Structure and oxygen permeability of a dual-phase membrane

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Abstract

The dual-phase membrane of La 0.15 Sr 0.85 Ga 0.3 Fe 0.7 O 3−δ–Ba 0.5 Sr 0.5 Fe 0.2 Co 0.8 O 3−δ (LSGF–BSCF) was prepared successfully. This membrane was characterized with X-ray diffraction (XRD), scanning electron microscopy (SEM) and electron probe micro-analyzer (EPMA). This membrane has a dense dual-phase structure: LSGF being the dense body of this membrane and BSCF as another phase running along the LSGF body. This structure is favorable for the oxygen permeation through the membrane. The oxygen permeation test shows that the oxygen permeation flux of LSGF–BSCF membrane (J O 2 = 0.45 ml/min cm 2 , at 915 °C) is much higher than that of LSGF membrane (J O 2 = 0.05 ml/min cm 2 ). Thickness dependence of oxygen permeation indicates that the oxygen permeation is controlled by the bulk diffusion. Compared to pure BSCF, the dual-phase membrane of LSGF–BSCF is stable in reducing atmosphere.

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1. Introduction

Some materials exhibiting oxygen ion and electron conductivity have been found to selectively permeate oxygen rather than other gases, such as nitrogen, at elevated temperatures. Dense membranes made of these materials have attracted a considerable and increasing attention due to their potential applications in the production of pure oxygen [1–7] and construction membrane reactors for catalytic conversion of light hydrocarbons [8–18]. For practical applications, a dense oxygen separation membrane should possess the following properties: (1) high oxygen permeation flux, i.e. having both high oxygen ionic and electronic conductivities; (2) structural stability within appropriate ranges of temperature and oxygen partial pressure; (3) sufficient mechanical strength and chemical compatibility. However, it is difficult to meet all these requirements in a single phase because improvement in one aspect is often accompanied by the deterioration in others. Therefore, the dual-phase composite membrane [19–23], in which oxygen ions are transported through the oxygen ion conducting phase (OIC-phase), while electrons are carried by the electron conducting phase (EC-phase), have been proposed to avoid this dilemma.

In general, stabilized zirconia and bismuth oxides, which exhibit high oxygen ionic conductivity at elevated temperature, were used as OIC-phase, and the noble metals, such as Ag, Pd, were used as EC-phase. In this kind of dual-phase system, at least 40 vol.% of the electronic conducting phase is required in order to...
obtain a dual-phase membrane with continuous metal and ceramic phases. This renders the dual-phase membranes too expensive for practical application. Furthermore, the structure of random packing of the particles of two phases with very different properties presents a compatibility issue making such composite membrane mechanically unstable under the conditions of swinging temperature and oxygen pressure.

Kim and Lin [19,20] reported preparation of dual-phase membrane with an OIC-phase formed by closed packing of yttria-stabilized zirconia particles (YSZ) and a continuous phase of Pd as a film covering YSZ particles or filling in the interparticle space of the YSZ phase. They first prepared a mesoporous YSZ membrane by the sol–gel method, and then coated Pd onto the grain surface of YSZ particles by dip-coating and solvent evaporation. Though the Pd phase becomes continuous at low Pd loading, they could not obtain a dense dual-phase membrane for effective oxygen transport. Kharton et al.[24,25] reported the dual-phase membrane with ceramic and a perovskite-structured La$_{0.5}$Sr$_{0.5}$Fe$_2$O$_{3-δ}$ as the OIC-phase and a perovskite-structured La$_{0.2}$Sr$_{0.1}$MnO$_{3-δ}$ as the EC-phase. However, the OIC-phase and EC-phase are different in the structure, making this kind of dual-phase membrane less stable for oxygen permeation. Moreover, this dual-phase membrane has a structure of random packing of the particles of the two phases, which may not offer a high oxygen permeation flux.

Ishihara et al. [26] found that the doubly doped LaGaO$_3$ perovskite oxide exhibited a notably high oxygen ion conductivity. They also found that the Fe-doped La$_{0.8}$Sr$_{0.2}$Ga$_{1-x}$M$_x$O$_{3-δ}$ was highly stable in a reducing atmosphere, while the oxygen permeation rate was smaller than that of Co-doped and Ni-doped. In order to meet with the need of the practical application for partial oxidation of methane (POM), it is necessary to increase the oxygen permeation flux of Fe-doped LaGaO$_3$. At the same time, Ba$_{0.8}$Sr$_{0.2}$Fe$_{1.3}$CoO$_{3-δ}$ (BSCF) developed in our group is a mixed-conductor with dominant electron conductivity. So, the oxygen permeation flux of Fe-doped LaGaO$_3$ (LSGF) may be improved by introducing a phase with high electronic conductivity such as BSCF. In this present paper, we report a new structure of dense dual-phase membrane. In this dual-phase membrane, OIC-phase is perovskite oxide made of La$_{0.5}$Sr$_{0.5}$Fe$_2$O$_{3-δ}$ (LSGF) and EC-phase is perovskite oxide made of BSCF. Furthermore, this new dual-phase membrane consists of an OIC ceramic phase defined by the closed packing of OIC ceramic particles and a three-dimensional film of an EC-phase covering the surface (or grain-boundary) of the OIC ceramic particles. As a result, this dual-phase membrane requires much lower loading of the EC-phase and may also offer improved oxygen permeability. Furthermore, it is very important for this paper to exhibit a favorable microstructure with conventional ceramic processing.

