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Structure, electrical conductivity and oxygen permeability of $Ba_{0.6}Sr_{0.4}Co_{1-x}Ti_xO_{3-\delta}$ ceramic membranes

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ABSTRACT

Cubic perovskite oxides, $Ba_{0.6}Sr_{0.4}Co_{1-x}Ti_xO_{3-\delta}$ (BSCT, $x = 0.12–0.30$) are prepared by conventional solid state reaction process as oxygen permeation membranes. The effects of Ti-doping on the crystal structure, electrical conductivity and oxygen permeability are investigated. The chemical stability in low oxygen partial pressure atmospheres is enhanced by Ti-doping. The partial substitution of Ti for Co is charge-compensated by the reduction of oxygen vacancy concentration in BSCT. Both the electrical conductivity and the oxygen permeation flux of BSCT decrease with Ti doping level. The large bonding energy of Ti–O and the decreased lattice free volume with Ti substitution lead to increased activation energy of oxygen permeation, which, combined with the decreased oxygen vacancy concentration, is responsible for the decreased oxygen permeation flux. Nevertheless, sufficiently high permeation fluxes, ca. 2.12 and 1.46 $mL\ cm^{-2}\ min^{-1}$ at 900 °C, are obtained for the samples with $x = 0.12$ and 0.30, respectively, which were comparable to that of the well known $Ba_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF5582) material. Furthermore the BSCT material shows much better phase stability compared to BSCF5582 material under oxygen permeation condition. The prepared BSCT materials are promising candidates for oxygen separation or POM applications.

1. Introduction

The perovskite oxides were dubbed as “inorganic chameleon” due to their rich diversity of chemical compositions and wide applications [1–8]. One family of these materials was used as oxygen permeation membranes [1–5,9–11] since that they can transport both the oxygen ion and the electron. Among this family, the materials with cubic perovskite structure were found to be the favorable candidates due to their high ionic conductivity, which was attributed to the high symmetry of the structure and thereby the relatively open path for ion transportation [9]. $BaCoO_3$ was found to be a suitable parent material for high performance oxygen permeation materials owing to the large free lattice volume and the weak Co—O—Co bond [10,11]. $BaCoO_3$, however, has a drawback of poor phase stability. At room temperature, $BaCoO_3$ takes the hexagonal structure, which almost does not have the ability to transport the oxygen ion [12]. With increasing temperature, the hexagonal structure will transform into cubic structure, according to the results by Yoshiya et al. [9], there will be about 10% of volume reduction accompanying with the phase transformation, which is sufficient to cause the cracking of an actual dense membrane. Meanwhile, the maintenance of excellent chemistry stability is the other challenge for $BaCoO_3$-based materials since that they always show poor chemistry stability when they were exposed to reducing atmosphere [10,13]. In order to improve its phase stability and chemistry stability, an effective approach is to modify the lattice structure of $BaCoO_3$ by doping at the *A*- or/and *B*-sites.

The existence of hexagonal structure can be partially attributed to the large tolerance factor $t = (r_A + r_O)/\sqrt{2}(r_B + r_O)$ of $BaCoO_3$ (higher than 1) [14,15], owing to the huge size of Ba^{2+} $r(CN = 12) = 1.61$ Å [16]). Thus, the substitution of small size ion for Ba, such as Sr, will make the tolerance factor *t* approach to 1.0, which will help to improve the phase stability [13]. For instance, $BaCo_{1-x}Fe_xO_{3-\delta}$ exists in hexagonal structure at room temperature [10,11,17], while $Ba_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ could take the cubic structure [18,19]. Taking into account the fact that most of the deterioration of $BaCoO_3$-based membranes in reducing atmospheres is due to the reduction of *B*-site ions, it is an effective strategy to improve the long term operational stability by substituting the *B*-site ion, Co, with some stable and high valence metal ions, such as Nb^{5+} [10], Ti^{4+} [20], and Zr^{4+} [17]. Considering that the strontium titanate was usually used as the anode materials (fuel electrode with strong

