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Oxygen permeability and CO_2-tolerance of $Ce_{0.9}Gd_{0.1}O_{2-\delta}$ – $SrCo_{0.8}Fe_{0.1}Nb_{0.1}O_{3-\delta}$ dual-phase membrane

Jianfang Zhou [a], Xia Tang [a], Daliang He [a], Chengzhang Wu [a, *], Yuwen Zhang [a], Weizhong Ding [a], Yonggang Jin [b], Chenghua Sun [c]

[a] State Key Laboratory of Advanced Special Steel, Shanghai University, Shanghai 200072, China
[b] CSIRO Energy Flagship, PO Box 883, Kenmore, QLD 4069, Australia
[c] School of Chemistry, Monash University, Clayton, VIC 3800, Australia

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ABSTRACT

$Ce_{0.9}Gd_{0.1}O_{2-\delta}$–$SrCo_{0.8}Fe_{0.1}Nb_{0.1}O_{3-\delta}$ dual-phase membranes (CGO-SCFN DPM) with different weight ratios were successfully prepared by solid-state reaction method. The microstructure, oxygen permeability, rate-determining step, and oxygen permeation stability using CO_2 as sweep gas were systematically investigated. It was found that the oxygen flux through DPM decreases with the increase of CGO content. For membranes of 80CGO-20SCFN with the thicknesses of 1.0 mm and 0.6 mm, the bulk-diffusion resistance and the interfacial exchange resistances of each side were determined according to a permeation mode. A stable oxygen flux of 0.80 mL $min^{-1}\cdot cm^2$ at 900 °C for the 0.6 mm thick membrane with a porous coating on the permeate side was achieved in comparison of 0.48 mL $min^{-1}\cdot cm^2$ for the 1.0 mm membrane without coating. The 80CGO-20SCFN DPM also shows a good tolerance to pure CO_2, the oxygen flux could reach 0.50 mL $min^{-1}\cdot cm^2$ at 900 °C.

1. Introduction

Mixed ionic-electronic conducting (MIEC) ceramic membranes have attracted increasing attention because of their potential applications in the field of oxygen separation [1,2], solid oxide fuel cells (SOFCs) [3,4] and especially in oxy-fuel process for CO_2 capture [5–7] due to greenhouse effect. In the present study, oxy-fuel technology using oxygen permeable membranes is considered as a promising carbon capture technology. In oxy-combustion process, fuel is combusted in permeated oxygen which is carried by CO_2 gas used as sweep gas. Fuel burned in this way will yield a pure stream of CO_2 which can be easily captured and stored [8]. In the past decades, numerous studies on oxygen transport membranes are available and intense research efforts have focused on (A, RE) $CoO_{3-\delta}$ (A = Ba, Sr; RE denotes rare earth elements) based perovskite oxides [9–12]. These well-researched traditional oxygen permeation membranes made of perovskite-type oxides generally show high oxygen permeation ability but are unstable in CO_2-containing atmosphere [13–16]. For instance, $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) is regarded as the state-of-the-art material in view of their high oxygen permeation fluxes. Nevertheless, an immediate stop of the oxygen permeation flux can be observed when using pure CO_2 as the sweep gas [14].

Obviously, the issue of pervoskite-based membranes limits their practical applications. Therefore, many studies have switched to dual-phase membranes (DPM), which comprise an ionic conducting phase and an electronic conducting phase or a mixed conducting phase [17–22]. In contrast to perovskite membranes, the desired dual-phase structure could maintain both the high oxygen permeability and structural stability under CO_2 atmosphere; therefore, well-defined DPM may offer excellent stability and relatively high performance [17–19] and several CO_2-tolerant dual-phase oxygen permeable membranes have been reported [20–23]. For instance, Xue et al. [22] made the composites of $60Ce_{0.9}Gd_{0.1}O_{2-\delta}$–$40Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$, whose oxygen permeation flux was up to 0.67 mL $min^{-1}\cdot cm^2$ at 950 °C with pure CO_2 as the sweep gas. Zhu et al. [6] reported that DPM with 25 wt.% $Sm_{1-x}Ca_xCoO_3$ (x = 0, 0.2, 0.4) – 75 wt.% $Ce_{0.8}Sm_{0.2}O_{1.9}$ showed excellent stability, and such improvement was attributed to the less calcium elements doped in the materials than in perovskite membrane. The above studies have proved that DPM could solve the dilemma of the perovskite oxides under CO_2-containing

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* Corresponding author.
E-mail address: wucz@shu.edu.cn (C. Wu).

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atmosphere.

Hence, it is expected that dual-phase oxygen membranes could have promising applications in oxy-fuel combustion for CO_2 capture. A number of studies have shown that Gd-doped ceria (CGO), the oxygen ion conductor, possesses inherently high chemical stability while its oxygen flux is limited by electronic conductivity [24]. It's also known that electronic conducting oxides such as $SrCo_{0.8}Fe_{0.1}Nb_{0.1}O_{3-\delta}$ (SCFN) shows high oxygen permeability [25]. In addition, in 2012, Zhu et al. [26] proposed a new oxygen permeation model based on the theoretical analysis by Virkar [27]. The model can well describe the permeation fluxes of oxygen transport membranes and easily distinguish the distribution of interfacial resistances on both sides and bulk resistance. Therefore, in this study, a series of DPM having the composition of CGO-SCFN with different weight ratios were prepared and the rate-determining step in oxygen permeation through the DPM was studied. In addition, the oxygen permeation ability and structural stability of the membranes were also investigated under He/CO_2 atmosphere. The results show that the 80CGO-20SCFN membrane is CO_2 tolerant and possesses high oxygen permeability.

