Oxygen permeability and CO_2-tolerance of $Ce_{0.8}Gd_{0.2}O_{2-\delta}$-$LnBaCo_2O_{5+\delta}$ dual-phase membranes

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Abstract

A series of oxygen permeable dual-phase composite oxides 60 wt% $Ce_{0.8}Gd_{0.2}O_{2-\delta}$-40 wt% $LnBaCo_2O_{5+\delta}$ (CGO-LBCO, Ln = La, Pr, Nd, Sm, Gd and Y) were synthesized through a sol-gel route and effects of the Ln^{3+} cations on their phase structure, oxygen permeability and chemical stability against CO_2 were investigated systemically by XRD, SEM, TG-DSC and oxygen permeation experiments. XRD patterns reveal that the larger Ln^{3+} cations (La^{3+}, Pr^{3+} and Nd^{3+}) successfully stabilized the double-layered perovskite structure of sintered LBCO, while the smaller ones (Sm^{3+}, Gd^{3+}, and Y^{3+}) resulted in the partial decomposition of LBCO with some impurities formed. CGO-PBCO yields the highest oxygen permeation flux, reaching 2.8×10^{-7} mol·s^{-1}·cm^{-2} at 925 °C with 1 mm thickness under air/He gradient. The TG-DSC profiles in 20 mol% CO_2/N_2 and oxygen permeability experiments with CO_2 as sweep gas show that CGO-YBCO demonstrates the best chemical stability against CO_2, possibly due to its minimum basicity. The stable oxygen permeation flux of CGO-YBCO under CO_2 atmosphere reveals its potential application in the oxy-fuel combustion route for CO_2 capture.

Key words

oxygen permeability; dual-phase membrane; fluorite; double-layered perovskite; chemical stability; CO_2 capture

1. Introduction

Global warming induced by the massive emission of greenhouse gases, especially CO_2, has aroused increasing anxiety in the past several decades [1,2]. Mixed ionic-electronic conductivity (MIEC) composite oxides have been widely investigated due to their potential applications in many fields such as separating pure oxygen from oxygen-containing gas [3], partial oxidation of methane to syngas [4] and solid oxide fuel cells [5] since the research of $La_{1-x}Sr_xCo_{1-y}Fe_yO_3$ by Teraoka et al. [6] in 1985. MIEC membranes integrated with oxy-fuel combustion in power plants, in which MIEC composites serve as oxygen provider, are proposed as a potential technique to reduce the emission of CO_2 [2,7]. In such an oxy-fuel combustion route, oxygen separated from air by MIEC composites is used for the combustion of fossil fuels, and a part of tail gas which contains large amount of CO_2 is recycled as sweep gas in the oxygen separation process. In this way, the concentration of CO_2 in the tail gas is greatly increased for carbon capture and storage.

Therefore, MIEC composites used in an oxy-fuel combustion route should possess not only good oxygen permeability, but also favorable chemical stability under CO_2 atmosphere.

Key problems restricting the application of MIEC composites in oxy-fuel technology are their poor oxygen permeability in the absence of CO_2. Up to now, the single-phase perovskite composite with ABO_3 chemical formulas and A-site occupied largely by alkaline metals is one of the most popular materials in the family of MIEC composites. Alkaline-earth-metal-containing single-phase perovskite membranes usually show good oxygen permeability, but alkaline-earth metals react easily with CO_2 and form carbonates on membrane surface, which results in the degradation or even failure of oxygen permeability [8,9]. Alkaline-earth-metal-free composites are usually more stable in CO_2, however, these composites usually demonstrate poor oxygen permeability [10]. Under the circumstances, dual-phase MIEC composites composed of ionic conducting (IC) and electronic conducting (EC) phases were proposed. Noble metals such as Pd and Ag were first chosen as EC materials [11]. However, the high cost of noble metals and the poor oxygen permeability have hindered the

further development of such dual-phase composites. In order to reduce the cost of EC phases, some perovskite and spinel oxides with good electronic conductivity were proposed as substitutes for noble metals [12,13]. Unfortunately, these oxides have poor ionic conductivity, therefore they impede the transporting of oxygen ions and thus lead to poor oxygen permeability. Perovskite-type MIEC oxides are now the most popular EC composites due to their excellent electronic conductivity and considerable ionic conductivity [14].

As for IC composites, lanthanides-doped CeO_2 have been widely studied because of their outstanding ionic conductivity, good chemical stability and low thermal expansion coefficient. So far, dual-phase MIEC composites composed of fluorite oxides such as $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ or $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ as IC phases, and perovskite MIEC oxides as both IC and EC phases have been widely investigated [15,16]. In a fluorite-perovskite dual-phase composite, one can take advantage of not only the excellent ionic conductivity and good chemical stability against CO_2 of fluorite oxides, but also the favorable electronic and ionic conductivity of perovskite oxides, and thus a high and stable oxygen permeation flux in CO_2 atmosphere can be expected from this kind of dual-phase composites [17].

