

# Oxygen permeability and phase stability of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ dense membrane

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**ABSTRACT:** A dense membrane of perovskite  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$  has been successfully prepared by polymerized complex method. Precursor of  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$  was analyzed by thermal gravimetric analysis and XRD to investigate optimum calcination temperature. The optimum sintering temperature of precursor is between 1000 and 1100 °C at which single perovskite powder is obtained without impurities. The oxygen flux of  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$  membrane increased with increasing temperature and decreasing thickness, and the oxygen permeation flux through 1.0 mm membrane with modified surface exposed to flowing air ( $P_{\text{H}_2} = 0.21$  atm) and helium ( $P_{\text{I}} = 10^{-5}$  atm) was ca. 1.4 ml/cm<sup>2</sup>·min at 950 °C. At high temperature over 850 °C surface reaction is more important than bulk diffusion. Membranes after permeation test were stable in view of crystal structure irrespective of surface modification but swollen part was formed in feed-side surface of non-modified membrane. Low oxygen permeation flux of non-modified membrane might be originated from low surface adsorption and barium surface diffusion in feed side.

**Keywords:**  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ , membrane, oxygen permeation, stability

## NOMENCLATURE

|                   |                                                    |
|-------------------|----------------------------------------------------|
| $F_{\text{perm}}$ | Permeation flux [ml/min]                           |
| $y_{\text{O}_2}$  | Oxygen concentration [v%]                          |
| $A$               | Effective membrane surface area [cm <sup>2</sup> ] |
| $P_{\text{O}_2}$  | Oxygen partial pressure [Pa]                       |
| $J_{\text{O}_2}$  | Oxygen flux [mol/cm <sup>2</sup> ·min]             |

## 1. INTRODUCTION

Carbon dioxide emitted by various source causes so called heat island phenomena in the city. Especially it is important to remove the carbon dioxide from CHP, combined heat and power system, because CHP is located in the city. Clean fuel such as natural gas is also used in CHP system to reduce emissions of pollutants but the method of CO<sub>2</sub> separation in CHP system is recently focused in view of environmental (heat island, climate change) and sustainable (low rank fuel adaptation) point.

Oxygen combustion is one of reduction methods of carbon dioxide from power system. However, the cost of production for pure oxygen is high so that oxy-fuel combustion is not commercialized until now. Mixed conducting membranes possessing oxygen ionic and electronic conductivities have been interested due to their oxygen separation ability. Especially, the ceramic dense membrane has a great potential to be applicable in petroleum industries and power generation system for oxygen separation from oxygen containing mixture gas[1]. It is very attractive technology economically and environmentally in industrial process with hot-turbine system. Many researches[2-6] have been deal with the perovskite type membrane with high oxygen permeability, and good stability at high temperatures condition. In this work,  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$  was prepared as membrane material. The purpose of this

work was to investigate the fundamental properties of  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ , including the oxygen permeability and stability in high temperature operation

## 2. EXPERIMENTAL

### 2.1 Membrane Preparation

All powder has been synthesized using polymerized complex method which can synthesizes a homogeneous and pure powder relatively low sintering temperature. The as-synthesized powders were compressed into disks of 20 mm in diameter and 1.0 ~ 2.0 mm of thickness in a stainless steel mold under a hydraulic load by unilateral press (model 25601 series, Specac Limited, U.K.). The green disk sintered at 1353 K for 5 hr. The sintered disk was polished to smooth the surface and to control the thickness of disk with 600 grit SiC. The face of membrane was modified by coating of same material powder. The phase of the powder and the disk before and after sintering was characterized with an X-ray diffractometer (XRD, Rigaku Co Model D/Max 2200-Ultimplus, Japan)

### 2.2 Experimental Procedure

The membrane permeation cell used in this work is shown in Fig. 1. A disk type permeation cell was used in this work for oxygen permeation study. Au ring (Au plate, 99.9 %, Aldrich) was used as the sealant to seal the disk onto the dense alumina tube.

Every membrane was tested to evaluate dense membrane with vacuum leakage apparatus. Prior to oxygen permeation test, the cell part is purged with He gas to remove the air in permeation cell tube and to confirm sealing of the assembly consisted of alumina tubes, membrane and sealant for 20 hr. The leakage test for the outer parts of apparatus such as line, fitting and valve was conducted with supplying  $\text{N}_2$  gas at feed side. The leakage through membrane during oxygen permeation test was also measured for all runs at each temperature and the oxygen permeation fluxes were corrected on

the basis of the measured leakage. Permeation study was performed within the temperature range of 750~950 °C. The temperature of the cell was increased up to 950 °C with a heating rate of 1.5 °C·min<sup>-1</sup> and held at desired temperature for 100 min to attain equilibrium flux. Synthetic air (21 vol.%  $\text{O}_2$ +79 vol.%  $\text{N}_2$ ) and pure He (99.999 %) were introduced into the different side of the membrane disk, which were controlled by the mass flow controller(MKS 247C). The feed flow rate was kept at 20 ml·min<sup>-1</sup>, and sweep flow rate was 20 ml·min<sup>-1</sup> on the permeated side. The oxygen content in the permeate stream was measured with a gas chromatograph (GC-TCD, Acme 6000, YoungLin, Korea). Helium was used as a reference gas, and a 1.8 m 5A molecular sieve was employed for gas separation. Using the results of GC, the oxygen flux was determined by following equation.

$$J_{\text{O}_2} [\text{ml/min} \cdot \text{cm}^2 (\text{STP})] = \frac{F_{\text{perm}} [\text{ml/min}] y_{\text{O}_2} [\text{v}\%] - \text{leakage correction}}{A [\text{cm}^2]}$$

Where  $F_{\text{perm}}$  is corresponding with the total flow rate of the permeation stream in which the oxygen concentration is  $y_{\text{O}_2}$ ,  $A$  is the effective membrane surface area, and leakage correction means the calculating oxygen flux from leakage.

