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Synthesis, oxygen permeability, and structural stability of $BaCo_{0.7}Fe_{0.3-x}Zr_xO_{3-\delta}$ ceramic membranes

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ABSTRACT

A series of mixed ionic–electronic conducting materials, $BaCo_{0.7}Fe_{0.3-x}Zr_xO_{3-\delta}$ ($x = 0$–0.12) were successfully synthesized and evaluated as potential ceramic membrane materials for oxygen separation applications. Effects of zirconium content on the crystal structure, internal and surface morphologies, electrical conductivity, structural stability and oxygen permeability of these membranes were systematically studied. A basic perovskite structure was for $x = 0.04$–0.12, and the grain size of the samples gradually decreases with increasing zirconium content. The structural stabilities of the membranes in different atmospheres (H_2, O_2 and CO_2) are significantly improved by substituting an appropriate amount of iron by zirconium. However, increase of the zirconium content also leads to a decrease in the electrical conductivity, which is confirmed by the first principles calculations. With increasing the zirconium content, oxygen permeation flux of the membranes increases and reaches a peak at $x = 0.06$, and then decreases. The highest oxygen permeation flux of 2.7 ml min^{-1} cm^{-2} at 925 °C is achieved by the 1 mm-thick $BaCo_{0.7}Fe_{0.24}Zr_{0.06}O_{3-\delta}$ membrane. With the same zirconium content, samples with larger grain sizes have remarkably higher oxygen permeation flux. Both theoretical and experimental works indicate that the oxygen permeability depends on the combined effect of the oxygen vacancy concentration, grain size and electrical conductivity.

1. Introduction

Mixed ionic–electronic conducting (MIEC) ceramic oxides have attracted research attention due to their potential applications in air separation to produce oxygen [1], in oxy–fuel combustion to capture carbon dioxide [2], in hydrocarbon oxidation [3]. On the other hand, MIEC ceramic oxides could be used as electrodes for gas sensors [4] or solid oxide fuel cells [5]. For oxygen separation, perovskite-type MIEC oxides of ABO_3 composition exhibit the best oxygen permeability due to their remarkable electronic and ionic conductivities over a wide range of temperatures [6,7], making the most promising materials for practical applications.

Teraoka et al. first reported MIEC perovskite-type oxide $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ (SCF) with good oxygen permeability [8]. Subsequently, many researches have been carried out on perovskite-type oxygen permeation materials. However, it is difficult to obtain both high oxygen permeability and good structural stability for perovskite-type materials, which limits their practical applications. In comparison with cobalt-free perovskite-type materials, cobalt-based ones in general have higher oxygen permeation fluxes but poor structural stability under reductive (such as hydrogen-containing atmosphere) and CO_2-containing atmospheres [9–12]. Nevertheless, because of their better oxygen permeability, cobalt-based perovskite-type materials have become one of the most popular researched materials in the family of MIEC membrane materials. Partial or full substitution of the A or B sites in the cobalt-based perovskite-type materials is used frequently to obtain membrane materials with both high oxygen permeability and good structural stability [13–16]. Shao et al. found that both the phase stability and oxygen permeability of SCF membranes could be improved by substituting a certain amount of Sr with Ba [17]. In recent years, cobalt-based perovskite-type materials with full Ba substitution for the A sites have been studied by many researchers and some progresses have been made. For instance, $BaCo_{0.7}Fe_{0.2}Nb_{0.1}O_{3-\delta}$ was successfully synthesized and demonstrated excellent oxygen permeability and high operational stability in a partial oxidation of

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methane membrane reactor [18]. A series of $BaCo_{0.7}Fe_{0.3-x}Nb_xO_{3-\delta}$ (BCFN, $x=0$–0.15) and $BaCo_{0.7}Fe_{0.3-x}Ta_xO_{3-\delta}$ (BCFT, $x=0$–0.2) membranes were systematically investigated in our previous studies [19,20]. We found that the oxygen permeability and stability of the BCFN and BCFT membranes could be enhanced by doping the B sites with a certain amount of Nb and Ta, respectively. In our recent studies of the $BaCo_{0.7}Fe_{0.2}M_{0.1}O_{3-\delta}$ (M=Ta, Nb, or Zr) membranes, a $BaCo_{0.7}Fe_{0.2}Zr_{0.1}O_{3-\delta}$ membrane exhibits the best oxygen permeability; however, its structural stability is unsatisfactory under a CO_2-containing atmosphere [21].

