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Enhancement of oxygen permeability by the introduction of a micro/nano surface reactive layer on the oxygen ion transport membrane

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Micro/nano surface reactive layers, $La_{0.6}Sr_{0.4}CoO_{3.\delta}$, are introduced on the surface of oxygen ion transport membranes to enhance the oxygen permeability of dense oxygen permeable perovskite-type ceramic membranes, $La_{0.7}Sr_{0.3}Ga_{0.6}Fe_{0.4}O_{3.\delta}$. An oxygen permeation flux of about 0.5 ml/minute·cm² is measured for the micro-sized surface-modified membrane with 1.7 mm of thickness, under a He/Air environment at 950°C. The membrane is also applied to the syngas (CO+H₂) production by the partial oxidation of methane. As a result, the complete selectivity of CO, 100%, over 50% of methane conversion and over 40% of syngas yield are obtained. The results show that the oxygen permeation flux is strongly influenced by the surface area of the surface reactive layer.

Key words: Oxygen Ion Transport Membrane, Surface Reactive Layer, Permeability.

Introduction

Dense oxygen ion transport membrane (ITM) has been drawing considerable attention because of its high oxygen selectivity and spontaneous oxygen mobility under an oxygen concentration gradient at high temperature [1-3]. As the membrane can separate oxygen molecules selectively from a gas mixture such as air, it is widely applicable for syngas production by the partial oxidation of methane gas, for hydrogen production, as a cathode material of solid oxide fuel cell, as an oxygen fuel burner, and for bio- and aero-applications for producing high purity oxygen. The gradient of oxygen pressure drop across the perovskite oxide results in a spontaneous oxygen flux through the dense membrane.

It has been reported that a perovskite-type ABO₃ membrane is a promising oxygen ion transport membrane due to its higher ionic conductivity than CeO₂ or ZrO₂ at high temperature [4-10]. To produce oxygen vacancies to facilitate mobility of oxygen, an other element, A', is replaced in the A site of ABO₃. For example, Sr²⁺ ion substitution for La³⁺ ion sites in the LaFeO_{3-δ} perovskite oxide forms oxygen vacancies and causes a change of valence states in B-site cations so that charge neutrality is maintained. However, even though they have higher oxygen permeation flux, the membranes showed lower stability in a severely reduced atmosphere, which results in phase transformation and microstructural changes

during long time operation.

More recently, a composition, $La_{0.7}Sr_{0.3}Ga_{0.6}Fe_{0.4}O_{3-\delta}$, has been reported to have a good chemical, structural stability, but also to have limited oxygen permeability [11-13]. We thus introduced micro/nano surface reactive layers on the surfaces of the $La_{0.7}Sr_{0.3}Ga_{0.6}Fe_{0.4}O_{3-\delta}$ with a cation-substituted perovskite-type composition, $La_{0.6}Sr_{0.4}CoO_{3-\delta}$, to enhance the oxygen permeability and investigated the factors affecting the surface reactivity.

In the present study, we selected La_{0.7}Sr_{0.3}Ga_{0.6}Fe_{0.4}O_{3-δ} as a representative membrane composition. We have evaluated the effects of surface reactive layers on its fundamental oxygen permeating properties at elevated temperature (>800°C). We also discuss the temperature dependence of the permeability and rate determining steps. All through the paper, La_{0.7}Sr_{0.3}Ga_{0.6}Fe_{0.4}O_{3-δ} perovskite oxide is designated by the abbreviation LSGF. Similarly, La_{0.6}Sr_{0.4}CoO_{3-δ} compositions are designated as LSC.

Experimental procedure

The starting materials for the synthesis of perovskitetype LSGF by conventional solid-state reaction were La_2O_3 (99.999%, Aldrich Chemical Co.), SrCO_3 (99.9%, Aldrich Chemical Co.), Ga₂O₃ (99.99%, Aldrich Chemical Co.), and Fe₂O₃ (99%, Aldrich Chemical Co.). The powders were mixed as slurry with 2-PrOH for 24 h in a planetary ball mill using zirconia balls in a polypropylene container. After mixing and drying, the softly agglomerated powder was crushed in an agate mortar and sieved using a 60-mesh screen. The powder mixture was calcined at 1250°C for 5 hr in air and uniaxially compressed into 1 inch (25.4 mm) diameter

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disks, followed by cold-isostatic pressing at a pressure of 140 MPa to enhance the green density. The LSGF green bodies were sintered at 1400-1500°C for 5 hr in air. Both sides of the sintered membrane were ground and polished to a 5 μ m finish to give a nominal thickness of 1.7 mm for permeation measurements.