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reducing atmosphere) for solid oxide fuel cell (SOFC) [21–24], the introduction of Ti to the *B*-site of the $BaCoO_3$ may be a feasible way to improve the chemistry stability of the membrane. In this work, Sr, and Ti were chosen as the *A*- and *B*-site dopants, respectively, and thus a new serial material $Ba_{0.6}Sr_{0.4}Co_{1-x}Ti_xO_{3-\delta}$ (BSCT, $x = 0.10–0.30$) for oxygen permeation membrane was designed. The electronic conductivity, oxygen nonstoichiometry, oxygen permeability, and chemistry stability of BSCT materials were investigated. In order to make a comparison, the well known $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_\delta$ (BSCF5582) material was also prepared and investigated.

2. Experimental

The powders of $Ba_{0.6}Sr_{0.4}Co_{1-x}Ti_xO_{3-\delta}$ (BSCT, $x = 0.10–0.30$) were prepared by conventional solid state reaction process, with $BaCO_3$, $SrCO_3$, TiO_2 and $Co(CH_3COO)_2{\cdot}4H_2O$ (all A.R. purity) as the raw materials. After accurately weighted, the raw materials were mixed by ball-milling at a rotational speed of 400 r min^{-1} for 2 h. Ethyl alcohol was used as the milling medium. After being dried, the obtained powders were sieved (140 mesh), and then calcined at 900 °C for 10 h in air. The so-obtained powders were ball-milled again for another 2 h, and then pressed into disks ($\Phi 19 \times 1.5$ mm^2) and bars ($4 \times 7.5 \times 42$ mm^3) under a uniaxial pressure of 110 MPa with appropriate amount of PVA (1 wt.%). Then, the green samples were sintered in air at 1115 °C for 10 h with both heating and cooling rates of 3 °C min^{-1}. The BSCF5582 material was prepared from $BaCO_3$, $SrCO_3$, Fe_2O_3 and $Co(CH_3COO)_2{\cdot}4H_2O$ by the same method, but sintered at a higher temperature, 1150 °C, to achieve the similar relative density with BSCT samples. Phase structures of the as-prepared materials were determined by X-ray diffraction (XRD, RIGAKU D/max-A diffractionmeter), using Cu-K_α radiation as the X-ray source. A Cambridge S250-MK2 scanning electron microscope (SEM) was employed to observe the microstructure of the sintered samples. Only the samples with a relative density higher than 90% were employed to study the electrical and oxygen permeability properties. Thermo-gravimetric analysis (TG, TA Instruments TGA2050) was performed on selected BSCT samples in air at a flow of 90 mL min^{-1} with a heating rate of 10 °C min^{-1}.

The electrical conductivity of samples was measured by four-terminal DC method in different atmospheres from 200 to 900 °C at a heating rate of 5 °C min^{-1}. And the oxygen permeation properties of the BSCT materials were investigated by gas chromatography (GC), as previously described in detail [11]. The room temperature and the high temperature oxygen nonstoichiometry of the samples were measured by iodometry titration technique.

3. Results and discussion

3.1. Phase structure and stability

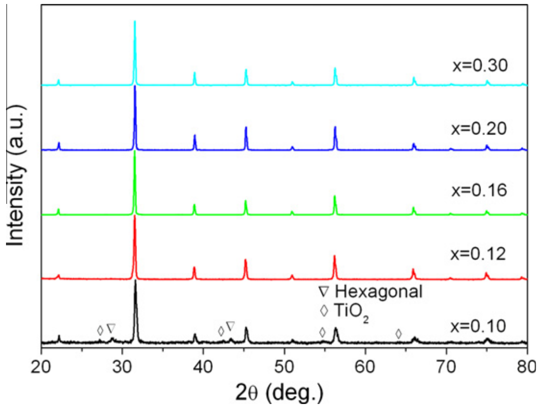

Fig. 1. XRD patterns of $Ba_{0.6}Sr_{0.4}Co_{1-x}Ti_xO_{3-\delta}$ ($x = 0.10–0.30$) after being calcined at 1115 °C in air for 10 h.

