

Improving the oxygen permeability of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ membranes by a surface-coating layer of $\text{GdBaCo}_2\text{O}_{5+\delta}$

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Abstract

A $\text{GdBaCo}_2\text{O}_{5+\delta}$ layer was coated on the $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ membranes to enhance their oxygen permeability by employing the fast oxygen adsorption/desorption surface-exchange properties of the $\text{GdBaCo}_2\text{O}_{5+\delta}$ material. The oxygen flux of the coated and uncoated $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ membranes was measured in the temperature range of 600–850 °C. The results reveal that the oxygen-permeation flux of the $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ membranes coated by a $\text{GdBaCo}_2\text{O}_{5+\delta}$ layer shows significant enhancement. The $\text{GdBaCo}_2\text{O}_{5+\delta}$ layer coated on the oxygen desorption side (He side) has much effect than that coated on the oxygen adsorption side (air side). At 850 °C, the oxygen flux with a single coating layer on the air side can rise 16%, while a single coating on the helium side will result into a rise of 23%.

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1. Introduction

Oxygen-permeation membranes have been of much interest due to the selected permeability of oxygen and its potential application in oxygen separation and partial oxidation of methane to syngas. However, only those membranes which have high oxygen-permeation flux can win practical applications. In recent years, research effort has been focused on materials and techniques that can provide high oxygen-permeation rate. The oxygen transport in a membrane is limited mainly by two resistive steps, i.e. oxygen exchange on the surfaces of the membrane and oxygen-ion diffusion in the membrane bulk. Therefore, the oxygen-permeation flux can be significantly improved by decreasing the membrane thickness when the oxygen permeation is mostly limited by bulk diffusion,^{1,2} or by coating the membrane with a catalytic layer to enhance oxygen surface exchanges when the oxygen permeation is mostly limited by the oxygen surface-exchange kinetics.^{3–5} The coated layer has two-fold functions depended on the material used. The first is that it can increase the effective surface area, thus increase the oxy-

gen exchange ability. The second is that coated materials have a higher oxygen activation (a higher oxygen surface-exchange rate) than the base membrane materials, thus can also enhance the oxygen exchange ability.

The oxygen-deficient double perovskite structure compounds $\text{RBaM}_2\text{O}_{5+\delta}$ (R = rare-earth element, M = Co, Fe, Mn), the so-called “112” phases, have attracted much attention in recent years because of their remarkable structure and oxygen transport properties. Their crystal structure can be regarded as a layered crystal $A'A''B_2O_6$ by doubling the unit cell of standard perovskite structure and consists of consecutive layers $[\text{MO}_2]$ – $[\text{BaO}]$ – $[\text{MO}_2]$ – $[\text{RO}_\delta]$ stacked along the *c* axis. The oxygen ions in the RO_δ layer can be easily varied in concentration $0 \leq \delta \leq 1$ by means of heat treatment under appropriate atmosphere.^{6–9} Taskin et al. have compared the oxygen diffusion behavior of the double perovskite $\text{GdBaMn}_2\text{O}_{5+\delta}$ phase with simple perovskite $\text{Gd}_{0.5}\text{Ba}_{0.5}\text{MnO}_{3-\delta}$ phase and they found that the oxygen-ion diffusion can be enhanced by orders of magnitude if a simple perovskite structure transforms into a layered one, because the layered structure reduces the oxygen bonding strength and provides disorder-free channels for ion motion.¹⁰ Kim et al. have also reported that $\text{PrBaCo}_2\text{O}_{5+\delta}$ bulk materials and thin films have unusually rapid oxygen transport kinetics at low temperature (300–500 °C).¹¹ In our previous work, we have

