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Investigation of phase structure, sintering, and permeability of perovskite-type $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ membranes

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Abstract

The high temperature phase structures of the perovskite-type oxide $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) were characterized by in situ high-temperature X-ray diffraction, which revealed that BSCF exhibits a good phase reversibility and structure stability in air from room temperature to 1273 K. The XRD patterns of BSCF oxide at 1173 K in different atmospheres (air, 2% O_2 in Ar and pure Ar) indicated that BSCF possesses an excellent phase stability at high temperatures not only in air but also in pure Ar. From the plot of the lattice constant against the temperature, the thermal expansion coefficient of BSCF was determined to be $11.5 \times 10^{-6}\,K^{-1}$, which is smaller than that of $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ (SCF) ($17.9 \times 10^{-6}\,K^{-1}$). Microstructures of the membranes sintered under different conditions were characterized by scanning electron microscopy (SEM). The effect of microstructure on the oxygen permeation flux through BSCF was observed by measuring the oxygen permeation flux using samples sintered under different conditions. The oxygen permeation flux increased considerably with the increase of the grain size of the membrane.

Keywords: Membrane; Oxygen separation; Mixed conductor; Perovskite

1. Introduction

Mixed ion and electron conducting membranes have attracted much interest in the last decades due to their potential applications in pure oxygen separation [1,2], and in the field of chemical processing, including partial oxidation of natural gas to syngas [3–6], oxidative coupling of methane to value-added products such as ethane/ethylene [7–11], selective oxidation of hydrocarbons [12–14], waste reduction and recovery [15]. Among the mixed-conducting ceramic membranes, perovskite-type (ABO_3) ceramic membranes exhibit the highest oxygen permeability due to their highest ionic and electronic conductivity. Teraoka et al. [16,17] were the first to report high oxygen permeation flux through several $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ perovskite membranes. The oxygen permeation flux through the membranes increases with increasing Sr and Co contents and the composition $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ (SCF) was found to exhibit the largest oxygen permeation flux of ca. 1×10^{-6} mol/s cm^2 at 1173 K. Unfortunately, it was found that this material has very limited chemical and structural stability in a reductive condition [18]. Proper substitutions of metal ions of the A-site in SCF may improve the phase and structure stability and/or oxygen permeability.

$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) was developed by partially substituting Sr in SCF by Ba which has a larger ion radius but the same valence state as Sr [19]. It was found that the phase stability of the membrane was remarkably improved while the oxygen permeation was still kept at a high level. The BSCF membrane was widely studied for oxygen separation [2,19] and as a membrane reactor for the partial oxidation of methane to syngas [20], and for the selective oxidation of light hydrocarbons [12,13,21]. But there are no information on the sintering behaviour of BSCF and in situ phase structures at high temperatures. It is very important to investigate the effect of sintering temperature and dwelling time on the microstructure because it could influence the

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oxygen permeability. On the other hand, the in-situ phase structures at elevated temperatures are important for the understanding of the stability of the membrane during oxygen permeation.

In this paper, we investigated the in situ phase structures of BSCF at high temperatures and the influence of the sintering conditions (temperatures and dwelling time) on the development of microstructures as well as on the oxygen permeation of BSCF membranes.

2. Experimental

The BSCF oxide powder was synthesized by a combined citrate and EDTA complexing method. Detailed information for the preparation of BSCF oxide powder can be found in reference [19]. The powders were pressed under 16 atm to prepare "green" membranes which were sintered at temperatures between 1273 and 1473 K for 5 h to study the effect of the sintering temperature on the microstructure of the membrane. Furthermore, the "green" membranes were also sintered at 1423 K between 0 and 50 h to investigate the effect of dwelling time (the time hold at an indicated temperature is defined as the dwelling time) on the membrane microstructure. During sintering, the membranes were heated to the indicated temperatures with a heating rate of 2 K/min and a cooling rate of 3 K/min.