Besides the chemical composition of membrane materials, optimization of the microstructure is another approach to improve the membrane properties. Influence of the grain size on membrane performance has been studied for different materials, although no consensus has been reached so far. Zhang et al. obtained SCF membranes with different grain sizes by varying the sintering temperatures. In their study, oxygen permeation flux increases with a decreasing average grain size [22]. Similar results were observed by Klande et al., in which sintering time was varied to achieve different grain sizes [23]. For $La_{0.5}Sr_{0.5}FeO_{3-\delta}$, $La_{0.1}Sr_{0.9}Co_{0.9}Fe_{0.1}O_{3-\delta}$, and $Ba_{0.95}La_{0.05}FeO_{3-\delta}$, smaller grain size also leads to higher oxygen permeation flux, which may be attributed to the faster diffusion of oxygen ions through the grain boundaries and the enhancement of the surface reaction rate with an increase in the number of grain boundaries [24–26]. On the contrary, $LaCoO_{3-\delta}$, $La_{0.3}Sr_{0.7}CoO_{3-\delta}$, $CaTi_{0.8}Fe_{0.2}O_{3-\delta}$, and $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$, exhibit higher oxygen permeation fluxes with larger grain sizes, suggesting that grain boundaries may act as the barriers for oxygen ionic transport in these materials [27–30]. On the other hand, grain boundaries of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) have been reported to have a negative impact [31] or no significant impact [32,33] on its oxygen permeability.

In this work, a series of $BaCo_{0.7}Fe_{0.3-x}Zr_xO_{3-\delta}$ (BCFZ, $x=0$–0.12) MIEC materials were prepared via sol–gel method. The effects of Zr content on the crystal structure, internal and surface morphologies, and stability of the BCFZ ceramic membranes were systematically investigated. The oxygen permeability of BCFZ membranes was examined under pure He- and CO_2-containing atmospheres. During our research, we found that the grain size of BCFZ membranes changed with the Zr content, which may affect their oxygen permeability. In order to comprehensively explore how Zr-doped content affect the oxygen permeability, the effect of grain size and first principle calculation were also researched.

2. Experimental

2.1. Membrane preparation

$BaCo_{0.7}Fe_{0.3-x}Zr_xO_{3-\delta}$ ($x=0$–0.12) powders were synthesized via sol–gel method. $Ba(NO_3)_2$, $Co(NO_3)_2\cdot6H_2O$, $Fe(NO_3)_3\cdot9H_2O$, and $Zr(NO_3)_4\cdot5H_2O$ were weighted stoichiometrically and dissolved in deionized water under heating and stirring. The necessary amounts of ethylenediaminetetraacetic acid (EDTA) and citric acid were then introduced to the mixed metal nitrate solution. The molar ratio of the total metal ions:EDTA:citric acid are 1:1:1.5. The pH value of the mixed solution was adjusted to 6–8 with the addition of $NH_3\cdot H_2O$. The mixed solution was stirred at 80 °C until a dark purple gel was obtained. The gel was dried overnight at 150 °C, then heated at 350 °C for 5 h, and finally calcinated at 900 °C for 5 h in air. The final powder was pressed into disks and bars using different stainless steel molds under hydraulic pressures of 150–200 MPa, followed by a final sintering at 1110 °C for 8 h in air. BCFZ membranes with $x=0.06$ and different grain sizes were obtained by sintering at 1110 °C for 5 h, 50 h, and 100 h, respectively.