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investigated the oxygen adsorption and desorption behavior of $\text{RBaCo}_2\text{O}_{5+\delta}$ ($\text{R} = \text{Pr, Gd, Y}$) over a wider temperature range (400–900 °C).¹² Our results show that the oxygen adsorption and desorption rate constants k_a and k_d of these R112 compounds are markedly larger than those of simple perovskite structure, commonly used, oxygen-permeation membrane materials, such as $\text{Ba}_{0.95}\text{Ca}_{0.05}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ and $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$.¹³ However, attempt to use $\text{RBaCo}_2\text{O}_{5+\delta}$ ($\text{R} = \text{Pr, Gd, Y}$) as oxygen-permeation membranes yielded negative results. Our experiments have shown that the $\text{RBaCo}_2\text{O}_{5+\delta}$ materials themselves are not good oxygen-permeation membrane materials. The oxygen permeability of $\text{RBaCo}_2\text{O}_{5+\delta}$ membrane is very lower comparing with the commonly used oxygen-permeation membrane materials. This means that even though $\text{RBaCo}_2\text{O}_{5+\delta}$ materials have a fast oxygen exchange ability on the membrane surface, but the oxygen-ion diffusion in the membrane bulk is not desirable because the difference of oxygen vacancy in oxygen and nitrogen ($\Delta\delta$, V mol) was smaller than that of the commonly used membrane materials, so their oxygen-permeation flux J_{O_2} was not as high as expected. On the other hand, the remarkable oxygen surface-exchange rates of these double perovskite R112 oxides opens a possibility to use them as a surface-coating layer on other oxygen-permeation membranes to obtain a more faster oxygen surface exchange of the membranes, and thus to enhance the oxygen-permeation flux membranes of the membranes.

$\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ was reported to be a promising oxygen permeation material with attractive oxygen permeability.^{14,15} The oxygen-permeation flux of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ membranes is about 1×10^{-7} mol/cm² s (~ 1 ml/cm² s) at 900 °C. Muydinov et al. have investigated the dependence of oxygen-permeation flux of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ membranes on their thickness.¹⁶ They found that due to the surface limited properties even for thin film membranes (2–5 μm thick) the oxygen-permeation flux of these thin film membranes can only reach a value of 1.6×10^{-7} mol/cm² s. They concluded that when the thickness of the membranes is 1 mm thick or larger the oxygen permeability is controlled mainly by the oxygen diffusion in the material. In Ref. ¹⁷ for a tubular BSCFO membrane with a wall thickness 1.7 mm, the authors also found the oxygen permeability is bulk diffusion limited with little or no contribution of the surface exchange at temperature of 700–900 °C. However, according to the investigation of Kharton et al., the oxygen flux of $\text{La}_{0.3}\text{Sr}_{0.7}\text{CoO}_{3-\delta}$ and $\text{La}_2\text{Ni}_{0.8}\text{Cu}_{0.2}\text{O}_{4+\delta}$ membranes with thickness ~ 1 mm are significantly affected by the oxygen surface-exchange rate.^{18,3} This may be indicated that for a middle thickness 1–2 mm both factors, the bulk diffusion and surface exchange, may be acted simultaneously.

The purpose of the present study is to use the double perovskite oxides $\text{GdBaCo}_2\text{O}_{5+\delta}$ as a coating layer on the $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ membrane hopefully to improve oxygen permeability of the membrane by increasing the oxygen exchange rate at gas/solid interfaces through $\text{GdBaCo}_2\text{O}_{5+\delta}$ coating. The experimental results show that the $\text{GdBaCo}_2\text{O}_{5+\delta}$ coating indeed enhances the oxygen-permeation flux of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ membrane; if coating is

used on both sides of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ membrane the oxygen-permeation flux is 41% higher than that of uncoated $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ membrane at 850 °C.

2. Experimental

2.1. Sample preparation

$\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCFO) and $\text{GdBaCo}_2\text{O}_{5+\delta}$ (Gd112) samples were prepared by the solid-state reaction method. $\text{GdBaCo}_2\text{O}_{5+\delta}$ (Gd112) samples were using Gd_2O_3 , BaCO_3 , and Co_2O_3 as starting materials. The stoichiometric mixture was mixed and ground in an agate mortar. After heated in air at 1000 °C for 20 h, it was ground into fine powder (average grain size about 1.41 μm) for membranes coating. $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCFO) samples used BaCO_3 , SrCO_3 , Fe_2O_3 , and Co_3O_4 as starting materials. The stoichiometric mixture was ground in an agate mortar. After decarbonation at 950 °C for 5 h, the powder was pressed into disks with diameter 22 mm under a pressure of 120 MPa and then were heated at 1100 °C for 5 h in air with heating and cooling rate 2 °C/min. The thickness of the membranes was controlled to 1.48 mm after calcinations in order to comparing their oxygen flux at the same thickness. The bulk density of the uncoated BSCFO membranes is 4.96 g/cm³ which is about 86% of its theoretical density.