2. Experimental

The oxide powders of BSCF and LSGF were prepared by a combined citrate and EDTA complexing method, which was described in detailed in previous report [27]. Dense BSCF–LSGF composites were prepared from the powders of BSCF and LSGF. The volume ratio of BSCF and LSGF is 1:12.8. The preparation route included mixing of the two powders of the two oxides, followed by ball-milling into disk-type pellets and sintering the disks in stagnant air at 1200 °C for 3–10 h (heating and cooling rate of 2 °C/min). The phase structure of the LSGF–BSCF membrane was characterized by X-ray diffraction (XRD, Rigaku D/Max-RB, Cu Kα radiation). The morphology of the LSGF–BSCF membrane was characterized by scanning electron microscopy (SEM, JEM-5600LV). The distribution of phases was analyzed by electron probe micro-analyzer (EPMA, Shimadzu-1600). The density of the sintered membrane was determined by the Archimedes method. The membranes with relative density higher than 95% were used for oxygen permeation. The oxygen permeation experiments were performed in a vertical high-temperature gas permeation cell as shown in the literature [28]. The permeator was put into a tubular furnace, and the operation temperature was controlled by a microprocessor temperature controller (Model AI-708, Xiamen Yuguang Electronics Technology Research Institute, China) to within ±1 K of the set points through a type K thermocouple encased in a quartz tube.

A ceramic–glass powder (Keramik-Glasur, UHLIG, Germany) was used as the ceramic binding agent to
seal the disc onto a dense quartz tube. This sealant solidified at 1040 °C. The effective inner surface of the membrane disc was controlled around 0.85 cm² for all the samples investigated. The side wall of the disc was also covered with a ceramic-glass powder to avoid radial contribution to the oxygen flux. Permeation studies were performed between 700 and 915 °C. We also found that the reaction between membrane and sealant is serious when the membrane was maintained at temperature higher than 925 °C for a long time. However, the reaction between the sealing material and the membrane is negligible at temperatures below 925 °C. In this paper, the highest temperature is 915 °C, so the reaction between sealant and membrane can be negligible.

Dried air was used as the feed at a flow rate of 150 ml/min. High purity helium (O₂ < 4 ppm) flowed on the other side of the membrane. The flow rates of the feed gases were controlled with mass flow controllers (Models D07-7AZM, Beijing Jianzhong Machine Factory, China). The permeate stream was analyzed by a gas chromatograph (GC, Agilent 6890) equipped with a 3 m 13X column. The GC was operated at 50 °C with helium as the carried gas. The oxygen concentration was calculated by the external standard method. The oxygen permeation flux through the membrane was calculated based on the helium flow rate and the oxygen concentration in the effluents.

3. Results and discussion

Dense BSCF–LSGF membranes were obtained after sintering under the present conditions. The sintered membrane maintains good integrity with no fracture, indicating good compatibility between BSCF and LSGF. The sintered membrane was heated to 1000 °C with 10 °C/min, and then it was cooled to room temperature with uncontrolled rate. However, we did not find cracks in the membrane. The experiment possibly demonstrated the two phases have a good compatibility. XRD pattern of the LSGF–BSCF composite is compared with those of pure LSCF and BSCF samples, as shown in Fig. 1. The pure BSCF and LSGF phases exhibit the same cubic perovskite structure, but with XRD peaks in different 2θ values due to the difference in the lattice parameter (0.399 nm for BSCF and 0.393 nm for LSGF). The LSGF–BSCF composite, however, does not exhibit the XRD patterns re-assembling those for the mixture of the two pure BSCF and LSGF phases. The XRD data show that the composite contains only one cubic perovskite phase with a lattice parameter (0.394 nm), essentially the same as that for the pure LSGF phase. It was found that BSCF still maintained its perovskite when it was melted. So there are no visible XRD peaks from the BSCF phase possibly due to small crystallite size of BSCF and low amount of BSCF phase in the dual-phase composite.

