

Oxygen permeability of perovskite-type $Y_{1-x}M_xBa_2Cu_3O_{7-\delta}$ ($M = La, Ca$) membranes

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Abstract

Oxygen permeability of dense perovskite-type $Y_{1-x}La_xBa_2Cu_3O_{7-\delta}$ ($x = 0.1, 0.3, 0.5, 0.8$ and 1.0) and $Y_{1-y}Ca_yBa_2Cu_3O_{7-\delta}$ ($y = 0.1, 0.2, 0.3$ and 0.4) membranes were investigated under an air/He gradient in a temperature range from 750 to 950 °C. The results indicate that doping of La or Ca has great effects on the oxygen permeability. Oxygen permeation flux of $Y_{1-x}M_xBa_2Cu_3O_{7-\delta}$ ($M = La, Ca$) membrane increases with M substitution for Y in $YBa_2Cu_3O_{7-\delta}$, and has an obvious increase at about 900 °C due to an order–disorder transition of the oxygen vacancies in the membrane material. Maximum oxygen fluxes of 0.92 and 0.77 $\mu\text{mol/s cm}^2$ are obtained for $LaBa_2Cu_3O_{7-\delta}$ ($x = 1.0$) and $Y_{0.8}Ca_{0.2}Ba_2Cu_3O_{7-\delta}$ ($y = 0.2$) membranes with thickness 1.0 mm at 950 °C, respectively.

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1. Introduction

Mixed ionic and electronic conductivity membranes (MIECM) can transport simultaneously of both ionic and electronic charge carriers, and thus, in the presence of an oxygen potential gradient, oxygen ions can migrate through the material without the need of external electrodes. In recent years, due to the selected permeability of oxygen of MIECM and its potential application in oxygen separation from air, partial oxidation of methane, MIECM have received more and more attentions [1,2]. However, only those membranes with high oxygen permeation flux (>0.744 $\mu\text{mol/s cm}^2$), good thermochemistry and structural stability can be possible to apply practically. Therefore, to find new oxygen permeation materials and improve the oxygen permeation properties is still a vigorous topic.

$YBa_2Cu_3O_{7-\delta}$ (YBCO, δ is oxygen-deficiency) is a high-temperature superconductor with layered perovskite-type structure. Its oxygen content can be easily changed when temperature

or surrounding oxygen partial pressure is changed. In the process of the change of δ from 0 to 1, the orthorhombic-to-tetragonal phase transition takes place, but its perovskite-type structure frame is still held [3]. Our previous study showed that the oxygen permeation rate of YBCO membrane is about 0.336 $\mu\text{mol/s cm}^2$ at 900 °C [4], is not as high as the doped $SrFeO_3$, such as, $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ and $La_{0.4}Sr_{0.6}Co_{0.8}Fe_{0.2}O_{3-\delta}$ [5,6].

In order to increase oxygen permeability and structural stability, many scientific researchers have done a lot of studies by element doping or element substituting. Some good results are consequently obtained [7–10]. Therefore, in the present work we investigate the effect of element doping at the Y site on the oxygen permeation properties of YBCO. La element is selected to substitute Y element, because La and Y have same chemical valence, the ionic radius of La 1.18 Å is close to the ionic radius of Y 1.015 Å in 8-fold coordination, and the La solubility x in $Y_{1-x}La_xBa_2Cu_3O_{7-\delta}$ can reach 1.0. We also select Ca element to substitute partially Y element in YBCO because the ionic radius of Ca 1.12 Å is close to the ionic radius of Y 1.015 Å in 8-fold coordination, and there is an increase in oxygen holes with the substitution of Y^{3+} by Ca^{2+} [11]. Our results show that substituting La and Ca for Y can enhance the oxygen permeation rate greatly.

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2. Experimental

$Y_{1-x}La_xBa_2Cu_3O_{7-\delta}$ ($x=0.1, 0.3, 0.5, 0.8$ and 1.0) samples were synthesized by the common solid-state reaction method. The raw material is a mixture powder of Y_2O_3 , La_2O_3 , $BaCO_3$ and CuO according to $Y:La:Ba:Cu=(1-x):x:2:3$. $Y_{1-y}Ca_yBa_2Cu_3O_{7-\delta}$ samples were also synthesized by the same method. Considering the Ca solubility in $Y_{1-y}Ca_yBa_2Cu_3O_{7-\delta}$ is about 0.25 [11,12], we selected $y=0.1, 0.2, 0.3$ and 0.4 . The raw material is a mixture of Y_2O_3 , $CaCO_3$, $BaCO_3$ and CuO according to $Y:Ca:Ba:Cu=(1-y):y:2:3$. The milled powder was pressed into disks in a stainless steel mold (20 mm in diameter) under a pressure of 8–15 MPa. Green disk compacts were sintered at $920^\circ C$ for 15 h and at $950^\circ C$ for 8 h in air, with heating and cooling rates of 5 and $2^\circ C/min$, respectively, and then were held at $500^\circ C$ for 5 h. To ensure the denseness of membrane material, the previous disks were ground into fine powder and pressed again into disks with different thickness. The disks were sintered at $970^\circ C$ for 8 h and were also held at $500^\circ C$ for 5 h.

Oxygen permeation fluxes of dense $Y_{1-x}La_xBa_2Cu_3O_{7-\delta}$ and $Y_{1-y}Ca_yBa_2Cu_3O_{7-\delta}$ membranes with varying thicknesses from 1.0 to 2.0 mm were measured by steady state permeation method in a vertical high-temperature gas permeation system as sketched in Ref. [4]. The experiments were performed on the sealed membranes by exposing one side to static air and the other side to flowing high purity helium. The helium flowing rate is about 40 ml/min.