The Gd112-coated BSCFO membranes were prepared with spin-coating method. The coating paste was a mixture of 23 wt% of Gd112 powder, 43 wt% of glycerol, 4 wt% of a glycol and 30 wt% of ethanol. The Gd112 layer was coated on one or both side surfaces of the BSCFO membrane using a spin-coating apparatus operated at 4000 rpm for 30 s. Post-heat treatment was conducted to remove the organic additives at 1100 °C for 5 h with heating and cooling rate 2° min⁻¹. The thickness of the Gd112 layer was about 6 μm observed by SEM.

2.2. Phase structure and microstructure observation

X-ray diffraction (XRD) analysis was carried out with X'tert Pro system using Cu K α radiation to investigate the phase structures of the powder samples. The microstructure of Gd112-coated BSCFO membrane was observed with a scanning electron microscope (SEM, Model JSM-5610LV, JEOL, Japan).

2.3. Measurement of oxygen surface-exchange rates

A particle size analyzer (BT-3000A, Better, China) was used to analyze the grain size distribution and specific surface of the Gd112 and BSCFO powder. The average grain size is 1.41 μm , and 1.40 μm and the specific surface 1.62×10^4 cm⁻¹, and 1.85×10^4 cm⁻¹ for Gd112 and BSCFO, respectively. The oxygen adsorption and desorption rate constants were measured with the thermogravimetry (TG) method. About 100 mg powder sample was put into a thermal analyzer (SETARAM LabsysTM) and heated to 600, 700, 800, and 900 °C, respectively, in oxygen (purity >99%) flow. When the weight of the sample did not change any more, oxygen was exchanged with nitrogen (purity

>99.999%) quickly. Then nitrogen was exchanged with oxygen again when the weight did not decrease remarkably. The flux of the nitrogen and oxygen was 30 ml/min.

2.4. Oxygen-permeation measurement

Oxygen permeability experiment was carried out in a vertical high-temperature gas permeation measuring system. Fig. 1 gives a sketch of the experiment setup. One BSCFO membrane disk was sealed to an alumina tube by high-temperature ceramic–glass glue which can result a perfect sealing and almost no air leak.¹⁹ In the permeation system, the membrane with seal was heated in air at a ramp rate of 5–10 °C/min to a temperature above the softening point of the Pyrex glass (920 °C), and kept at that temperature for 0.5 h. And then cooling down to temperature range (850 °C) at which the oxygen permeation experiment will be performed. High-purity helium streams were introduced to the inner sides of the membrane at a flow rate of 50 ml/min with the aid of a mass flow controller, and the outside of the membrane was exposed to static ambient air. The composition of the effluent helium stream was analyzed with an Agilent T1790 gas chromatograph and the oxygen partial pressure was calculated based on the oxygen content in He stream. The oxygen permeation experiment was performed in the temperature range of 600–850 °C with a temperature interval 50 °C.

3. Results and discussion

The crystallographic phases of BSCFO and Gd112 powders were verified by XRD as shown in Fig. 2. Perovskite and double perovskite structures were found for BSCFO and Gd112 samples, respectively. Moreover, a superlattice structure ($a_p \times 2a_p \times 2a_p$, a_p being the cell parameter of the cubic perovskite) was formed in Gd112 due to ordered distribution of oxygen vacancies along b axis.⁶

Fig. 3 shows the weight change ($[(w(t) - w(0))/w(0)] \times 100$) with time during the gas changing cycle (oxygen → nitrogen → oxygen) at different temperature for Gd112 and BSCFO samples. It can be seen that the weights of two samples decrease (releasing oxygen) when gas flow is changed from

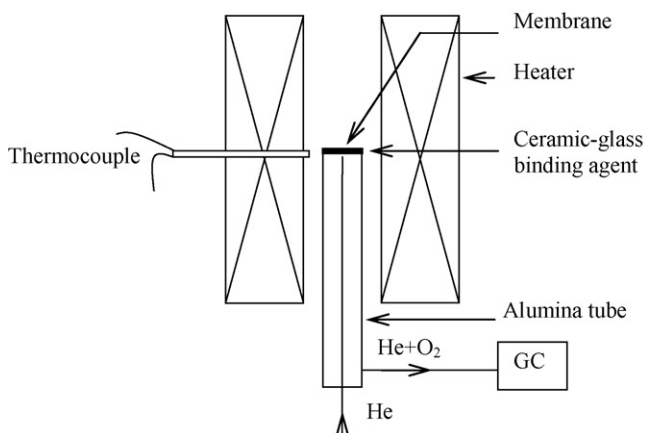


Fig. 1. Sketch of oxygen permeation experiment setup.