2. Experimental

2.1. Membrane preparation

Commercial $Ce_{0.9}Gd_{0.1}O_{2-\delta}$ powder was purchased from Xuancheng Jingrui New Materials Co. Ltd., and $SrCo_{0.8}Fe_{0.1}Nb_{0.1}O_{3-\delta}$ oxide was synthesized by the conventional solid-state reaction method [28]. Firstly, stoichiometric amounts of $SrCO_3$, Co_3O_4, Fe_2O_3 and Nb_2O_5 (Purity $\geq$ 99.0%, from Sinopharm Chemical Reagents Co. Ltd) were ball-milled in ethanol, then the mixed powder was dried and pressed into disks under 100–150 Mpa, followed by a calcination at 1230 °C for 10 h. Secondly, the CGO and SCFN powders were mixed with weight ratios of 6:4, 7:3 and 8:2, and the mixtures were isostatically pressed into pellets. Finally, DPM were prepared by sintering the pellets at 1220 °C for 10 h. All the membranes used for oxygen permeation have relative densities no less than 95%.

Before oxygen permeation measurement, the calcined discs were carefully polished with 800 mesh sandpapers to get membranes with the thicknesses of 1.0 mm and 0.6 mm. After polishing and cleaning in ethanol, permeate side of membranes was coated with a porous layer with the same composition as bulk dense DPM to improve the oxygen surface exchange rates. The slurry was made by mixing terpineol and the as-prepared CGO-SCFN powder with a weight ratio of 1:1. Porous layers were calcined at 1220 °C for 5 h. Thickness of porous layer are usually ~10 μm.

2.2. Membrane characterizations

Phase structures of the as-prepared materials were determined by X-ray diffraction (XRD) on a Rigaku D/MAX-2200 diffractometer in the range of 2θ (Cu Kα radiation operating at 40 kV and 200 mA) from 20° to 80°. The surface morphologies of the DPM were observed by a back-scattered scanning electron microscopy (BSEM, FEI Quanta 250 FEG, Germany). TG-DSC experiments were conducted in a flowing atmosphere (the flow gas: 50 mol% CO_2/50 mol %N_2) at a heating rate of 10 °C/min up to 1000 °C.

2.3. Oxygen permeation measurement

The DPM were sealed onto a quartz tube with silver rings at their melting points [2]. The effective inner surface areas of the membrane discs were around 1.3 cm^2. One side of the membrane was exposed to air and the other side was swept by CO_2 or He. The flow rates of the gases were controlled by mass flow controllers. Effluents were analyzed by a gas chromatography (GC 9160). Oxygen permeation fluxes through the membranes were calculated based on the effluent flow rate and the concentrations of oxygen in the effluents. The contribution of molecular O_2 flux from the leakage at high temperatures was subtracted from the overall flux values by measuring the N_2 concentration. Thus, the oxygen permeable fluxes were determined using the equation as follows:

$$J_{O_2} = \left(C_{O_2} - C_{N_2} \times \frac{21}{79}\right) \times \frac{F_{He}}{A} \tag{1}$$

where C_{O_2} and C_{N_2} are measured oxygen and nitrogen concentrations in the gas on the permeate side, respectively, and F_{He} is the flow rate of permeate stream (ml/min) and A is the active membrane area (cm^2). The leakage was no more than 1.0% for all the oxygen permeation experiments.

2.4. Rate-determining step

Oxygen permeation model proposed by Zhu et al. was used for determining the rate-limiting step in oxygen permeation. Oxygen partial pressures in the feed side were adjusted by changing the flow rates of pure oxygen and pure nitrogen and controlled in the range of 0.2–0.9 bar. The flow rate of synthesized air was 100–200 mL min^{-1}. Oxygen partial pressures of the permeate side were adjusted by changing the flow rate of helium (sweep gas) and controlled in the range of 0.005–0.01 bar, corresponding to the helium flow rates of 30–100 mL min^{-1} . Then, total permeation resistance, $r^{tot} = r' + r^b + r''$, can be calculated from the following equation:

$$r^{tot} = -\frac{\Delta\mu_{O_2}^{tot}}{4^2F^2j_{O_2}} = -\frac{RT}{4^2F^2j_{O_2}} ln\frac{P''_{O_2}}{P'_{O_2}} \tag{2}$$

Usually, a simple power function can been used to describe the relationship between interface specific resistance and the oxygen partial pressure by following two equations:

$$r^{tot} = r'_0\left(P'_{O_2}/P_0\right)^{-\frac{1}{2}} + \left(r^b + r''\right) \tag{3}$$

$$r^{tot} = r''_0\left(P''_{O_2}/P_0\right)^{-\frac{1}{2}} + \left(r^b + r'\right) \tag{4}$$

Where r', r'' and r^b are permeation resistances of interface region of feed side, interface region of permeation side and of the membrane bulk, respectively; $-\frac{\Delta\mu_{O_2}^{tot}}{4^2F^2}$ is the total driving force across the membrane. P_0, r'_0 and r''_0 are the oxygen partial pressure of 1.0 bar, area specific resistances of the feed side and permeation side at oxygen partial pressure of 1.0 bar, respectively.

3. Results and discussion

3.1. Microstructural analysis

Fig. 1 presents the XRD patterns of the CGO-SCFN DPM with different ratios after being calcined at 1220 °C for 10 h. The XRD patterns show that the membranes consist of only the flourite CGO phase and the cubic perovskite SCFN phase, indicating that the coexistence of the CGO and the SCFN is stable, and the peaks intensity of the fluorite oxide increases obviously with the increase of its content in the DPM. Zhu et al. [29] reported that barium doped perovskite oxides easily react with ceria to produce $BaCeO_3$, however, due to a higher chemical potential in $SrCeO_3$ than that in