Synthesis and Characterization of \( \text{La}_{1-x}\text{Sr}_{x}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3 \) and \( \text{La}_{1-x}\text{Ba}_{y}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3 \) (0.0 ≤ \( x \) ≤ 0.4) Dense Membranes

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Abstract

Dense membranes of perovskite-type oxides \( \text{La}_{1-x}\text{Sr}_{x}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3 \) (LSCF) and \( \text{La}_{1-x}\text{Ba}_{y}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3 \) (LBCF) where 0.0 ≤ \( x \) ≤ 0.5, have oxygen ion transfer capability and active as catalysts for partial oxidation of small hydrocarbons. The oxides were synthesized by solid state methods from their corresponding metal oxides or nitrates at a stoichiometric composition and calcined between 1150 and 1250 °C. X-ray diffraction analysis showed that the resulting powders have perovskite structure for LBCF at all percentage of barium substitution. On the other hand, non-perovskite structure appeared on LSCF when Sr substitution exceeds 30%. The perovskite powders were used to prepare dense membranes by pressing the corresponding powders in a hardened stainless steel mold into green membranes (12 mm diameter and 2 mm thick) by applying 2 to 8 ton pressure followed by sintering process at temperature between 900 and 1250 °C. Morphology analysis by SEM showed that the density of membranes depends on the percentage of Sr and Ba substitution and calcination temperature. The density and hardness of the membranes increases, while their thermal expansion coefficient decrease when the amount of Sr substitution was higher. Higher applied pressure and sintering temperature increase the density of the resulting membranes.

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Introduction

\( \text{La}_{1-x}\text{M}_{y}\text{Co}_{1-y}\text{Fe}_{y}\text{O}_3 \) is one of the perovskite-type oxides that can be used as membrane materials for oxygen ion conductors with high oxygen flux (Zeng et al., 2007). Oxygen ion conductivity of 10\(^{-2}\) to 1.0 \( \Omega^{-1}\)cm\(^{-1}\), which is considered very high, was exhibited by \( \text{La}_{1-x}\text{Sr}_{x}\text{Co}_{1-y}\text{Fe}_{y}\text{O}_3 \) at 800 °C.

Oxygen ion conductivity in the perovskite oxide membrane is influenced by the density of the membrane. The conductivity is directly related to the presence of grain boundaries that constrain the displacement of oxygen ions in the membrane (Kharton et al., 2000). The density is strongly influenced by the compressive force given to raw materials in the mold during the manufacture of green membrane and the sintering process (Zhang et al., 1999). Mobius et al. (2009) reported that dense membranes from the family of \( \text{La}_{1-x}\text{Sr}_{x}\text{Co}_{1-y}\text{Fe}_{y}\text{O}_3 \) can be made when sintered at 1150 °C. Meanwhile, Mosadeghkhah et al. (2007) reported that \( \text{La}_{1-x}\text{Sr}_{x}\text{Co}_{1-y}\text{Fe}_{y}\text{O}_3 \) membranes have relative density up to 93% when they were prepared by pressing them in a mold using 2.3 to 2.9 tonnes of compressive force and sintered at 1100 °C for 7 to 8 hours.

The density of the membrane can also be increased if the membrane raw material contains elements that act as a flux. These elements can lower the melting point of the material in the same way sodium which can significantly reduce the melting point of quartz. In this case the sodium is a flux element. These elements are usually of the group of alkaline and alkaline earth group. Strontium and Barium is an alkaline earth elements that are likely to have properties as flux and widely reported as components of perovskite oxides. Both of these elements are in the oxidation state of 2\(^+\) in perovskite oxides.

Given its nature as a flux and the component of perovskite oxides it is necessary to study on the effect of the presence of such elements in the perovskite oxide group of \( \text{La}_{1-x}\text{M}_{y}\text{Co}_{1-y}\text{Fe}_{y}\text{O}_3 \) and its influence on the density of the resulting membrane. Knowledge of the relationship between the densities of the membrane by the presence of elements of lowering the melting point is needed in the preparation of the oxygen ion conductor membrane that has a high
oxygen ion conductivity as well as density. This paper reports the results of research on the effect of the concentration of Ba\(^{2+}\) and Sr\(^{2+}\) substituents in perovskite oxide La\(_{1-x}\)M\(_{x}\)Co\(_3\)Fe\(_2\)O\(_y\) (M = Ba\(^{2+}\) or Sr\(^{2+}\)) against the density of the resulting membrane.

