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Oxygen separation from air using $Ba_{0.95}La_{0.05}FeO_{3-\delta}$ membranes fitted with porous $La_{1-x}Sr_xFeO_{3-\delta}$ layers

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Abstract

Selective oxygen separation from air was performed using perovskite-type oxide membranes made of $Ba_{0.95}La_{0.05}FeO_{3-\delta}$. We demonstrated that surface modification of $Ba_{0.95}La_{0.05}FeO_{3-\delta}$ membranes with $La_{1-x}Sr_xFeO_{3-\delta}$ catalyst layers led to an increase in oxygen permeation fluxes at 700–930 °C. We studied the effects of oxygen vacancy amounts, surface area, particles size, surface treatment of $La_{1-x}Sr_xFeO_{3-\delta}$ on the oxygen permeability of the membranes fitted with $La_{1-x}Sr_xFeO_{3-\delta}$ catalyst layers. Among the catalyst layers tested, the membranes fitted with $La_{0.9}Sr_{0.1}FeO_{3-\delta}$ ($x=0.1$) showed the highest oxygen permeation flux probably because of its higher porosity and uniform morphology without open voids, which would increase the number of surface reaction sites. The obtained results suggest the feasibility of further upgrading the membrane performance by using surface catalyst layers having a homogeneous morphology and a different composition from that of the mother membrane.

Keywords: A. Films; D. Perovskites; E. Membranes

1. Introduction

Oxygen is one of the most widely used commodity gases in many industrial sectors, including metal processing, steel, chemical, and pharmaceutical industries. One major way to produce oxygen in a large scale is low-temperature liquefaction separation, which fractionally distills liquefied air into its primary components, typically nitrogen and oxygen.

Membrane separation methods have also been proposed for separation of oxygen from air [1–5]. Among them, ceramics membranes based on electron- and ion-conducting perovskite-type oxides are attracting much attention[1–3] because of their superior properties over other membranes based on polymers [4] and zeolites [5]. Electrical and ionic conduction in oxide membranes allow for bulk diffusion of oxygen ions in membranes. This oxygen diffusion occurs only with the help of oxygen partial pressure differences between the oxygen supply side and the extraction side of the membrane as shown in Scheme 1, thus eliminating the need of employing electrodes that are used to drive the oxygen diffusion. On the basis of the operating mechanism, the membranes have an ability to selectively extract oxygen from air. The high thermal stability of oxides also makes it possible to extract oxygen from high-temperature exhaust gases from industries.

However, the oxygen permeability of the membranes still remains low for practical applications. To improve the performance, we have been studying the membrane composition and structure. Recently, we have developed a new Fe-based membrane, La-doped $BaFeO_3$ ($Ba_{0.95}La_{0.05}FeO_{3-\delta}$) [6,7], which has higher oxygen permeation

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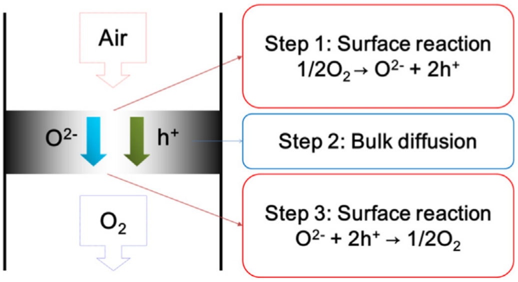

Scheme 1. Oxygen permeation mechanism via surface reactions and bulk diffusion.

properties than conventional Co-based membranes such as $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$, $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$, and $Sr_{0.9}Ca_{0.1}CoO_{2.5+\delta}$ [8–10]. The Fe-based material also shows superior stability than Co-based membranes that are not stable under reducing conditions because of Co reduction at high temperatures. In addition, La-doped $BaFeO_3$ is currently regarded as promising cathode materials for solid-oxide fuel cells (SOFCs) [11–14]. We also revealed that the oxygen permeability can be further upgraded by reducing the membrane thickness as a result of a decrease in the oxygen diffusion length [15].