The morphology of the fresh LSGF–BSCF membrane was observed with the optical microscope. Low magnification morphology analysis of the two-dimensional surface of the dual-phase membrane clearly shows a two-dimensional view of the membrane surface characterized by a continuous netlike “film” running between the boundaries of many grains of about 30–50 µm in size. Fig. 2 is a higher magnification SEM micrograph of the top view of the dual-phase membrane. This figure shows a section of the continuous netlike “film” running in the boundaries of three larger ceramic grains. It is important to note that the continuous netlike “film” is very fine (only 2.5 µm) and uniform throughout the membrane surface observed.

The surface of the dual-phase membrane analyzed by EPMA shows different compositions in the regions of the netlike “film” and the grains, as shown in Fig. 3. The EPMA picture of the two-dimensional view of the dual-phase membrane is very similar to the SEM picture in Fig. 2, i.e. a continuous netlike
“film” (black region) running along the boundary of the bulk grains (white region). Qualitative EPMA analysis shows only the elements of La, Sr, Ga, Fe, O in the white region, and Ba, Sr, Co, Fe, O in the black region, confirming that the white grains are the LSGF phase and the netlike “film” is the BSCF phase.

The structure of this dual-phase membrane is very interesting. All of the dual-phase membranes reported in the literature have the structure of random packing of the particles. However, we prepared the dual-phase membrane with the structure of closed packing particles by taking the advantage of the fact that the melting point of LSGF (∼1250 °C) is higher than that of BSCF (∼1180 °C). The melting points of BSCF and LSGF were determined by increasing temperature step by step. Fig. 4 illustrates the formation process of this dual-phase membrane. The green-body containing particles of two phases are sintered together to form connected larger grains with clear grain-boundaries (Fig. 4a) because the sintering temperature is lower than, but close to, the melting point of LSGF. At the same time, the EC-phase (BSCF) becomes molten and spreads over the grain surface of the larger OIC particles (LSGF). Finally, the sintered grains of the OIC-phase (LSGF) developed to a dense bulk body and the liquid EC-phase (BSCF) forms a continuous three-dimensional film running through the grain-boundaries of the connected OIC-phase (LSGF), as shown in Fig. 4c. The EC-phase (BSCF) is expected to be percolated. In this way, the oxygen permeation of the dual-phase LSGF–BSCF membrane should be much higher than that of LSGF membrane.

The oxygen permeation data for the LSGF membrane and the LSGF–BSCF membrane were measured.
Fig. 4. The primary idea for the formation process of the LSGF–BSCF membrane.

Fig. 5. Comparison of oxygen permeation flux at different temperatures for the dual-phase membrane with the pure phase membrane. Air flow rate in air side is 150 ml/min and helium flow rate in permeation side is 30 ml/min. Membrane thickness is 1.99 mm, membrane area is 0.85 cm².
the LSGF and BSCF phases and within the BSCF phase. Fig. 6 shows oxygen permeation flux (J_{O_2}) versus reciprocal of membrane thickness (1/L) at different temperatures for constant \(\ln(P_h/P_l)\). The oxygen permeation flux through the mixed electronic-ionic conducting membrane is theoretically expressed by the following equation:

\[
J_{O_2} = \frac{RT}{16F^2(\sigma_e + \sigma_i)L} \ln \frac{P_h}{P_l}
\]

where \(R\) is the gas constant; \(F\) is the Faraday constant; \(T\) is the temperature; \(L\) is the thickness of the membrane; \(P_h\) is the oxygen partial pressure of the air side; \(P_l\) is the oxygen partial side in the He side, which depends on the oxygen permeation flux and He flow rate finally. \(\sigma_e\) and \(\sigma_i\) are the electronic and ionic conductivity, respectively. When \(\ln(P_h/P_l)\) is constant, the oxygen permeation flux (J_{O_2}) plotted against the reciprocal of thickness (1/L) is linear and go through the origin of the coordinates if the limiting step of the oxygen permeation is bulk diffusion. In order to determine the rate-limiting step of the oxygen permeation of LSGF–BSCF, the oxygen permeation flux with different thickness at different temperatures was measured. From Fig. 6, it can be seen that the relation of oxygen permeation flux (J_{O_2}) with the reciprocal of thickness (1/L) is linear and go through the origin of the coordinates at the temperatures between 800 and 900 °C. This result indicated that the rate-limiting step of LSGF–BSCF is the bulk diffusion rather than surface exchange. Consequently, it is expected that further higher oxygen permeation flux can be achieved by decreasing thickness of membranes.