**Methodology**

1. **Preparation of L\(_{1-x}\)Sr\(_x\)Co\(_3\)Fe\(_2\)O\(_y\) (LSCF) and L\(_{1-x}\)Ba\(_x\)Co\(_3\)Fe\(_2\)O\(_y\)**

Powders of LSCF and LBCF synthesized by solid state method from La\(_2\)O\(_3\), Co\(_3\)O\(_4\), Fe\(_2\)O\(_3\), BaO and Sr(NO\(_3\))\(_2\).6H\(_2\)O, following the method reported by Zawadski (2010) and Maulidah (2010). The preparation begins with the mixing of all the powder material with a composition according to the molar composition of targeted LSCF and BSCF. Mixing was carried out by milling the powders in a ball mill for 24 hours at a speed of 400 rpm. Methanol was added before milling to disperse the powder in the mill. The result of milling was dried on a hot plate at a temperature of 75 °C to evaporate the methanol. The dried mixture was then calcined at 1000 °C for 2 hours. Calcination process was repeated three times to improve the crystallinity of the reaction product. The products were analysed by X-ray diffraction at 20 between 20 and 100° with a step size 0.02° and a rate of 1 °C.min\(^{-1}\). The perovskite oxides were named according to the following rule: LSCF (or LBCF) ab82. For example, LSCF 7382 represents La\(_{0.8}\)Sr\(_{0.2}\)Co\(_3\)Fe\(_2\)O\(_y\), and LBCF 6482 represents La\(_{0.8}\)Ba\(_{0.2}\)Co\(_3\)Fe\(_2\)O\(_y\).

2. **Preparation and characterization of LSCF and LBCF membranes**

LSCF and BSCF powder that has been formed was molded into coin-shaped membrane using KBr pellets press. The diameter of the membrane was 12 mm with a thickness between 1 and 2 mm. The applied pressure to press the pellets was 4 tons and held for 15 minutes. The resulting green membrane then sintered at 1250 °C for 2 to 16 hours at a rate of temperature rise of 3°.min\(^{-1}\). The effect of temperature and duration of sintering as well as applied pressure during pelletizing process to the physical properties of membranes were studied on LSCF 7382. Morphology of the resulting membranes was observed by SEM-EDX. Thermal expansion coefficient (TEC) and hardness of the membranes were observed with Thermomechanical Analyser (TMA) and Vickers Micro Hardness Tester.

**Results and Discussion**

The results of X-ray diffraction analysis of the oxide powders synthesized by solid state method are shown in Figure 1. It can be seen that all the diffractogram has a pattern with diffraction peaks typical of LaCoO\(_3\) with perovskite oxide structure shown by the typical diffraction peak at 29 23°, 32.62°, 40.3°, 47°, 53° and 58.2° as reported by Thoriyah (2010).

Based on the diffraction data, it is hardly found any impurities except on LSCF 7382 (marked by arrows in Figure 1a). The presence of impurities is shown by the diffraction peaks at 36.5°, 37°, 38.5° and 42°. This indicates that the LBCF and LSCF are pure. In the case LSCF 7382, the impurities are relatively small as seen from the very small intensity of the non-perovskite phase. Further evaluation to the LSCF 7382 diffractogram using the year 2012 ICDD data base shows that the peaks of non-perovskite phase at 36.5°, 37° and 38.5° are belong to CoO\(_2\) and peaks at 42° are belong to La\(_2\)O\(_3\). This indicates that there is still a cobalt and lanthanum oxides that has not reacted perfectly into perovskite oxide that is possible by not homogeneous mixtures prepared from metallic oxides. Nevertheless, the existence of non-perovskite phase is negligible so that both LSCF and LBCF perovskite oxides can be used in the preparation of perovskite oxide membranes.

Powders of LBCF and LSCF perovskite oxides were used to mould into 12 mm diameter pellets. The resulting green membranes were sintered at 1100 °C for LSCF as reported by Setiawati (2012) and 1250 °C for LBCF. The sintered membranes have darker colour than their original green pellets. Testing the sintered results with water drops shows that the membrane porosity is very low as indicated by the persistence of water droplets on the surface of the grains of the membrane. If the membrane is porous, water droplets will disappear into the pores of the membranes.

