The structure and oxygen permeation performance of Ba$_{0.5}$Sr$_{0.5}$Ga$_{1-x}$Fe$_x$O$_{3-\delta}$ perovskite-type oxides

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Abstract. Solid-state reaction was used to prepare mixed-conducting Ba$_{0.5}$Sr$_{0.5}$Ga$_{1-x}$Fe$_x$O$_{3-\delta}$ (BSGF) perovskite-type membranes. They were characterized by SEM, XRD and DSC and their oxygen permeation performance was examined. The experiments showed that the doping content of the Ga can play an important role in the structure of BSGF. It was found that the perovskite structure was sustained when Ga doping was lower than 0.4 or a little higher, but when Ga doping reached 0.6, the samples will not be perovskite structure. The oxygen permeation experiment showed that the temperature can affect the oxygen permeation of the BSGF membrane remarkably. At high temperature (about 940°C), its oxygen permeation property was higher and its oxygen permeation property will decrease with the temperature. The measured oxygen desorption activity energy of the Ba$_{0.5}$Sr$_{0.5}$Ga$_{0.2}$Fe$_{0.8}$O$_{3-\delta}$ measured is about 306.314 kJ·mol$^{-1}$.

1. Introduction

Partial oxidation of methane (POM) to syngas is a potential alternative to steam reforming processes. Since mixed-conducting oxygen permeation membranes can separate oxygen from air at an elevated temperature, using oxygen permeation membranes as reactor can combine the separation of air with POM into a single step, thus simplifying the process and reducing the cost by about 20–30%[1-3]. Over past years, extensive efforts have been focused on developing new mixed-conducting oxygen permeation membranes and improving their performance in POM processes. Many mixed conductors with the perovskite-type have shown notably high oxygen permeability[4, 5]. Unfortunately, most of them are unstable under methane conversion conditions. This is an inevitable concomitant of the expansion of the perovskite unit cell volume with reduction of the transition metal ions to their larger lower-valent forms as the oxygen partial pressure is lower[6, 7]. The membrane will eventually crack due to the volume change. The perovskite-type Ba$_{0.5}$Sr$_{0.5}$Co$_{0.3}$Fe$_{0.7}$O$_{3-\delta}$ (BSCFO) is one of the mixed conductive materials with high permeability[8-10]. However the stability of this material is poor in reduced atmosphere. Hendriksen et al.[11] reported that a strong contraction was observed when exposing SrFeCo$_{0.3}$O$_{3-\delta}$ even to mildly reducing conditions. It is obvious that the cobalt-containing perovskite oxides suffer from stability problems in a syngas environment, which might cause membrane failure during long-term operation. This forms a major incentive in several recent studies for either lessening the relative amount of cobalt in the perovskite phase to co-dope the material with less reducible ions, such as Zr$^{4+}$, Ga$^{3+}$ and Al$^{3+}$, or to add a toughening material such as zirconium or gallium[12-14].
It was reported that the oxygen permeation membranes with gallium-containing perovskite exhibit excellent stability in the POM process\cite{15, 16}. The average metal–oxygen bonding energy of Ga ion in perovskite structure is \(-143\) kJ·mol\(^{-1}\)\cite{17}, smaller than that of Co ion. The Ga ions only take the +3 valence state in perovskite structure. The lower metal–oxygen bonding energy is beneficial to promote the conductivity of oxygen ions. The stable valence state could avoid the expansion of the perovskite unit cell volume. It is conjectured that replacing Co by Ga may improve the stability of BSCFO membrane in the POM process. Therefore, the main objective of the present work is to develop new membrane materials \(\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Ga}_{1-x}\text{Fe}_{x}\text{O}_{3-\delta}\) and investigate their structure and oxygen permeation performance.