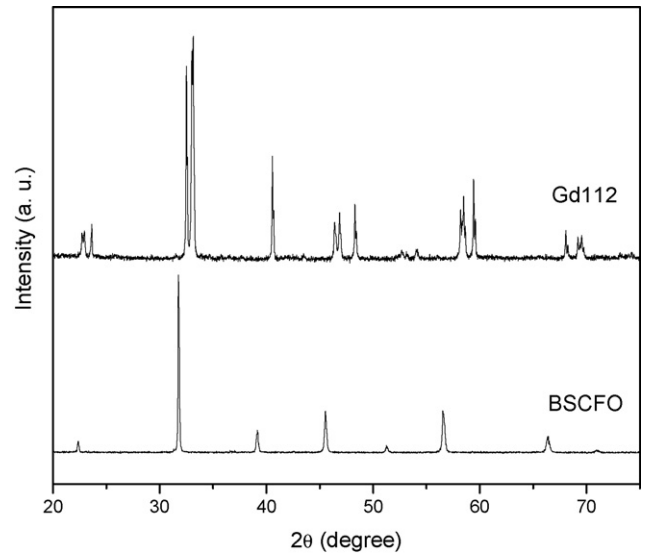


Fig. 2. XRD patterns of Gd112 and BSCFO powder samples.

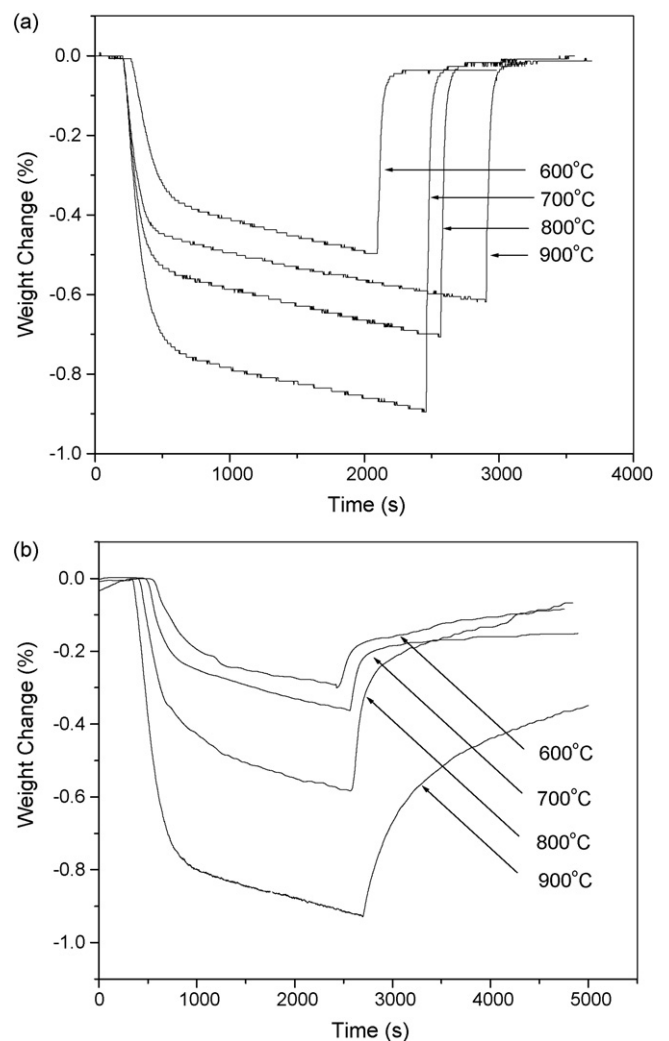


Fig. 3. Weight change of the samples during oxygen → nitrogen → oxygen cycle at different temperature for (a) Gd112 and (b) BSCFO powder samples.

