Available online at www.sciencedirect.com

Materials Letters 59 (2005) 2285–2288

materials letters

www.elsevier.com/locate/matlet

Oxygen permeability and structural stability of Zr-doped oxygen-permeable $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ membrane

Hui Lu, Zengqiang Deng, Jianhua Tong, Weishen Yang*

State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, P.O. Box 110, Dalian 116023, P.R. China

Received 8 October 2004; accepted 6 March 2005

Abstract

Oxygen-permeable ceramic membrane materials of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCFO) and Fe-substituted partially $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.1}Zr_{0.1}O_{3-\delta}$ (BSCFZO) were synthesized by solid state reaction method. The BSCFO material possess purely cubic perovskite structure, while minor impurity phase $(Ba,Sr)ZrO_3$ exists in the perovskite-type BSCFZO material. Oxygen permeability of these dense membrane disks was measured at different temperatures (973–1123 K). The reduced oxygen permeability of BSCFZO was resulted from the decrease of the oxygen vacancy concentration and ionic conductivity due to the dissolution of Zr^{4+} in the B-sites of BSCFO. However, good stability of oxygen permeation of BSCFZO membrane was achieved at the temperature lower than 1123 K. Structural stability of the BSCFZO material was studied by the high temperature XRD technique, which demonstrated that its stability was significantly improved when the Fe ions in the B-sites of BSCFO were substituted partially by Zr^{4+} ions.

Keywords: Ceramics; Membrane; Oxygen permeability; Crystal structure; Stability

1. Introduction

Perovskite-related solid state oxides based on the strontium cobaltite ($SrCoO_{3-\delta}$) and strontium ferrite ($SrFeO_{3-\delta}$) were of considerable interests as material of ceramic mixed-conducting membranes for the high purity oxygen separation and partial oxidation of light hydrocarbons [1–6]. The mixed-conductor involved the simultaneous transport of both ionic and electronic charge carriers. In the presence of an oxygen potential gradient, oxygen ions can be mobile through the material without any external electrodes or circuits [2]. Meanwhile, this system had an advantage in simple structure, no consumption of electric energy and high purity in the obtained oxygen, since no other gases (such as nitrogen) could be permeable. Along with predominant electronic conductivity, these mixed-conducting materials exhibited a high level of oxygen ionic diffusion [2,7]. One of the highest known levels of ionic conduction and oxygen permeability was characteristic of perovskite-type $SrCo_{1-x}Fe_xO_{3-\delta}$ (x=0.2–0.35) [1–4]. For practical application, mixed conducting oxygen-permeable membrane must possess sufficiently high oxygen permeability and sustainable structural stability to withstand harsh conditions (syngas, carbon oxide, etc.). However, these ceramics possessed a number of significant disadvantages, including high thermal expansion coefficients, insufficient mechanical strength, and phase decomposition/segregation on the reduced oxygen partial pressures and temperatures [2,7–9].

Attracted by the usually high permeability of $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ (SCFO) material, many researchers had studied extensively the physic-chemical properties, such as the surface exchange kinetics, nonstoichiometry, and phase stability [1–6]. Unfortunately, it was found that the material has very limited chemical and structural stability in the reducing environment [5,6]. Proper substitution of metal ions in SCFO might lead to improvement in phase stability or oxygen permeability. Recently, we had developed

---

* Corresponding author. Tel.: +86 411 84379073; fax: +86 411 84694447.

E-mail address: yangws@dicp.ac.cn (W. Yang).

0167-577X/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.matlet.2005.03.004

$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCFO) membrane material with improved oxygen permeability and phase stability [9]. However, the decay in the oxygen permeation stability of BSCFO occurred at the temperature lower than 1123 K, which was caused by phase transition and surface segregation of the BSCFO membrane [9].

Our interests for partially substituted BSCFO perovskite material are associated with the improvement of mechanic, structural, and stable performance of it [8,10–12]. In the present work, BSCFO and Zr-doped $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.1}Zr_{0.1}O_{3-\delta}$ (BSCFZO) membrane materials were synthesized by solid state reaction method, and oxygen permeability and stability of these membranes were studied. The structural stability of BSCFZO material was significantly improved as confirmed by the high temperature XRD technique.

2. Experimental

$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCFO) and Fe-substituted partially $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.1}Zr_{0.1}O_{3-\delta}$ (BSCFZO) powders were synthesized using solid state reaction method with appropriate amounts of metal oxides, followed by milling and calcination at different temperatures for 10 h. Monoaxially pressed membrane disks (diameter ~17 mm, thickness 1–2 mm) were sintered in SiC muffle oven at 1423 K for 5–10 h, and about 90% relative density for these membrane disks were obtained.