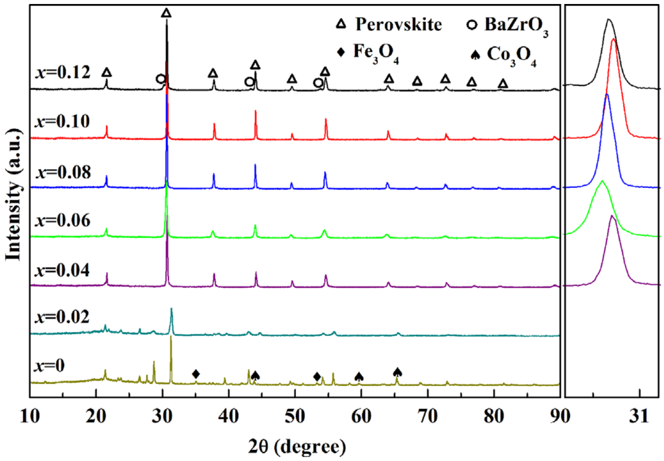

Fig. 1. (Left): XRD patterns of $BaCo_{0.7}Fe_{0.3-x}Zr_xO_{3-\delta}$ ($x=0$–0.12) sintered at 1110 °C in air for 8 h. (Right): the XRD pattern of the amplified perovskete phase around 30°.

2.2. Materials characterization

The crystal structures of the BCFZ membranes were characterized using X-ray diffraction (XRD, Rigaku D/Max-2550) technique equipped with Cu-Kα radiation at 40 kV and 250 mA. The surface and cross-section morphology of the fresh and spent BCFZ membranes were studied with a field emission scanning electron microscope (JEOL JSM-6700F) at an excitation voltage of 15 kV. The structural stability of the BCFZ membranes under a reductive atmosphere was determined with hydrogen temperature-programmed reduction (H_2-TPR) (Micrometrics AutoChem II 2920). The sample powders (about 0.1 g) were prepared by grinding the sintered membranes into powder, treating the powders in a flow of pure Ar at 300 °C for 10 min, and then cooling them to 50 °C. The H_2-TPR experiments were performed by increasing the temperature from 100 to 900 °C at a rate of 10 °C min^{-1} in a gaseous mixture of 10-mol%-H_2/Ar with a flow rate of 30 ml min^{-1}. The oxygen desorption properties of these membranes were investigated with oxygen temperature-programmed desorption (O_2-TPD) experiments (Micrometrics AutoChem II 2920). The sample powders (about 0.5 g) were pretreated by heating to 120 °C for 10 min in a flow of pure He, with the temperature slowly decreased to 50 °C. The O_2-TPR experiments were performed by increasing the temperature from 50 to 1000 °C at a rate of 10 °C min^{-1} in pure He with a flow rate of 30 ml min^{-1}. The structural stability of these membranes was investigated with TG-DSC (NETZSCH STA 449 F3 Jupiter). The sample powders (about 30 mg) were heated from 40 to 1150 °C and from 40 to 1000 °C in 10-mol%-CO_2/N_2 and 10-mol%-O_2/N_2 atmospheres, respectively, at a rate of 10 °C min^{-1}. The electrical conductivity was measured using four-terminal DC method on sintered bars in Air or pure Ar atmosphere. The temperature increased from 100 to 900 °C at a heating rate of 5 °C min^{-1} and the interval between two measurements was 50 °C. For each datum acquisition, 15 min was allowed for the conductivity stabilization.

2.3. Experimental setup

The integrated installation used to investigate the oxygen permeability of the synthesized disk-shaped membranes was described in our previous work [34–36]. Prior to the test, the membrane was uniformly polished with 180 and 800 mesh emery paper on both sides to a thickness of 1.0 mm, then sealed into the