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A CO_2-tolerance oxygen permeable $60Ce_{0.9}Gd_{0.1}O_{2-\delta}$–$40Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ dual phase membrane

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ABSTRACT

A CO_2-tolerant dual phase membrane with composition of 60 wt% $Ce_{0.9}Gd_{0.1}O_{2-\delta}$–40 wt% $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (60CGO–40BSCF) was successfully developed. The 60CGO–40BSCF dual phase membrane showed good reversibility of the oxygen permeation fluxes and good stability in CO_2 atmosphere. A stable oxygen permeation flux of 0.67 mL/min cm^2 was obtained with pure CO_2 as the sweep gas during a 250 h oxygen permeation at 950 °C. The electronic conductivity results confirmed the concept that the electronic conductivity of the BSCF perovskite oxide could be partly reserved in CO_2 atmosphere. Due to the high oxygen permeation fluxes and the good stability in CO_2-containing atmosphere, the 60CGO–40BSCF dual phase membrane has great potential application in oxyfuel techniques for CO_2 capture and storage.

1. Introduction

Recently, CO_2 capture and storage technologies have received great interest for the purpose of reducing the emission of CO_2. Because 30–40% of CO_2 emissions come from coal-fired power plants, technologies for the capture of CO_2 from coal-fired plants have received great interest [1–3]. Nowadays, there are three major concepts for CO_2 sequestration: post-combustion capture, pre-combustion separation and oxyfuel techniques [1,2]. The oxyfuel process, i.e., O_2 instead of air for combustion, has rapidly attracted a number of attentions because of the high thermal efficiency and low capital cost. Mixed oxygen ionic–electronic conducting ceramic membranes (MIECMs) have gained increasing attention due to their potential applications in the oxygen supply to power stations for the oxyfuel combustion according to the oxyfuel concept [4–6]. In the oxyfuel process, a part of the CO_2 is recycled and used as the sweep gas, therefore, the MIECMs that are applied in the oxyfuel process should not only show good oxygen permeation, but also good stability, especially under the CO_2-containing atmosphere [5–10].

In the last decades, intense studies focus on the perovskite oxides with dominant electronic conductivity to obtain high oxygen permeability [11–15]. Among the perovskite membranes, the composition of $(Ba_xSr_{1-x})(Co_{0.8}Fe_{0.2})O_{3-\delta}$ is regarded as state-of-the-art materials in view of their high oxygen permeation fluxes [11,12,16]. Unfortunately, the $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) perovskite membrane is not stable in the CO_2-containing atmosphere [17,18].

In order to solve the dilemma of the perovskite oxides like the BSCF, we developed a CO_2-tolerant dual phase oxygen separation membrane, which is composed of the fluorite oxide $Ce_{0.9}Gd_{0.1}O_{2-\delta}$ (CGO) as the oxygen ionic conductor and a mixed oxygen ionic–electronic BSCF perovskite oxide as the electronic conducting phase. In this dual-phase membrane, oxygen ions could be transported through both phases and electrons could transport through the perovskite phases [19–21].

Although the Sr and Ba ions on the A site tend to form carbonates in CO_2 atmosphere that destroy the structure of perovskite oxides, their electronic conductivity contributor of continuous equipotential passages –O–B–O–B–O– chains might be still maintained because the B site ions such as Co or Fe formed cobalt oxides or ferric oxides, which are still good electronic conductors, so that the network of the electron transmissions could be reserved, as shown in Fig. 1B [17,18,22,23]. Moreover, the oxygen ion conductor (CGO) possesses inherently high chemical stability against the acidic gases and it will not be destroyed in the CO_2, as shown in Fig. 1. Therefore, it is expected that this dual phase membrane could possess both high oxygen permeability and good stability under CO_2 atmosphere.

2. Experimental

2.1. Synthesis of powder and membrane

The $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ powder was synthesized via a combined citrate and ethylenediaminetetraacetic acid complexing method which was described in our previous work [24,25].

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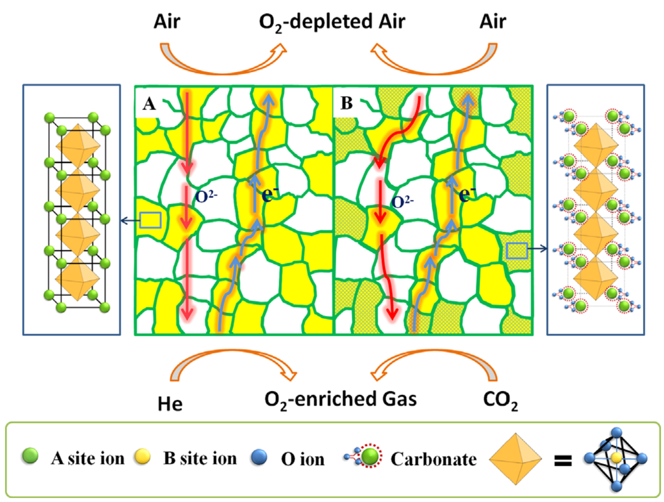

Fig. 1. Diagrams of the novel concept for CO_2-tolerance oxygen permeable dual phase membranes.

Commercial $Ce_{0.9}Gd_{0.1}O_{2-\delta}$ powder (Yitong New Material Co. Ltd., Weifang, China) was used as raw material. The CGO and the BSCF powders were mixed in a mortar at a weight ratio of 60:40 and carefully ground to prepare the 60CGO–40BSCF dual phase oxides. The as-obtained powders were isostatically pressed into pellets in a stainless steel module at 20 MPa, and then sintered at 1100 °C in air for 10 h. The densities of the sintered membranes were determined by the Archimedes method using ethanol. Only those membranes with relative density higher than 95 % were used for oxygen permeation studies.