The crystal structure of the powders and sintered membranes were characterized by XRD (Cu Kα, 0.1542 nm, Rikagu, Japan) in the 2θ range of 10–80°. The XRD output power was 30 kV × 15 mA. The high temperature XRD (HT-XRD) experiments were performed by using a RINT D/MAX-2500/ PC XRD instrument (Cu K_a Rigaku, Japan), which was equipped with a Rigaku PTC-30 heating unit. The HT-XRD output power was 40 kV × 100 mA, and the heating rate of the sample was 5 K/min. The temperature was held constant from the room temperature to 1373 K with an accuracy of about ± 1 K for the given values.

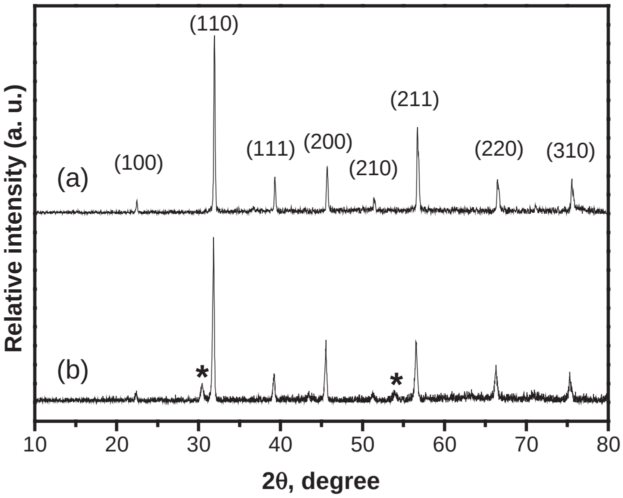

Fig. 1. The room temperature XRD patterns of sintered BSCFO and BSCFZrO membrane disks. (a) BSCFO and (b) BSCFZO, *: $(Ba,Sr)ZrO_3$ phase.

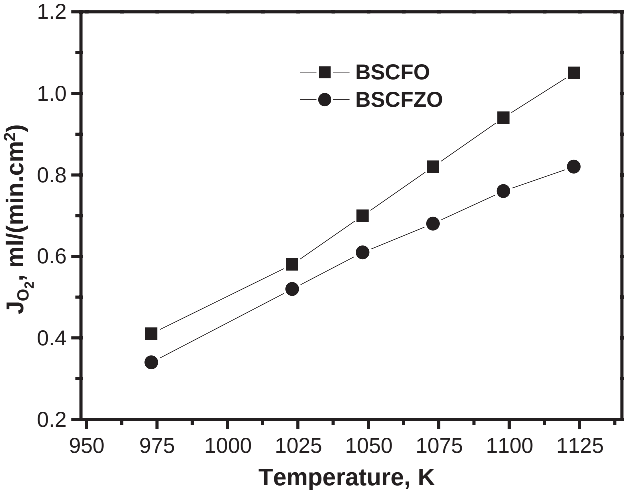

Fig. 2. Temperature dependence of oxygen permeation fluxes of BSCFO and BSCFZO ceramic membranes (thickness, 1.46 mm).

Oxygen permeation fluxes were measured for the sintered dense membranes, which had been sealed to the stainless steel tube using two special high-temperature ceramic sealants. The leakage was below 5% for all measurements, and the calculated oxygen permeation fluxes were corrected based on the measured leakage. Oxygen partial pressure difference across the membranes was established by using air on the primary side and pure He gas on the secondary permeable side. The air flow rate was kept at 150 ml/min, and He flow rate was 40 ml/min on the permeated side. The effective membrane surface area was 0.80–1.0 cm^2. The oxygen permeation fluxes were calculated from gas chromatography analysis (GC, Agilent 6890, equipped with TCD and a 13 × molecule sieve column) of O_2 and possible N_2 in the effluent of the permeated side of the membrane disc [9].

3. Results and discussion

Fig. 1 gives the XRD patterns of the sintered BSCFO and BSCFZO membrane disks. The XRD pattern of BSCFO shows that all diffraction peaks can be given a Miller index of a cubic structure (see Fig. 1a), indicating that the sample had a single cubic perovskite phase. The lattice parameter (a) is 0.3977 nm, which is in good agreement with that (a=0.3980 nm) of BSCFO prepared by the improved EDTA-citric acid complexing method [9]. The lattice parameter is larger than that of SCFO (a=0.3863 nm), and it might be due to the larger ion size of Ba^{2+} (175 pm) than that (158 pm) of Sr^{2+}. While for the BSCFZO material (Fig. 1b), minor impurity phase $(Ba,Sr)ZrO_3$ exists in it.