3. Results and discussion

Fig. 1 shows the X-ray diffraction (XRD) patterns for $Y_{1-x}La_xBa_2Cu_3O_{7-\delta}$ samples, all of them show mainly Re-123 phase, but little impurity phase can also be observed. The formation of $La_{1+x}Ba_{2-x}Cu_3O_{7-\delta} + Ba_2Cu_3O_{5+\delta}$ impurity phase is due to the occupation of La ions on the Ba site with the increase in La content. In addition, the preparation of La-123 sample is difficult, and pure phase cannot be obtained by sintering in air [13].

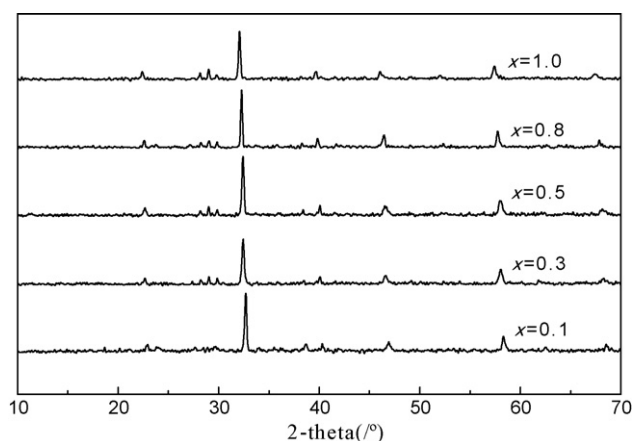


Fig. 1. XRD patterns for $Y_{1-x}La_xBa_2Cu_3O_{7-\delta}$ samples.

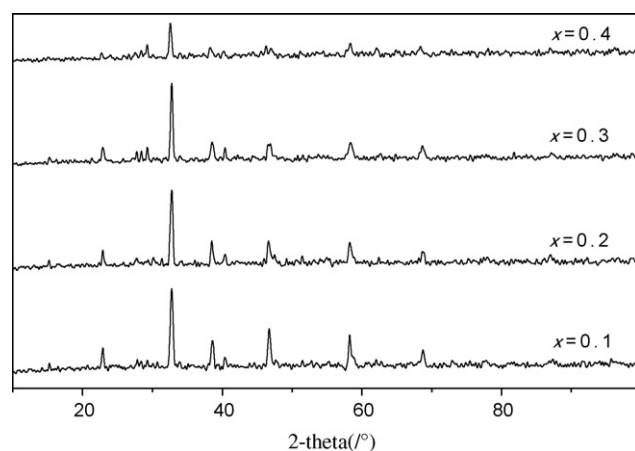


Fig. 2. XRD patterns for $Y_{1-y}Ca_yBa_2Cu_3O_{7-\delta}$.

Fig. 2 shows the XRD patterns for $Y_{1-y}Ca_yBa_2Cu_3O_{7-\delta}$ samples. From the Fig. 2, we can see that the XRD pattern for $Y_{0.6}Ca_{0.4}Ba_2Cu_3O_{7-\delta}$ ($y=0.4$) is obviously different to the others. The samples are mainly 123 phase when $y=0.1, 0.2$ and 0.3 , but the sample with $y=0.4$ has more impurity phase $BaCuO_2$. The appearance of impurity phase $BaCuO_2$ is due to a small amount of Ca that occupies the Ba site and new phase $Y_{1-y}Ca_{1.1y}Ba_{2-0.1y}Cu_3O_{7-\delta}$ is also formed [14,15]. Therefore, when $y>0.3$ the single 123 phase cannot be obtained.

In a MIECM, the oxygen transport can be described as the surface exchange reactions between the surrounding gas phase and the oxygen ion transport through the body of the membrane. The oxygen permeation flux density J_{O_2} can be theoretically calculated by the formula (in our research, no nonaxial transport of oxygen, taking $G=1$) [16]:

$$J_{O_2} = \frac{\sigma_{amb}}{4Fd}(E - \eta) \quad (1)$$

where d is membrane thickness, η driving force consumed by surface oxygen exchange, σ_{amb} ambipolar conductivity, F Faraday constant and E is driving force for oxygen permeation, respectively. According to Aasland [17], if the surface process is much faster than the bulk process, η in Eq. (1) is negligible, bulk controlled diffusion in a mixed conductor is given by:

$$J_{O_2} = \frac{1}{16F^2} \frac{RT\sigma_e\sigma_o}{(\sigma_e + \sigma_o)d} \ln \frac{p_1}{p_2} \quad (2)$$

where the symbol σ_e is electronic conductivity, σ_o oxygen ionic conductivity, T absolute temperature, R gas constant, p_1 high oxygen partial pressure and p_2 is low oxygen partial pressure, respectively.

The oxygen permeation flux as a function of La substitution proportion (La content x) measured at $950^\circ C$ across the disc-shaped $Y_{1-x}La_xBa_2Cu_3O_{7-\delta}$ ($x=0.1, 0.3, 0.5, 0.8$ and 1.0) membranes of thickness 1.0 mm is shown in Fig. 3. It can be seen that the oxygen permeation fluxes of $Y_{1-x}La_xBa_2Cu_3O_{7-\delta}$ membranes increase with the increase in La content. When La substitutes totally for Y, the oxygen permeation flux through $LaBa_2Cu_3O_{7-\delta}$ membrane reaches $0.92 \mu mol/s cm^2$. It is much higher than that through the YBCO membrane at the same tem-

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