The micro-sized LSC powder was synthesized by mixing La₂O₃, SrCO₃, and Co(NO₃)₂·6H₂O and calcining at 1000°C for 5 hr. The micro-sized powder mixtures were mixed into a paste with an organic solvent, binders, plasticizer and dispersant. The paste was used to modify the surface of the membrane by a screen-printing method. Post-heat treatment was conducted at 600°C for 5 hr to remove the organic additives and at 800-1250°C for 2 hr to control the porosity of the coating layer.

The nano-sized polycrystalline perovskite-type oxide LSC power was prepared by using a co-precipitaion method. Each hydroxide, La(OH)₃, Sr(OH)₂, and Co(OH)₂, were prepared from the co-precipitate by adding NH₄OH solution to La(NO₃)₃·6H₂O, Sr(NO₃)₂, and Co(NO₃)₂·6H₂O. The reaction mixture was stirred using a magnetic stirrer for 30 minutes, filtered and washed with deionized water, and then dried for 1 day. The mixtures with a molar composition La:Sr:Co=6:4:10, from each hydroxide, were mixed into a paste with an organic solvent, binders, plasticizer and dispersant for screen printing. Post-heat treatment was conducted at 600°C for 5 hr to remove the organic additives and at 950°C for 2 hr.

The other nano-sized LSC layer was obtained by EB-PVD (electron beam physical vapor deposition). A 10 kW EB-PVD instrument was used for making nanosized LSC. Ingots were prepared from the calcined LSC powder which had started as La_2O_3 , $SrCO_3$, and $Co(NO_3)_2 \cdot 6H_2O$. LSC ingots from LSC of 150 mm length and 25.4 mm diameter were bottom fed into the crucibles during evaporation. The maximum power was maintained at 713 W. The average substrate temperature during deposition was 800°C.

The microstructures of the membranes were investigated using a scanning electron microscope (SEM, XL30 Philips). The apparent densities of the sinteref thed

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Fig. 2. SEM micrographs of the surface of (a) LSGF membrane, (b) porously surface-modified LSC layer, and (c) densely surfacemodified LSC layer.

2(b) and 2(c). The relative density of the LSC layer was controlled from 70% to above 95% according to the control of the heating schedule. Figure 2(b) shows the surface from the top view of the surface-reactive LSC layer heat-treated at 800°C. The microstructure includes many pore volumes. On the other hand, we could obtain a fully dense and large-grained LSC microstructure by heat-treating at 1250°C as shown in Fig. 2(c).

The oxygen permeation fluxes of the LSGF surfacemodified by porous LSC (Porous LSC/GF) or dense LSC (Dense LSC/GF) with micrometer-sized particles are compared with that of an unmodified specimen (LSGF) in Fig. 3. The LSGF membrane showed signi-



Fig. 3. Oxygen permeation fluxes of LSGF membrane, LSGF membrane surface-modified by porous LSC (Porous LSC/GF), and LSGF surface-modified by dense LSC layer (Dense LSC/GF) as a function of temperature. The oxygen partial pressure of feed and permeate side was around 0.21 and 10^{-3} atm, respectively, and the thickness of membranes is 1.7 mm.

ficant enhancement in the oxygen permeation flux by the introduction of a porous LSC layer. In the case of a densely surface-modified LSGF membrane, the permeation flux was improved even though the improved value was not very high. On the other hand, the oxygen permeation flux increased dramatically by the introduction of the porous LSC layer. The highest oxygen flux, 0.48 ml/ minute·cm², was obtained at 950°C for the LSGF surface-modified by porous LSC. This result indicates that the oxygen flux was strongly influenced by the introduction of the LSC layer, and especially by the microstructure. Particularly, in the porous LSC/GF, oxygen started to permeate from 700°C and the oxygen



Fig. 4. Arrhenius plots of oxygen permeation fluxes of LSGF membrane surface-modified by porous LSC (P-LSC/GF), dense LSC (D-LSC/GF), or outer-porous/inner-dense LSC layer (PD-LSC/GF). The oxygen permeation flux of unmodified LSGF membrane is also inserted in the graph.

 Table 1. Apparent activation energies of oxygen permeation fluxes of unmodified LSGF membrane and modified LSGF membranes

Membrane type	Activation energy, E (kJ/mol)
LSGF	103.6
D-LSC/GF	73.7
P-LSC/GF (at lower temperature region)	48.8
P-LSC/GF (at higher temperature region)	20
PD-LSC/GF (at lower temperature region)	43.4
PD-LSC/GF (at higher temperature region)	19.9

fluxes were 6 times higher than that of the unmodified specimen at 950°C (0.08 ml/cm² for LSGF and 0.48 ml/cm² for porous LSC/GF). These increases in the oxygen fluxes may have been caused both by the increase in the effective surface area and by the increase in surface activity to oxygen dissociation and association with the application of porous LSC for both surfaces [14].