The crystal structures and lattice constant of the BSCF perovskite were characterized by in situ high-temperature X-ray diffraction (PHILIPS-PW1710) using Cu Kα radiation. The sample was tested in a high temperature cell (Bühler HDK 2.4 with REP 2000) with a heated Pt sample holder up to 1273 K in different atmospheres (air, 2% O_2 in Ar and Ar). The heating and cooling rates amounted to 5 K/min. At each temperature step, the temperature was hold for 70 min. Data were collected in a continuous scan mode in the range of 20–90° with intervals of 0.05°. The peaks of Pt were used as an internal standard to calculate the lattice constant of the BSCF perovskite. The microstructures of membranes were observed by scanning electron microscopy (Jeol-JSM-6700F). The grain size distribution has been estimated from series of secondary electron micrographs by putting a threshold on an 8-bit gray scale that is implemented in the Image J software. Experimental densities were estimated from the dimensions and the masses of the sintered disks. The relative densities of the samples were estimated with the reference to the theoretical density of 5.81 g/cm^3, which was calculated from the lattice constant of the BSCF powder at room temperature.

The oxygen permeation was conducted on a self-made high temperature oxygen permeation cell, as shown in Fig. 1. The membrane was sealed on a quartz tube (Ø = 16 mm). Another quartz tube (Ø = 24 mm) served as the air side of the permeator. A tubular furnace was used to heat the permeator. The temperature was controlled by a microprocessor temperature controller (Eurotherm) within ±0.5 K of the set points and monitored by a K-type thermocouple encased near

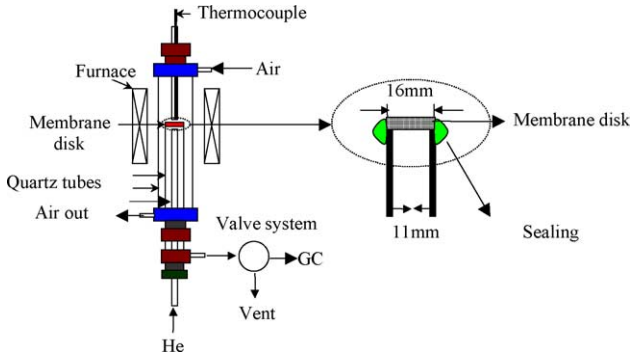

Fig. 1. Scheme of the membrane reactor for oxygen permeation at high temperatures.

the discs. A ceramic-glass powder (Keramik-Glasur, UHLIG) was used as the ceramic binding agent to seal the disk onto a quartz tube at 1313 K. The inlet gas flow rates were controlled by mass flow controllers (Bronkhorst). Air was fed to the air side of the permeator and high purity helium (>99.995%) and 0.46 ml/min Ne (>99.995%) as an internal standardization gas were fed to the sweep side of the permeator. The effluents were analyzed by a gas chromatograph (Agilent 6890) equipped with a Carboxen 1000 column (Supelco). The total flow rate of effluents can be calculated from the change in the Ne concentrations before and after the permeator. Nitrogen was also determined in the effluents by the gas chromatograph because of the slight imperfections of the sealing. Due to the N_2 traces of the corresponding amount of O_2 was subtracted when the O_2 permeation flux was calculated. The relative leakage oxygen was found to be less than 0.5%.

3. Results and discussion

In situ high temperature XRD technique provides an effective and direct way to characterize the high temperature phase structure during increasing and decreasing temperatures. Fig. 2 shows the XRD patterns of BSCF oxide in air as the temperature was increased from 303 to 1273 K indicating that this material remained in its perovskite structure over the examined temperature range. The XRD patterns during temperature increase and decrease are almost the same. In turn, this means that BSCF exhibits good phase reversibility and structure stability in air at high temperatures.

During the oxygen permeation experiments, one side of the membrane was exposed to air (higher oxygen partial pressure); the other side of the membrane was exposed to Ar or He (lower oxygen partial pressure). The phase stability of BSCF in air alone is not sufficient to reflect its actual stability as a candidate for oxygen separation. Therefore, it is necessary to study the high temperature phase stability of BSCF in a lower oxygen partial pressure, e.g., 2% O_2 in Ar or pure Ar. The XRD pattern of BSCF powder at 1173 K in the atmospheres of different oxygen partial pressures shows that BSCF oxide can remain its perovskite structure both in