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Re-evaluation of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ perovskite as oxygen semi-permeable membrane

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Abstract

$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF), a mixed oxygen ionic and electronic conducting ceramic derived from $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ (SCF), was re-evaluated for its possible application as an oxygen semi-permeable membrane and membrane reactor for partial oxidation of light hydrocarbons. The partial substitution of Sr^{2+} with Ba^{2+} in SCF led to an increase in the phase stability of the cubic perovskite structure. Both BSCF and SCF were found to have high oxygen nonstoichiometry. However, BSCF possessed a higher oxygen nonstoichiometry than SCF at room temperature, but a similar value at high temperatures. This resulted in the lower chemical expansion for BSCF than SCF. The doping of Ba^{2+} in SCF led to the decrease of the electronic conductivity, but an increase in the oxygen ionic conductivity. The oxygen permeation study of the BSCF membrane demonstrated that the permeation rate was mainly rate-determined by the slow surface exchange kinetics at the oxygen lean side (or reaction side) membrane surface. The high ionic conductivity and the slow surface exchange kinetics resulted in the surface oxygen partial pressure at the reaction side membrane surface to be much higher than the surrounded atmosphere, therefore protecting the BSCF membrane from reduction.

Keywords: Perovskite; Ceramic membrane; BSCF; Oxygen permeation; Mixed conductivity

1. Introduction

The oxygen semi-permeable, dense ceramic membranes, based on the composite oxides with mixed oxygen ionic and electronic conductivity at high temperature, have been received considerable attention during the past decade [1–10]. An ever increasing interest in such membranes is driven from their intrinsic advantages for oxygen generation. In comparison with the cryogenic oxygen separation process, the oxygen production based on the conducting ceramic membrane is simpler, more energy-saving, and provides a continuous production of oxygen with infinite selectivity. Furthermore, the conducting membranes can also act as catalytic membrane reactors for the partial oxidation of hydrocarbons to value-added products with increased selectivity and improved operation safety by avoiding of direct mixing of fuel with molecular oxygen.

Since Teraoka et al. first reported the remarkable high oxygen permeation flux through the ceramic disks based on the $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ (LSCF) perovskite oxides in the 1980s [11,12], cobalt-contained perovskite membranes have been widely investigated [13–20]. The LSCF membrane is currently cited as a typical example of the mixed conducting ceramics with high oxygen permeability. However, the practical application of cobalt-based perovskite membranes has been doubted by some researchers [21,22] because of two main drawbacks. First, such materials usually have a high thermal expansion coefficient, which may introduce high internal stress across the membrane reactor under asymmetric atmospheres. Cracks are then easily formed, especially under a large oxygen gradient, which could result in the failure of the membrane during the operation [23]. Secondly, they usually have low chemical stability [24]. It was found that the perovskite structure could start to collapse at an oxygen partial pressure as high as 10^{-8} atm [25], although the dopant might also have a significant impact on their phase stability [26,27]. For the coupling reaction, such as the methane partial oxidation to syngas, the oxygen partial

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pressure can be as low as 10^{-19} atm [25]; cobalt ion is intrinsically unstable under such a reduced atmosphere. The reduction of cobalt ions to metal could take place and destroy the material's phase structure and simultaneously the oxygen permeability. Therefore, instead of trying to improve the phase stability of cobalt-based conducting membranes via the strategy of doping, some researchers are trying to develop new cobalt-free perovskite materials with intrinsically improved structural and chemical stability, such as La–Sr–Ga–Fe [28], Be–Ce–Fe [29] and Ba–Sr–Zn–Fe [30]. However, thus far, none of the oxygen permeation fluxes could reach the level of cobalt-contained materials. On the other hand, although the cobalt-based materials are generally recognized to have low chemical stability, long-term operation stability of such membrane reactors have been reported in the literature [31–33], illustrating that cobalt-based mixed conducting membranes are able to operate stably under the stringent partial oxidation condition. Among the various cobalt-based oxygen separation membrane compositions, BSCF, as first reported by Shao et al. [34], have attracted much interest due to its ultrahigh oxygen permeability and favorable structural stability. Recently, Shao et al. also found out BSCF to be an excellent cathode material for intermediate-temperature solid oxide fuel cells [35].

In this paper, we present a detailed re-evaluation of the BSCF membrane. The main purpose is to have a more clear illumination of its feasibility as the oxygen separation membrane and partial oxidation membrane reactor. The reason for their stable operation under a highly reducing atmosphere and the high thermal expansion coefficient is discussed.