2.2. Characterization of membrane materials

For the conductivity measurements, two parallel silver wires were glued to the sample with a silver paste for better contact, and then they were calcined at 800 °C in air. The samples were heated in a tubular furnace with ramp rates of 5 °C/min from 100 °C to 950 °C in different atmospheres, and the resistance was measured by an electrochemical workstation (Zahner IM6ex, German) using a dc two-probe method. The phase structures of the sintered disks before and after oxygen permeation were characterized by X-ray diffraction (XRD, Bruker-D8 ADVANCE, CuKα radiation). The spent CGO–BSCF dual phase membrane was observed by a scanning electron microscope (SEM, S-3700N, Japan) and the elemental compositions of the membrane were determined by energy dispersive spectroscopy (EDS).

2.3. Oxygen permeation

The oxygen permeation fluxes through the membranes were investigated by the gas chromatography (GC) method in a home-made high-temperature oxygen permeation cell as shown in Refs. [26,27]. A commercial ceramic sealant (Huitian, Hubei, China) was used to seal the disk-shaped membranes onto the corundum tube. Gases were delivered to the permeation cell by mass flow controllers (MFC, Seven star D08-4F/ZM) calibrated by a soap bubble flow meter. Air was fed to the air side of the membrane, and He/CO_2 was fed to the sweep side. The effluents were directed to an on-line gas chromatograph (GC, Agilent Technologies, 7890A). The flow rates of the effluents were also measured by the soap bubble flow meter. The leakage of the oxygen due to the imperfect sealing at high temperatures was less than 0.5% during all the experiments and it was subtracted when the oxygen permeation flux was calculated. The calculation of oxygen permeation flux was also presented in detail in our previous paper [11,26].

3. Results and discussion

Fig. 2 presents the XRD patterns of the commercial CGO powder, the BSCF powder, the 60CGO–40BSCF dual phase powder after being calcined at 950 °C for 10 h and the 60CGO–40BSCF dual-phase membrane after being sintered at 1100 °C for 10 h. The characteristic peaks corresponding to the BSCF oxides and the fluorite CGO are obvious and no other peaks resulting from undesirable reaction phases can be observed, revealing that the coexistence of the BSCF and the CGO is stable [24,28].

The temperature dependence of the total electrical conductivity of the 60CGO–40BSCF and the BSCF under N_2 and CO_2 atmospheres are presented in Fig. 3. Because the mobility of oxygen ions is much lower than that of the electron holes in N_2 and CO_2 atmospheres, it can be assumed that the measured electrical conductivities represent only the electronic conductivity [29,30]. In both cases, the conductivity variation tendencies of 60CGO–40BSCF and the BSCF are similar. The conductivity increases from 100 °C to 750 °C, presenting a p-type semi-conductivity, and there exists a transition at high temperatures due to the reduction of Fe^{4+} to Fe^{3+} or Co^{4+} to Co^{3+} [29,30]. The highest conductivities of the BSCF and the 60CGO–40BSCF reach 8.2 S/cm and 5.0 S/cm in N_2 atmosphere, and 7.5 S/cm and 4.0 S/cm in CO_2 atmosphere at around 750 °C. Similar results were also found by other researchers [31]. Most importantly, only a slight decrease of the electronic

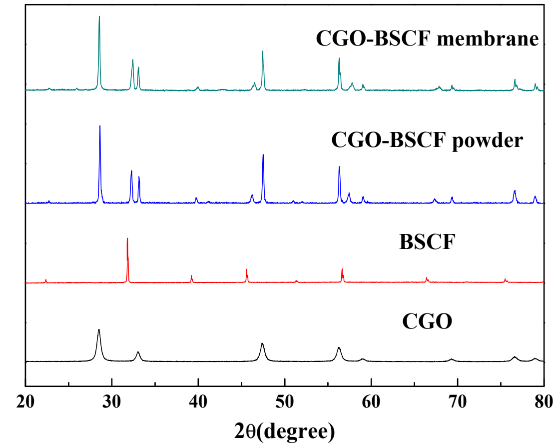

Fig. 2. XRD diffraction patterns of the commercial CGO powder, the BSCF powder, the 60CGO–40BSCF powder calcined at 950 °C for 10 h and the fresh 60CGO–40BSCF dual phase membrane sintered at 1100 °C for 10 h.

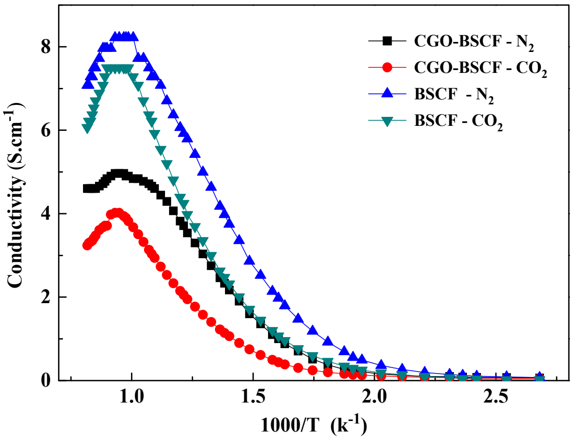

Fig. 3. Temperature dependence of total conductivity of the 60CGO–40BSCF and the BSCF under N_2 and CO_2 atmospheres.