Another way to improve the performance is attaching catalyst layers to the membrane surface [16–18]. We reported that $Ba_{0.95}La_{0.05}FeO_{3-\delta}$ membranes attached with porous $Ba_{0.95}La_{0.05}FeO_{3-\delta}$ layers showed improved oxygen permeability because of an enhancement in the rate of oxygen surface reactions (steps 1 and 3 in Scheme 1) on the membrane surface [19]. The result suggests the possibility of improving the membrane performance with modification of the composition and structure of porous layers. In this study, we studied the oxygen permeability of $Ba_{0.95}La_{0.05}FeO_{3-\delta}$ membranes attached with porous $La_{1-x}Sr_xFeO_{3-\delta}$ layers. It is expected that attachment of $La_{1-x}Sr_xFeO_{3-\delta}$ onto the membrane surface improves the oxygen permeability due to its good oxygen ion and electrical conductivity that promote oxygen exchange and diffusion kinetics [20–23]. $La_{1-x}Sr_xFeO_{3-\delta}$ has also been used for SOFC cathodes [24], implying its ability to facilitate the oxygen surface reaction at the membrane surface. Here, the composition of $La_{1-x}Sr_xFeO_{3-\delta}$ was controlled to investigate effects of oxygen deficiency and microstructure on the oxygen permeability.

2. Experimental

$Ba_{0.95}La_{0.05}FeO_{3-\delta}$ powders were prepared by a pyrolysis method, as follows. The constituting La and Fe nitrates and Ba acetates were dissolved in water. The pH of the solution was adjusted to 2 using a NH_3 solution. The solution was evaporated to dryness at 350 °C, and the dried powder was calcined at 850 °C for 5 h in air. The calcined powder was ground and crushed in ethanol with a planet-type ball-mill at 300 rpm for 15 h. After drying, the ball-milled powders (ca. 1 μm) were press-formed into a disk (diameter: 10 mm), and sintered at 1175 °C for 5 h in air. Dense disks were obtained using the above procedure. The surface of the membranes was polished with an emery paper (80) to adjust their thickness to 0.67 mm.

For the coating of porous layers on the membranes, $La_{1-x}Sr_xFeO_{3-\delta}$ powders were prepared by the pyrolysis method. The constituting metal nitrates were dissolved in water. The pH of the solution was adjusted to 2 using a NH_3 solution. The solution was evaporated to dryness at 350 °C, and the dried powder was calcined at 900 °C for 5 h in air. The calcined powder was dispersed in ethanol to make a coating ink (1–3 wt%). A designated amount of the ink was applied to the $Ba_{0.95}La_{0.05}FeO_{3-\delta}$ membranes. Porous layers were formed after drying and calcination at 1000 °C for 5 h in air. The thickness of the layers was approximately 8–10 μm. In some cases, sample powders were treated with a planetary ball mill at 300 rpm for 5 h using zirconia beads to reduce the particle size and increase the surface area.

The crystal structure was characterized on a X-ray diffractometer using Cu Kα radiation (RINT2100, Rigaku Co., Ltd.). The oxidation state of Fe and the total oxygen content in the $La_{1-x}Sr_xFeO_{3-\delta}$ system were determined by iodometry. Samples were dissolved in a deaerated solution consisting of KI and HCl. The liberated I_2 was titrated with a standard sodium thiosulfate solution with starch as the end point indicator. The procedure was performed under N_2 flow. The samples were quenched with liquid nitrogen after heating at 930 °C prior to chemical analysis. The chemical analysis was performed in triplicate, and the average values of oxygen vacancies (δ) in the mixed oxide systems were estimated. The surface area of samples was measured by a nitrogen-gas-adsorption method using a specific surface area/pore size distribution analyzer (BELSORP-mini II, Bell, Japan).

The oxygen permeability through the membranes was measured using a flow apparatus previously reported [6,19]. The membrane was fixed to a quartz tube by welding with a silver ring at 960–965 °C. For permeation tests, synthetic air ($200\ cm^3\ min^{-1}$) and He ($150\ cm^3\ min^{-1}$) were flowed to each side of the membranes, respectively. The oxygen concentration in the He flow was below 0.05 ppm. The amount of oxygen passing through the membrane from the air side to the He side was monitored with a thermal conductivity detector connected to a gas chromatography system. The measurement was performed at 700–930 °C.

3. Results and discussion

Coating a surface catalyst layer on the membrane surface is effective in improving the oxygen permeability by increasing the surface reaction rate. However, it is necessary to optimize the composition of the catalyst layer to avoid the mismatch of the junction between the mother membrane and the catalyst layer. Attachment of a layer, whose composition is largely different from that of the membrane, results in peeling off of the layer from the membrane surface due to a large difference in their heat expansion coefficients. We found that the compatibility of $La_{1-x}Sr_xFeO_{3-\delta}$ with $Ba_{0.95}La_{0.05}FeO_{3-\delta}$ was good enough to form a stable layer on a $Ba_{0.95}La_{0.05}FeO_{3-\delta}$ membrane probably due to similar heat expansion coefficients of the both materials.