We compared three kinds of LSC layer configurations: (i) porous, (ii) dense, and (iii) outer-porous/inner-dense layers (abbreviated as PD-LSC/GF) to both surfaces of the LSGF membrane. The oxygen permeation fluxes of the three kinds of surface-modified specimens are given with that of unmodified LSGF as a function of reciprocal temperature in Fig. 4. The slope of the curve corresponds to the activation energy for oxygen permeation. The calculated activation energies for each membrane are shown in Table 1. Note the lower slope in P-LSC/GF at higher temperature. Although the activation energy of D-LSC/GF is lower than that of unmodified LSGF, it is not as low as P-LSC/GF in the higher temperature region. The difference in the fluxes between D-LSC/GF and P-LSC/GF can be explained by the disparity in effective surface area. On the other



Fig. 5. Methane conversion and syngas yield of LSGF membrane surface-modified by porous LSC as a function of temperature.



Fig. 6. Methane conversion and syngas yield of LSGF membrane surface-modified by porous LSC as a function of long-time duration.

hand, the fluxes and activation energies of PD-LSC/GF were almost identical with those of P-LSC/GF over the entire temperature range measured. This result means that it is not the population of triple phase points but rather the effective surface area that is the decisive factor in surface exchange reactivity of LSC.

Figure 5 plots methane conversion and syngas (H₂+ CO) yield of the LSGF membrane deposited with micro-sized porous LSC as a function of operating temperature from 825°C to 950°C. The methane conversion and syngas yield increases with increasing operation temperature, reaching about 50% of conversion and over 40% of yield at 950°C with 100% of CO selectivity. The fact that the H₂/CO ratio is less than 2 is probably due to the carbon deposition. The high ratio of CH₄/O₂ could cause deposition of large amounts of carbon [15]. Nevertheless, the higher conversion and yield rate in Fig. 5 are closely related with increased oxygen permeation at higher operation temperatures. This result indicates that the conversion and yield rate depend on the oxygen permeation flux.

The syngas production using a LSGF membrane surface-modified by a porous LSC layer was measured with air fed in the one side of the reactor and helium and methane in the other side of the membrane. Figure 6 shows CH_4 conversion and syngas yields of the samples measured at 950°C for longtime operation to the maximum 600 hr. It can be concluded that the conversion and yield maintain stable values for long-time duration even though slight deviations are observed. The stable syngas yield indicates that the LSGF membrane surface-modified by a porous LSC layer is a candidate material with high stability and high oxygen permeability for ITM.



Fig. 7. SEM micrographs of the surface of (a) nano-sized LSC layer deposited by coprecipitation method and (b) nano-sized LSC layer deposited by EB-PVD method.

Figure 7 shows top views of a nano-sized LSC surface reactive layers deposited on the LSGF membranes. Nano-sized particles are deposited by screen-printing after co-precipitation (Fig. 7(a)), and EB-PVD (Fig. 7(b)). It is observed that the precipitated nano-powder is agglomerated during drying and calcination. On the other hand, the particles prepared by EB-PVD consist of a several tens of nanometer-sized with a relatively narrower size distribution. However, the stoichiometric composition of LSC is not easily obtained due to rapid evaporation of the ingots by electron-beam radiation. The composition uniformity of nano-sized LSC particles is a current theme to be solved for higher oxygen permeation by increasing the surface reactive area as foreshadowed in Fig. 3 and Fig. 4.

Conclusions

The oxygen permeability of dense perovskite-type

ceramic membrane, $La_{0.7}Sr_{0.3}Ga_{0.6}Fe_{0.4}O_{3-\delta}$, was enhanced by the introduction of a surface reactive layer, $La_{0.6}$ - $Sr_{0.4}CoO_{3-\delta}$. The enhanced oxygen fluxes were 6 times higher than that of an unmodified specimen at 950°C (0.48 ml/minute·cm² than 0.08 ml/minute·cm² for unmodified LSGF) by the modificaton with a surface reactive composition and an increase of reactive surface area. Syngas, CO+H₂, was successfully obtained from methane gas, CH₄, using a $La_{0.7}Sr_{0.3}Ga_{0.6}Fe_{0.4}O_{3-\delta}$ membrane surface-modified by a porous $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ layer, with over 40% of CH₄ conversion and syngas yield. The surface-modified $La_{0.7}Sr_{0.3}Ga_{0.6}Fe_{0.4}O_{3-\delta}$ membrane was stable even when it was exposed to a reducing environment, for 600 hr at 950°C.

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