2. Experimental

$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF)/$SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ (SCF) membranes were prepared by the powder/pressing method. The corresponding composite oxide powders were synthesized by a combined citrate and EDTA complexing method. $Ba(NO_3)_2$, $Sr(NO_3)_2$, $Co(NO_3)_2{\cdot}6H_2O$ and $Fe(NO_3)_3{\cdot}6H_2O$ (analytical grades) were used as the raw materials for metal sources with EDTA and citrate both served as the complexing agents. The detail preparation procedure can be found elsewhere [31]. The synthesized powder was pressed into disk shape membranes in a stainless steel mold (15 mm in diameter) under a hydraulic pressure of approximately 1.5×10^8 Pa. These green disk-shape membranes (~1.5 mm in thickness) were sintered in an electrical oven at 1130–1160 °C for 2–5 h under stagnant air at a heating/cooling rate of 1–2 °C $\min^{-1}$. The sintered membranes had a diameter of ~12 mm with relative density >90% as measured by the Archimedes' liquid displacement technique using pure water as the medium.

The crystal structure of the synthesized powders or sintered membranes was characterized with an X-ray diffractometer (XRD, Bruker D8 Advance). The room temperature oxygen nonstoichiometry was measured by the iodometry titration technique. The method involves dissolving the samples in HCl with the presence of potassium iodide in excess and heating in an oxygen-free environment. During this process, the cobalt ion (Co^{3+}, Co^{4+}) was reduced to Co^{2+}, while Fe^{4+} to Fe^{3+}, and oxidizing I^- to I_2. The amount of I_2 released is subsequently quantitatively determined by redox titration using tiosulfate as the titrant agent. The oxygen nonstoichiometry was calculated based on the amount of I_2 formed. The oxygen nonstoichiometry under various atmospheres at high temperature was determined by the TGA process using a NETZSCH STA 409 thermal gravity analyzer.

The electrical conductivity was measured by the four-probe D.C. method on sintered bars of approximate dimensions 2 mm × 5 mm × 12 mm. The measurements were performed under controlled atmosphere upon cooling from 900 to 300 °C at steps of 5 °C. At each temperature step, 2 min was allowed for the conductivity stabilization. Silver paste was painted on the square cross sectional edges of the sample or along the rectangular edges (separated by a distance L) to form current and voltage electrodes. Two silver wires acted as current contacts and the other two silver wires acted as the voltage contacts and were attached to the electrodes using silver paste. The sample was placed in a vertical split tube furnace. A constant current was applied to the two current wires and the voltage response on the two voltage wires were recorded using a Keithley 2420 source meter. The current was increased from 1 μA to a maximum value of 2 μA. The conductivity was calculated based on the following equation:

$$\sigma = \frac{L}{AK} \tag{1}$$

where A is the cross-sectional area, L the length, and K the slope of the curve of current versus voltage.

Permeation properties of the membranes were investigated by the gas chromatography (GC) method using a high-temperature oxygen permeation apparatus as shown in Fig. 1. A ceramic glass powder was used as the sealant to fix the membrane disk onto a dense quartz tube (A) and expose an effective geometric membrane surface area of around 0.7 cm^2 at the sweep side for permeation study. The sidewall of the membrane disk was also covered with the paste to avoid radial contribution to the oxygen flux. Quartz tube A was surrounded with another quartz tube (B) to form the chamber for gas feeds with defined oxygen partial pressures to the membrane surface. A third quartz tube (C) was inserted into quartz A for the outlet of gases from the sweep side. Compressed air was used as the feed gas at a flow rate of 100 ml $\min^{-1}$ ([STP]). The chamber formed by tubes A and C was used for the inlet of the sweep gas (helium), which first passed through tube A, swept the membrane surface, carried the permeated oxygen to the quartz tube C, and then conducted to a GC fitted with a molecular sieve with a 5 Å capillary column for analysis. The oxygen permeation flux was calculated by

$$J_{O_2}(\mathrm{mol\,cm^{-2}\,s^{-1}}) = \left[C_O - C_N \frac{0.21}{0.79}\left(\frac{28}{32}\right)^{1/2}\right]\frac{F}{S} \tag{2}$$

where C_O and C_N are the measured concentrations of oxygen and nitrogen in the gas on the sweep side (mol ml^{-1}), respectively, F the flow rate of the exit gas on the sweep side (ml s^{-1}), and S is the membrane geometric surface area of the sweep side (cm^2).