oxygen to nitrogen and increase (absorbing oxygen) when gas flow is changed from nitrogen to oxygen at each temperature. Reaching an equilibrium state in nitrogen is more difficult than in oxygen. Moreover, the rate of weight change for BSCFO is obviously smaller than that for Gd112. From these TG curves, one can calculate the oxygen adsorption rate constant k_a and oxygen desorption rate constant k_d based on the theoretical model proposed by Zeng and Lin²⁰ and van Hassel et al.²¹ and the detail of the calculation can be found in Refs. 12 and 13. For a comparison the k_a and k_d values of Gd112 BSCFO are presented in Table 1. It can be observed that the k_a and k_d values of Gd112 are larger significantly than those of BSCFO at each temperature, which indicates that Gd112 has faster oxygen surface-exchange kinetics than BSCFO.

The oxygen surface-exchange rate constant k of Gd112 have been measured by Taskin et al. by examining the weight change of single crystals of Gd112 as a function of time over a temperature range 250–600 °C¹⁰ and by Tarancon et al. using 18O/16O isotope exchange depth profile (IEDP) method over a temperature range 299–686 °C.²² The tracer experiments result in much lower values of k (7.4×10^{-8} , 2.8×10^{-7} , 1.3×10^{-7} cm/s for 496, 575, 686 °C) than that of the chemical diffusion experiments (3×10^{-5} , 8×10^{-5} , 1×10^{-4} cm/s for 500, 550, 600 °C), and Tarancon et al. attributed this difference to the method used because much higher values can be expected for the kinetic parameters determined by chemical diffusion experiments as theoretically shown by Maier.²³ Despite of the large difference of k , the activation energies in both methods are almost same, which is about 0.8 eV. Comparing our results (11×10^{-7} cm/s for 600 °C, which is obtained using the method proposed by Zeng et al.²⁰ and Hassel et al.²¹) with the results of Taskin et al. and Tarancon et al., it can be found that our result is very close to the Tarancon's results. However, our result shows very weak temperature dependence. If assumes the Arrhenius relation $k = k_0 \exp(-E/k_B T)$, the activation energy is about 0.035 eV (3.3 kJ/mol) which is one order smaller than the values obtained by Taskin et al. and Tarancon et al. This may be caused by the following reason. The temperature range we measured is different to Tarancon et al., in our case it from 600 to 900 °C, while from 299 to 686 °C in the measurement of Tarancon et al. A single activation energy may not be used to cover a larger temperature range because the activation energy may change with temperature. In the Tarancon's measurements the value of k at 686 °C (1.3×10^{-7} cm/s) is obviously smaller than the value at 575 °C (2.8×10^{-7} cm/s). The same situation can be found in our BSCFO sample, for which the k_a decreases with the increase of temperature. In these cases, the decrease of k with the increase of temperature does not mean a negative activation