2. Experimental

The \(\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Ga}_{1-x}\text{Fe}_{x}\text{O}_{3-\delta}\) (BSGFO, \(0<x<0.8\)) samples were prepared by the common solid-state reaction method. Briefly, \(\text{BaCO}_3\), \(\text{SrCO}_3\), \(\text{Ga}_2\text{O}_3\) and \(\text{Fe}_2\text{O}_3\) were mixed and ground in an agate mortar. Then the mixture was pressed into disk, which was then sintered at 900–1000\(^\circ\text{C}\) for 10–15 h. The disk was then ground into fine powder, and pressed into disk again at a diameter of 20 mm by a thickness of 1.0–1.4 mm. The disk was sintered at 1000–1200\(^\circ\text{C}\) for 5 h with a heating rate of 2 \(^\circ\text{C}\cdot\text{min}^{-1}\) once again and then annealed at 500\(^\circ\text{C}\) for 5 h. The phases of membranes were determined by X-ray diffraction (XRD, Model D/MAX-3B, RIGAKU, Japan) with Cu-K\(\alpha\) radiation. The morphology of membranes was examined by scanning electron microscope (SEM, Model JSM-5610LV, JEOL, Japan).

![Figure 1. Schematic diagram of ceramic membrane reactor](image)

The oxygen permeation experiments were performed in a vertical high-temperature gas permeation system as shown in figure 1. BSGFO disks (efficient surface area 2.0 cm\(^2\)) were sealed onto the top of alumina tubes by using a homemade ceramic binder\cite{18}. High purity helium was introduced into alumina tube at atmospheric pressure. The effluent gas was analyzed by an on-line gas chromatograph (Agilent 1790, TCD detector). Helium was used as carrier gas and a molecular sieve 5A column was used to separate oxygen and nitrogen. The densities of the sintered membranes were determined by the Archimedes method using ethanol.

3. Results and Discussion

3.1. The influence of Ga doping on the phase structure

The influence of Ga doping on the phase structure of \(\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Ga}_{1-x}\text{Fe}_{x}\text{O}_{3-\delta}\) was investigated. Figure 2 shows the X-ray diffraction patterns of \(\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Ga}_{1-x}\text{Fe}_{x}\text{O}_{3-\delta}\) powders with varying Ga-contents obtained from calcining the precursors at high temperatures under stagnant air atmosphere. Pure phase perovskite was formed at \(x=0.2\), besides the basic perovskite, a few additional peaks differed were also observed at \(x=0.4\), and obviously different diffraction patterns from that of perovskite were found at...
x≥0.6. If the Ga and Fe ions take the valence state +3 and +4 respectively, the effective ionic radii of Ga and Fe are 0.62 and 0.585 Å, respectively. Furthermore, the calculation of the tolerance factor showed that the tolerance factor decreased from 0.946 to 0.936 with increasing Ga-content (See Table 1). Besides the ionic radii requirement, another condition to be fulfilled is electroneutrality[19], i.e., the sum of charges of A and B equals the total charge of oxygen anions. It is evident that with the increasing of Ga content, an anion-deficient perovskite structure tends to failure eventually due to the increasing of oxygen ions vacancy.

**Table 1. The tolerance factor of materials**

| Ga content x | r_A(Å) | r_B(Å) | r_O(Å) | t     |
|--------------|--------|--------|--------|-------|
| 0.2          | 1.265  | 0.592  | 1.40   | 0.946 |
| 0.4          | 1.265  | 0.599  | 1.40   | 0.943 |
| 0.6          | 1.265  | 0.606  | 1.40   | 0.939 |
| 0.8          | 1.265  | 0.613  | 1.40   | 0.936 |

![Figure 2. X-ray diffraction patterns of BSGFO](image1)

**Figure 2.** X-ray diffraction patterns of BSGFO

**Figure 3.** XRD patterns of BSGFO sintered at different temperatures

3.2. The influence of sintering temperature on the phase structure

Figure 3. shows the XRD patterns of Ba$_{0.5}$Sr$_{0.5}$Ga$_{0.2}$Fe$_{0.8}$O$_{3-δ}$ membranes sintered at different temperatures. Almost a pure phase perovskite was observed for temperature above 1100°C. The intensity of XRD diffraction peaks at 2θ of about 32°, 46° and 56° increases directly with the sintering temperature, which reflects the content of the corresponding phase. However, some other peaks could also be observed when temperature is 1000°C. Therefore, it can be concluded that the increases of sintering temperature are beneficial to the formation of perovskite phase. In this case proper sintering temperature is 1100°C.