Table 1
Calculated lattice parameter and cell volume of $Ba_{0.6}Sr_{0.4}Co_{1-x}Ti_xO_{3-\delta}$ ($x = 0.12–0.30$).

x	Lattice parameter/Å	Cell volume/Å^3
0.12	4.0043	64.21
0.16	4.0028	64.13
0.20	4.0015	64.07
0.30	4.0007	64.03

Fig. 1 shows the room temperature XRD patterns of $Ba_{0.6}Sr_{0.4}Co_{1-x}Ti_xO_{3-\delta}$ after being calcined at 1115 °C in air for 10 h. For the sample with low Ti doping level ($x = 0.10$), the cubic perovskite structure is the dominant phase, however, some diffraction peaks corresponding to hexagonal structure and TiO_2 were found at the same time. Considering that the sample without Ti-doping, for example, $Ba_{0.5}Sr_{0.5}CoO_{3-\delta}$ [25], usually takes the hexagonal perovskite, Ti doping at the Co-site should remarkably stabilize the cubic structure down to room temperature. However, a 0.1 mol Ti-ion in $Ba_{0.6}Sr_{0.4}Co_{1-x}Ti_xO_{3-\delta}$ was insufficient. A single cubic perovskite structure was formed for samples with a Ti doping level ranging from 0.12 to 0.30. The calculated parameters and cell volumes were list in Table 1. The lattice parameter and the cell volume decreases slightly with increasing Ti doping level. Because that the ionic radius of Ti^{4+} (${}^{VI}r_{Ti^{4+}} = 0.605$ Å) was lager than that of Co ions (${}_{HS}{}^{VI}r_{Co^{4+}} = 0.53$ Å, ${}_{HS}{}^{VI}r_{Co^{3+}} = 0.61$ Å, ${}_{LS}{}^{VI}r_{Co^{3+}} = 0.545$ Å) [16], it is a little unaccountable for the decreased lattice parameter. It is well known that the formation of oxygen vacancies will result in lattice expansion [26–31]. Thus, the effect of Ti-doping on the oxygen nonstoichiometry is quiet important, and was studied by the iodometry titration technique. The oxygen nonstoichiometry measurement results were list in Table 2. It is revealed that the oxygen nonstoichiometry (δ) decreases with increasing Ti content. The reduction in oxygen vacancy concentration will cause the lattice contraction [26,28,29–31], hence resulting in the decrease in lattice parameter. The two opposite factors, the substitution by large size ion and the decrease of oxygen vacancy concentration, make the lattice parameter change not evidently.

The oxygen nonstoichiometry at high temperature (800 °C) was also measured in this work. The sintered samples of $Ba_{0.6}Sr_{0.4}Co_{1-x}Ti_xO_{3-\delta}$ ($x = 0.12–0.30$) were heat-treated at 800 °C in air for 2 h to achieve oxygen balance, and then were quenched to room temperature in order to maintain the structure state of BSCTs at high temperature. The measurement results were list in Table 2. The oxygen nonstoichiometry at 800 °C is higher than that at room temperature, revealing the lattice oxygen loss with temperature. The oxygen vacancy concentration still decreases with increasing Ti content, while the reduction tends to be much more sluggish ($\Delta\delta$ decreases with increasing Ti content), which indicates that Ti-doping mitigates the lattice oxygen loss at elevated temperature, i.e. increases the structure stability of the materials. This can be well reflected by the TG results, as illustrated in Fig. 2. Sample with $x = 0.3$ exhibits a slow weight loss compared to sample

Table 2
Oxygen nonstoichiometry (δ) and average valence of Co ions in $Ba_{0.6}Sr_{0.4}Co_{1-x}Ti_xO_{3-\delta}$ ($x = 0.12–0.30$), measured by iodometry titration technique.

x	δ			Average valence of Co ions	
	R.T.	800 °C	$\Delta\delta$	R.T.	800 °C
0.12	0.410	0.455	0.045	3.068	2.965
0.16	0.390	0.427	0.037	3.071	2.983
0.20	0.358	0.391	0.033	3.105	3.022
0.30	0.309	0.335	0.026	3.117	3.043