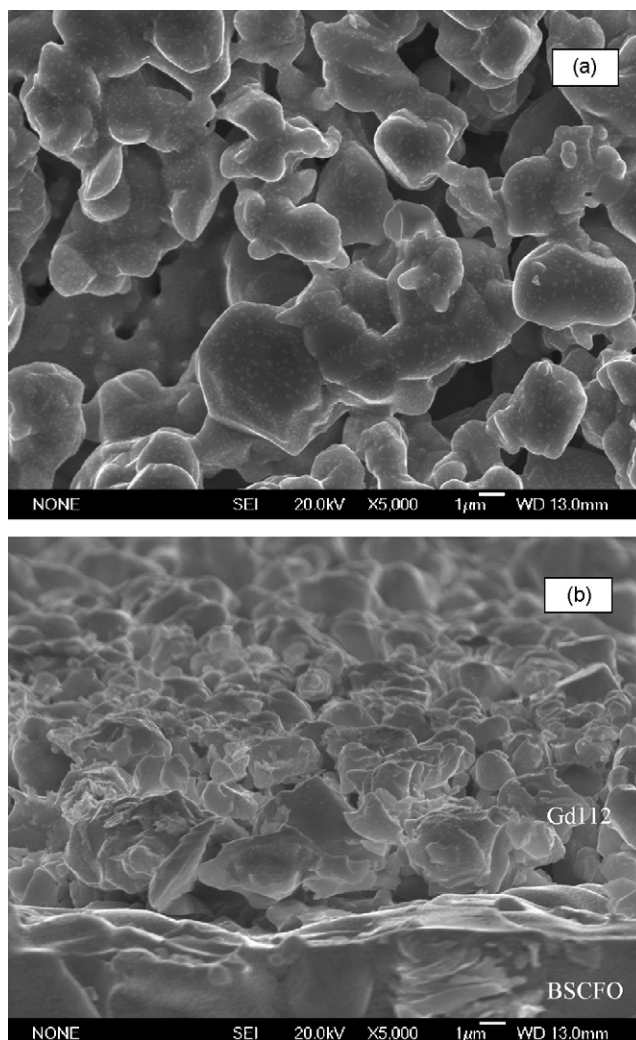


Fig. 4. SEM micrographs of porous Gd112 layer coated on dense BSCFO membrane, (a) surface of Gd112 layer and (b) cross-section.

energy according to the Arrhenius relation, but a change of activation energy with temperature. Even though different methods may result different k for the same material at same temperature, using the same method to comparing k values for different materials is relatively creditable. Therefore, we calculated that the oxygen surface-exchange rate constants of Gd112 are higher than that of BSCFO.

Fig. 4 shows SEM micrographs of Gd112-coated BSCFO membrane. As seen in Fig. 4(a), Gd112 layer is porous due to the volatilization of organic solution during post-heat treatment. This porosity would provide adequate diffusion pathway near the surface and increase the effective surface area of Gd112

Table 1
Oxygen adsorption and desorption rate constants k_a and k_d for Gd112 and BSCFO samples

	Gd112 sample				BSCFO sample			
	600 ^a	700 ^a	800 ^a	900 ^a	600 ^a	700 ^a	800 ^a	900 ^a
k_a (10^{-7} cm s ⁻¹)	11.09	12.13	12.10	12.59	4.76	4.27	4.22	3.98
k_d (10^{-7} cm s ⁻¹)	1.86	2.40	2.90	3.07	1.08	1.16	1.19	1.54

^a T (°C).

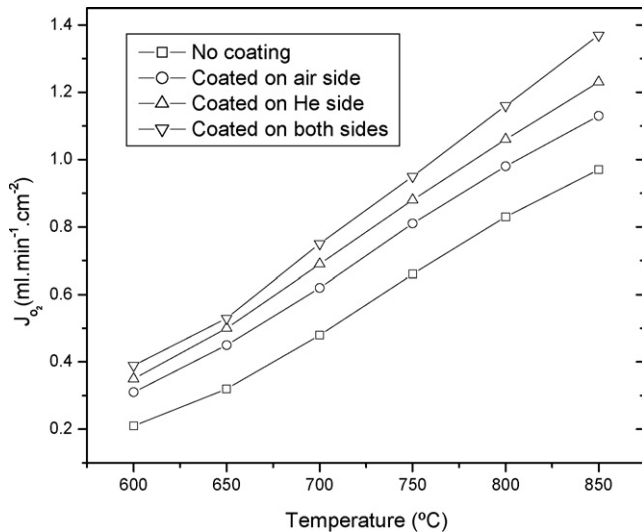


Fig. 5. Oxygen-permeation fluxes of unmodified BSCFO and Gd112-coated BSCFO membranes with temperature.

layer. From the cross-section of Gd112-coated BSCFO membrane (Fig. 4(b)), we can distinguish the porous Gd112-coating layer, which has approximately 6 μm thickness, from the dense BSCFO membrane.

The oxygen-permeation fluxes of the uncoated BSCFO membranes and Gd112-coated BSCFO membranes are shown in Fig. 5. The BSCFO membranes show significant enhancement in oxygen-permeation flux by coating Gd112 layer within the entire studied temperature. The value of oxygen flux through uncoated BSCFO membrane is 0.97 ml/min cm at 850 °C, whereas the values through the membranes of Gd112 coated on air side, helium side and both sides are 1.13, 1.23 and 1.37 ml/min cm, respectively, i.e. 16%, 27% and 41% higher than that of uncoated BSCFO membrane. The effect of the Gd112-coating layer on the increasing of oxygen-permeation flux is remarkable.