3.3. The influence of sintering condition on the micrographs of membrane

A dense body is desirable for an oxygen permeation membrane. The morphology of membrane sintering with a heating rate of 2 °C·min$^{-1}$ was showed in figure 5(a). We can see that there are some pores on the surface of membrane. The formation of pores may be the volatilization of organic reagent (PVA) added as molding of membrane and the secondary recrystallization. Figure 4 shows the DSC/TG data of the composite precursor powders and BSGFO powders. Endothermic peaks present at about 220°C showing the decomposition of PVA and 796~1070°C showing the formation of mixed oxides. In order to volatilize organic reagent completely before sintering and form mixed oxides at mild condition, the modified sintering condition should be heating to 220°C with a heating rate of 2 °C·min$^{-1}$ and hold for 2 h first, then heating to 800°C and hold for 2 h and finally sintering at 1100°C.
for 5 h. The morphology of membrane with new condition was shown in figure 5(b), from which it can be seen that for the fresh membrane, ceramic grains with clear grain boundaries are visible and there are few pores on the surface of membrane. The relative density of membrane reaches to 5.538 g·cm⁻³, close to that of theoretical value.

![Figure 4. DSC curves of the composite precursor powders (a) and BSGFO powders (b)](image)

**Figure 4.** DSC curves of the composite precursor powders (a) and BSGFO powders (b)

![Figure 5. SEM pictures of BSGFO membrane with different sintering conditions](image)

**Figure 5.** SEM pictures of BSGFO membrane with different sintering conditions

3.4. The oxygen permeation performance of Ba₀.₅Sr₀.₅Ga₀.₂Fe₀.₈O₃-δ

The value of oxygen permeation flux is a key parameter for an oxygen permeable membrane to obtain real applications. Figure 3 presents the dependencies of oxygen permeation fluxes of Ba₀.₅Sr₀.₅Ga₀.₂Fe₀.₈O₃-δ membranes on temperature under atmosphere. It can be seen that the oxygen permeation flux is about 0.04 ml·min⁻¹·cm⁻² only at 800°C. With the increase of temperature the oxygen permeation flux reaches to about 0.11 ml·min⁻¹·cm⁻² at 940°C. The activation energy of BSGFO estimated by Freemen-Carroll method using the TG data[20] was 306.314 kJ·mol⁻¹ for 800–900°C. That explained the reason of the oxygen permeation at lower temperature.
4. Conclusions

The doping content of the Ga can affect on the structures of Ba$_{0.5}$Sr$_{0.5}$Ga$_{1-x}$Fe$_x$O$_{3-δ}$ significantly. It was found that the perovskite-type ceramic membrane was sustained only when Ga content x≤0.4. Indicating a stable perovskite-type structure depended on not only the geometric structure but also the oxygen ions deficiency. The temperature can affect the oxygen permeation of the BSGF membrane remarkably. At a high temperature of 940°C, its oxygen permeation reaches to about 0.11 ml·min$^{-1}$·cm$^{-2}$. However, at a lower temperature of 800°C, it can also exhibit some performance of oxygen permeation. The oxygen desorption activity energy of the Ba$_{0.5}$Sr$_{0.5}$Ga$_{0.2}$Fe$_{0.8}$O$_{3-δ}$ calculated using TG data is about 306.314 kJ·mol$^{-1}$.

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