Lee et al. [29] investigated the oxygen permeability of LSGF; it was found that the oxygen permeation flux of LSGF membrane is only 0.08 ml/min cm^2 (1.5 mm thickness) at 950 °C, which is similar to the pure \(La_{1-x}Sr_xGa_{1-x}Fe_xO_3-\delta\) studied by our group. However, the oxygen permeation flux is much smaller than that of LSGF–BSCF presented in this paper. Ishihara et al. [30] found the oxygen permeation flux can be increased greatly when the surface of \(La_{1-x}Sr_xGa_{1-x}Fe_xO_3-\delta\) was coated with \(La_{0.8}Sr_{0.2}CoO_3-\delta\). The oxygen permeation reached 2.5 ml/min cm^2 at 1000 °C when the thickness of the LSGF membrane was 0.3 mm. In our experiments, the thickness of LSGF–BSCF is about 2 mm and the oxygen permeation flux is 0.45 ml/min cm^2 at 915 °C. Considering the bulk diffusion is the rate-limiting step, we can say that the oxygen permeation flux of LSGF–BSCF is similar to that of Ishihara.

The LSGF membrane exhibits high absolute stability because Ga is only +3, and it can restrain the valence state change of Fe [27]. The membrane reactor for the POM to syngas based on LSGF was operated steadily for more than a year [31]. This indicated the LSGF membrane has good stability in the reducing
conditions. The LSGF–BSCF membrane contains the body of LSGF, and therefore is expected to exhibit the same stability as that of the LSGF membrane in the reducing conditions. So the phase stability of the LSGF–BSCF membrane under reductive atmosphere should be tested. The sample was treated for 1 h at 900 °C in the 5% H₂–Ar mixture gas, then the sample was quenched to room temperature. XRD analysis was carried out after this treatment. Fig. 7 shows the XRD patterns of the LSGF–BSCF membrane. As shown in Fig. 7b, the LSGF–BSCF membrane almost retains the perovskite structure after the membrane was treated for 1 h at 900 °C in the 5% H₂–Ar mixture gas. In our previous study [32], we found that pure BSCF is unstable in the reduction conditions. This result indicated LSGF–BSCF exhibits good stability under the reducing atmosphere.

For industrial applications, the membrane material must be operated steadily for long time. Few literatures reported the lifetime experiment of dual-phase membranes. Fig. 8 shows the oxygen permeation flux of the LSGF–BSCF membrane operated in an air/helium gradient. During the 120 h run, the oxygen permeation flux was fairly stable at 850 °C, with a value of about 0.32 ml/min cm² this demonstrates the excellent stability of the dual-phase membrane. Furthermore, the membrane was also operated at 900 °C for about 180 h, as shown in Fig. 8. It can be seen that the oxygen permeation flux increases slowly with time during the first 20 h and then levels off at a constant flux of ∼0.6 ml/min cm². The stability data after the time shown in Fig. 8 were not obtained due to the failure of the power supply.

The structure stability for oxygen permeation can be demonstrated by the XRD of the LSGF–BSCF membrane after permeation for 120 h at 850 °C. The membrane was quenched from permeation conditions to room temperature. Fig. 7c and d is the XRD patterns of the surface exposed to helium and the surface exposed to air of the LSGF–BSCF membrane after permeation for 120 h at 850 °C. The membrane was quenched from permeation conditions to room temperature. Fig. 7c and d shows that both the surface exposed to helium and the surface exposed to air after permeation for 120 h still maintain perovskite structure. This demonstrates that the LSGF–BSCF membrane exhibits a high stability for oxygen permeation. These results also indicate that no reaction or little reaction occurred between the LSGF and BSCF phases during the 120 h operation.

4. Conclusion

We have synthesized a new dual-phase LSGF–BSCF composite membrane with a structure defined by the closed packing of LSGF grains with a three-dimensional thin BSCF film running between the boundaries of the connected LSGF grains. The film phase is percolated at a volume percent as low as 7.2%. Since the majority phase is the chemically more
stable LSGF with the pervoskite structure and the second phase is made of a mechanically and chemically compatible BSCF rather than a metal. In this way, the oxygen permeation of the dual-phase LSGF–BSCF membrane is much higher than that of LSGF membrane. The oxygen permeation flux of LSGF–BSCF membrane (∼0.45 ml/min cm²) is nine times higher than that of the LSGF membrane (∼0.05 ml/min cm²) at 915 °C. H₂ reduction experiment shows that the LSGF–BSCF membrane has a good stability in the H₂-containing atmosphere. The LSGF–BSCF membrane can be operated steadily for 180 h of oxygen permeation. After permeation, the membrane retains its cubic pervoskite structure. This dual-phase membrane will offer many applications including in membrane oxygen separators, fuel cells, and membrane reactors. The concept of the dual-phase membrane and its synthesis method can also be extended to composite materials for other applications.

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