Figure 2 shows the surface of the LSCF membrane after sintering at 1100 °C for 8 hours. In the figure it is shown that the density of LSCF 10082 (La\(_{1-x}\)Sr\(_x\)Co\(_3\)Fe\(_2\)O\(_y\)) membrane still contains many pores while LSCF 6482 had no visible pores. This shows that the density increases with increasing number of substituent Sr\(^{2+}\).

Unlike the LSCF that were sintered at 1100 °C, the density LBCF at all compositions is very high which is made possible by the use of higher sintering temperature (1250 °C) as shown by SEM images in Figure 3. There is no significant difference in the density of the LBCF membrane.
Figure 1. Diffractogram of (a) La_{1-x}Sr_xCo_{0.8}Fe_{0.2}O_3 and (b) La_{1-x}Ba_xCo_{0.8}Fe_{0.2}O_3

Figure 2. Surface morphology of LSCF membranes
Although in general the LBCF membranes are dense, each membrane has a surface porosity that is different. Figure 3 shows that the surface of LBCF varies depending on the number of Ba$^{2+}$ substituent. The lower the number of Ba$^{2+}$ substituents, the lower the density of the surface of resulting membrane is. This is caused by the ability of Ba as a flux agent in lowering the melting point of the materials.

Variation in the number of Sr$^{2+}$ substituent also affects the coefficient of thermal expansion and hardness of the membranes. Figure 4 and 5 show the coefficient of thermal expansion measured by TMA (Thermomechanical Analyser) and Vicker’s hardness by Vicker’s micro hardness tester. in both image, $x$ indicates the fraction of Sr$^{2+}$ in accordance with the general formula La$_{1-x}$Sr$_x$Co$_{0.8}$Fe$_{0.2}$O$_3$.

Thermal expansion coefficients of all LSCF membranes up to 800 °C have no significant difference except on LSCF without any Sr$^{2+}$ substitution (LSCF 10082). The coefficient of LSCF 10082 is higher than other LSCF indicating that the addition of Sr$^{2+}$ is slightly lower the coefficient of thermal expansion. However, at 1000 °C, there was a huge increase in the thermal expansion coefficient. At this temperature, in general it can be seen that the higher the number of substituent Sr$^{2+}$, the higher the heat expansion coefficient. This again proves that the Sr$^{2+}$ acts to lower the melting point and the increase of thermal expansion coefficient of LSM at 1000 °C LSCF is caused by softening of LSCF.
Effects of increased Sr$^{2+}$ in the sintering process are also indicated by the results of hardness testing of the membranes where denser membrane will show higher hardness. Figure 5 shows that the hardness increased with increasing number of substituent Sr$^{2+}$.

The density of the membrane also increases when a higher pressure was applied in the moulding of the green membrane. Figure 6 shows a cross section of the LSCF 7382 which was membrane sintered at 1100 °C with a pressure of 4 and 8 tons. A membrane with 8 tons of moulding pressure is denser than the same membrane moulded at 4 tons.

**Conclusions**

Based on the results of this study it can be concluded that the calcination temperature affects the crystallinity and purity of the synthesized perovskite oxide La$_{1-x}$Ba$_x$Co$_{0.8}$Fe$_{0.2}$O$_3$ (LBCF) and La$_{1-x}$Sr$_x$Co$_{0.8}$Fe$_{0.2}$O$_3$ (LSCF) with 0,0 ≤ x ≤ 0.4. Both LBCF and LSCF perovskite oxides with high crystallinity can be produced at 1150 °C calcination. Analysis results of membranes made from LBCF and LSCF show that the density of the membrane is influenced by the number of Ba$^{2+}$ and Sr$^{2+}$ substituents. The greater the number of substituents, the denser the resulting membranes is. The substituent also affects the density and hardness of the membranes. Higher density and hardness were achieved at higher Sr$^{2+}$ substituent. On the other hand thermal expansion coefficient of LSCF decreases when the amount of Sr$^{2+}$ substitution was higher. In overall, higher applied pressure and sintering temperature increase the density of the resulting membranes.
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