If the oxygen-permeation flux of BSCFO membranes are bulk diffusion limited when their thickness are larger than 1 mm according to Refs. ¹⁶ and ¹⁷ it will be vary hard to understand the present experimental results because increasing the surface-exchange rate is useless for a bulk diffusion limited membrane. We propose two possibilities hear. Firstly, the BSCFO membranes we used may not be totally bulk diffusion limited. We measured the oxygen-permeation flux for other three BSCFO membranes with thickness 1 mm, 1.5 mm and 2 mm, respectively, and found their oxygen-permeation flux were 1.11 ml/min, 0.97 ml/min and 0.78 ml/min at 850 °C. A departure from an inversion relationship between the oxygen-permeation flux and thickness is remarkable. Therefore, the surface exchange limited effect also present in our samples. But what cause the difference between our sample and those of Refs. ¹⁶ and ¹⁷ is not clearly known at the present time. Secondly, a coating layer may change the “effective” oxygen pressure imposed on the membrane surface. On the high oxygen pressure side of the membranes, if the coating layer has a fast oxygen adsorption ability while the membrane body has a lower oxygen diffusion rate the oxygen ions will accumulate in the coating layer, thus the surface of body membrane below

the coating layer will be subject a high oxygen “pressure”. This oxygen “pressure” enhances the oxygen flux and a new equilibrium state will be reached between the oxygen “pressure” and the enhanced oxygen flux. On the low oxygen pressure side of the membranes, the fast desorption ability of the coating layer can lower the “effective” oxygen pressure, thus also enhance the flux. If this conjecture is true, it means that a coating layer can also be used to enhance the oxygen-permeation flux even for a bulk diffusion limited membrane. However, further experiments are needed to investigate this point carefully.

Therefore, we concluded that the increase of the oxygen fluxes for our sample should be caused by the fast oxygen surface-exchange ability of Gd112-coating layer as well as the increase of the effective surface area. However, it is difficult to distinguish which factor is the main factor that is responsible for the increase of the oxygen fluxes. We have coated a BSCFO layer on BSCFO membrane using the same method as coating Gd112 layer. However, the increase of its oxygen flux is not obvious. This may indicate that the fast oxygen surface-exchange ability of Gd112 is an important factor besides the increase of the effective surface area.

It should be noted that the increase of oxygen flux for the membrane of Gd112 coated at the helium side is more remarkable than that of Gd112 coated air side. Single coating the air side will results a rising 16% for the oxygen flux at 850 °C, but single coating the helium side will results a rising 23% for the oxygen flux at 850 °C. This is because that the oxygen desorption rate constant k_d of BSCFO is much smaller than its oxygen adsorption rate constant k_a , so that the oxygen desorption at the helium side will be a dominant control factor for the oxygen flux. Thus, improving the oxygen desorption rate of the helium side will be more effective. A similar result was also found by Muydinov et al. They found that applying a Pt sublayer on the low $p(\text{O}_2)$ surface of the membrane of BSCFO, it will increase the oxygen flux. While when applying the Pt sublayer on the high $p(\text{O}_2)$ surface, it does not alter the oxygen flux obviously.¹⁶

According to Tsai et al.²⁴ the higher the oxygen-permeation rate, the lower the flux activation energies. The flux activation energy, if assuming the Arrhenius relation $J_{\text{O}_2} = J_0 \exp(-E_J/k_B T)$ that can cover the whole temperature range measured, will be 51.0 kJ/mol for the uncoated BSCFO membrane and 41.6 kJ/mol for the Gd112-coated (both sides) BSCFO membrane. This little decrease of flux activation energy seems cannot fully account the 41% increase of oxygen flux for the Gd112-coated BSCFO membrane. The same situation can be found in Ref. ¹⁴ where the BSCFO membranes synthesized by three different methods resulting in different oxygen-permeation flux but almost the same flux activation energies. Therefore, sometimes the change of the oxygen flux may not be explained only by the change of flux activation energies.

4. Conclusion

Thermogravimetric analysis reveals that the oxygen surface-exchange rates of Gd112 are markedly larger than that of BSCFO, which suggests that Gd112 is potential catalytic coating materials on membranes to enhance oxygen permeability.

Comparing the oxygen fluxes of uncoated BSCFO membrane with the Gd112-coated BSCFO membranes leads to the conclusion that deposition of catalytic Gd112 layer can improve the membrane performance significantly. The values of oxygen-permeation fluxes for BSCFO membranes surface-modified by a Gd112 layer on air side, helium side and both sides are 16%, 27% and 41% higher than that for uncoated BSCFO membrane, respectively, at 850 °C.

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