Recently, $LnBaCo_2O_{5+\delta}$ (Ln = rare earth elements) has aroused much interest due to its special double-layered structures. In a $LnBaCo_2O_{5+\delta}$ composite oxide, Ln^{3+} and Ba^{2+} cations occupy the A-site lattices orderly, and layers of BaO, CoO_2 and LnO_δ stack successively in a sequence of $|LnO_\delta|CoO_2|BaO|CoO_2|$ with oxygen vacancies located only in the LnO_δ layer [18]. Compared with non-ordered perovskites, the special layered structure of $LnBaCo_2O_{5+\delta}$ can enhance the diffusivity of oxygen ions, and increase the oxygen surface exchange kinetics [19]. $LnBaCo_2O_{5+\delta}$ has excellent electronic and ionic conductivity at intermediate temperatures, and been widely studied as cathodes for intermediate-temperature solid oxide fuel cells [20,21]. Researches show that $LnBaCo_2O_{5+\delta}$ can also be used as the EC phases of dual-phase MIEC composites [22,23]. However, to the best of our knowledge, no literatures have focused on effects of the rare earth elements on their properties as oxygen permeation composites.

In this paper, a series of $Ce_{0.8}Gd_{0.2}O_{2-\delta}$-$LnBaCo_2O_{5+\delta}$ dual-phase oxygen permeable membranes with CGO as IC phase and LBCO as both IC and EC phases were successfully synthesized. The effects of Ln^{3+} cations on their structure/stability, oxygen permeability and chemical stability against CO_2 were systemically investigated by XRD, thermogravimetry-differential scanning calorimetry (TG-DSC) and oxygen permeation experiments.

2. Experimental

2.1. Membranes fabrication

CGO powders were synthesized through a sol-gel route as reported elsewhere [16]. Briefly, Stoichiometric amount of

Gd_2O_3 powders and $Ce(NO_3)_2 \cdot 6H_2O$ were added to distilled water. Excess concentrated nitric acid was introduced until all the Gd_2O_3 powders were dissolved and a homogeneous solution was formed. Afterwards calculated amount of citric acid and EDTA at a molar ratio of citric acid : EDTA : total metal ions = 1.5 : 1 : 1 were added to the mixed solution, followed by the addition of ammonia until its pH reached about 6 and a clear and transparent solution was formed. The mixed solution was heated at 80 °C with vigorous stirring until a dry gel was formed. The dry gel was fired at 350 °C in air to remove the organic compounds, followed by carefully grinding and pre-calcination at 600 °C for 5 h in air. LBCO powders were fabricated through a similar route except that the pre-calcination temperature is 850 °C.

The as-obtained CGO and LBCO powders were weighted at a weight ratio of 60 : 40 and carefully mixed in a mortar for 4 h to ensure the homogeneous distribution of the two powders. The mixed powders were uniaxially pressed into green disks under 150 MPa for 3 min. The green disks were sintered at 1150 °C for 6 h in air with a heating and cooling rate of 3 °C·min^{-1}. The sintered membranes were polished to desired thickness for oxygen permeation experiments by abrasive paper.

2.2. Samples characterization

X-ray diffraction (XRD, Rigaku D/MAX2550 powder diffractometer, Cu K_α radiation, $\lambda = 1.54056$ Å) measurements were carried out in an angle range between 10º and 90º with a step of 0.02º to identify the crystal structures of the as-prepared powders and sintered membranes. The morphology of the membranes were examined by scanning electron microscope (SEM, JEOL-JSM-6700F). In order to study the chemical stability of CGO-LBCO against CO_2, all sintered membranes were crushed and milled into fine powders in a agate mortar and heated in 10 mol% O_2/N_2 or 20 mol% CO_2/N_2 mixture gas from 30 °C to 1100 °C at a heating rate of 10 °C·min^{-1} in a thermogravimetry-differential scanning calorimetry (TG-DSC, NETZSCH STA 449 F3).

2.3. Oxygen permeation flux measurement

Oxygen permeation fluxes through the membranes were measured by an on-line gas chromatography (GC-9160). The oxygen permeation experiments were carried out in a home-made high temperature cell as mentioned in literature [24]. The polished membrane disks were sealed onto a quartz tube with a silver ring softened at 948 °C. No nitrogen was detected in the permeating gas before the oxygen permeation experiments, which ensured that no oxygen could leak through the membrane and contribute to the oxygen permeation fluxes. Compressed ambient air was introduced to the feed side of the membranes at a flow rate of 300 mL·min^{-1}, and He or He/CO_2 mixture gas was used as sweep gas at a flow rate of 100 mL·min^{-1}.