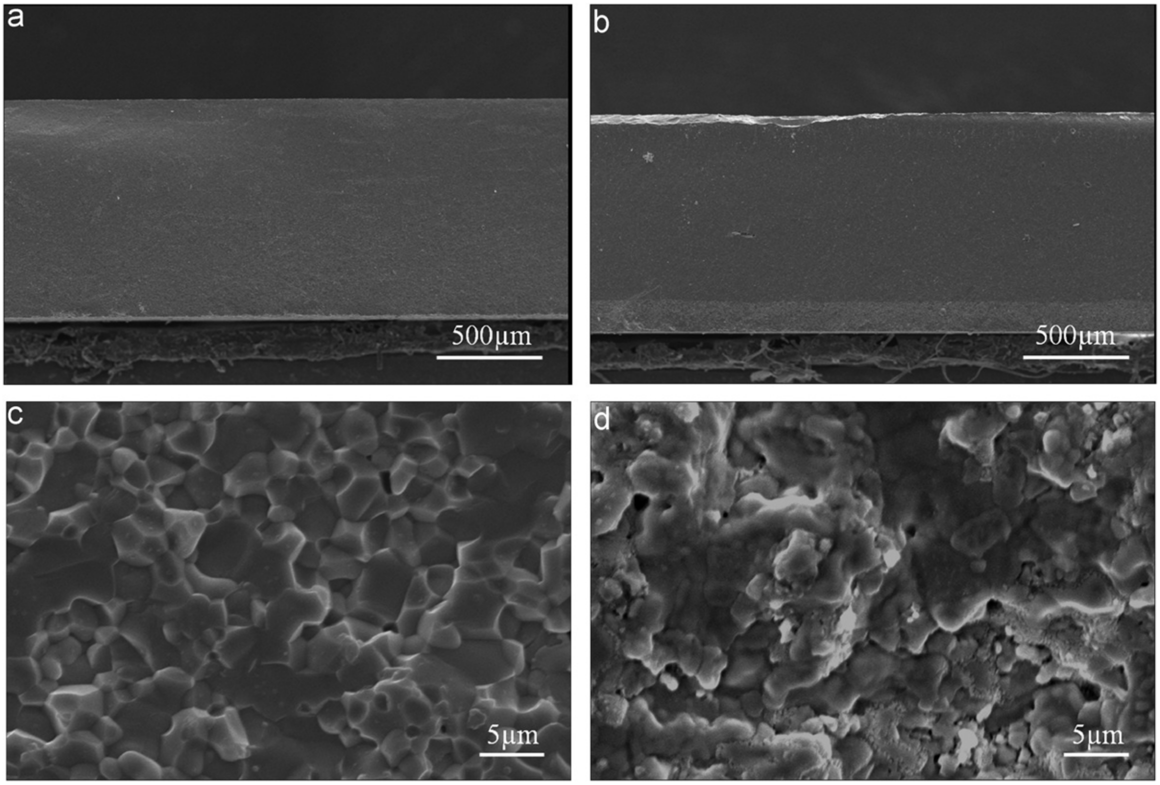

Fig. 2. SEM images of membrane, cross-section of pre- (a) and post-tested membrane (b), cross-section of the corroded region on the CO side (c) and the surface on the CO side (d).