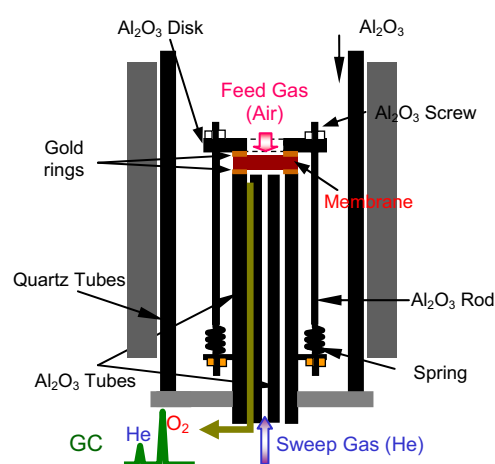


**Figure 1:** The schematic diagrams of test cell.

### 3. RESULTS AND DISCUSSION

#### 3.1 Sample Characteristics

$\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ , (BSCF-5582) was successfully synthesized by using polymerized complex method. Fig. 2 shows TGA and DSC results of BSCF-5582 precursor powders. It was reported that BSCF-5582 was synthesized at 1100 °C [7]. TGA result in Figure 2 also showed BSCF-5582 was melted at 1225 °C. However, we have a slightly melted surface after sintering over 1100 °C. It indicates that polymerized complex method might lower the sintering temperature of BSCF-5582.

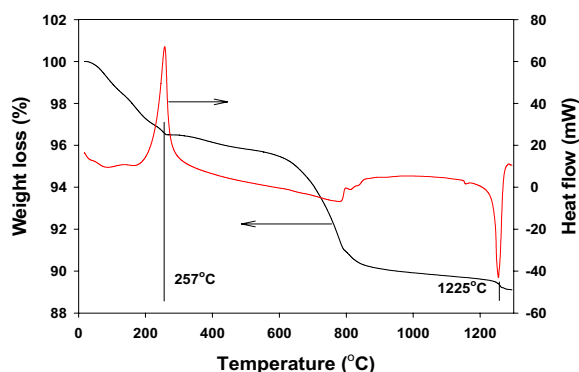


**Figure 2:** TGA result of BSCF-5582 precursor prepared by polymerized complex method.

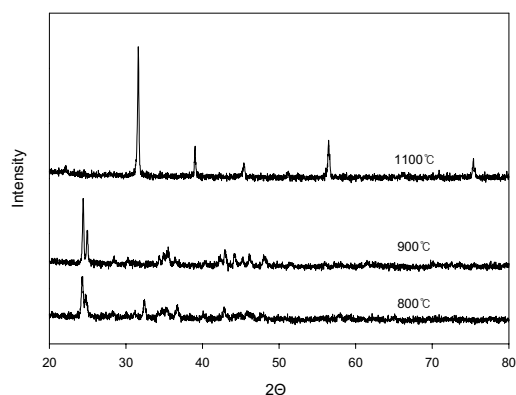


**Figure 3:** XRD patterns of BSCF-5582 powders according to sintering temperature.

Fig. 3 shows XRD patterns of BSCF-5582 powders according to sintering temperature.

The XRD results below 900 °C shows carbonate peak. Therefore the sintering window of BSCF-5582 is very narrow and the region of optimum sintering temperature is between 1000 and 1100 °C.

#### 3.2 Oxygen Permeation

Fig. 4 shows oxygen permeation flux of BSCF-5582 with membrane thickness. In this case, all membrane was modified. As membrane thickness decreased from 1.6 mm to 1.0 mm, the permeation flux increased about 80 % (from 0.74 to 1.33 ml/cm<sup>2</sup>·min at 900 °C). The increasing rate is almost same in all the temperature region. It indicates that the membrane is controlled by bulk diffusion with Wagner equation[1].

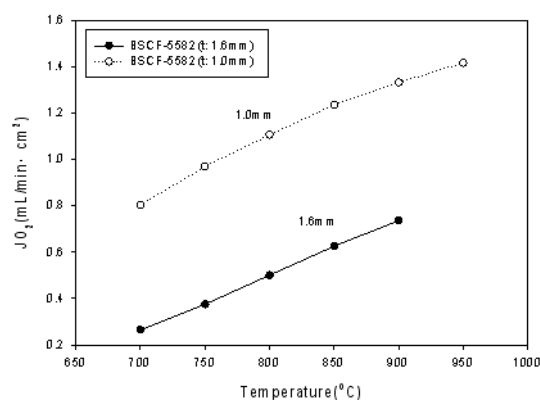


**Figure 4:** Oxygen permeation flux of according to membrane thickness

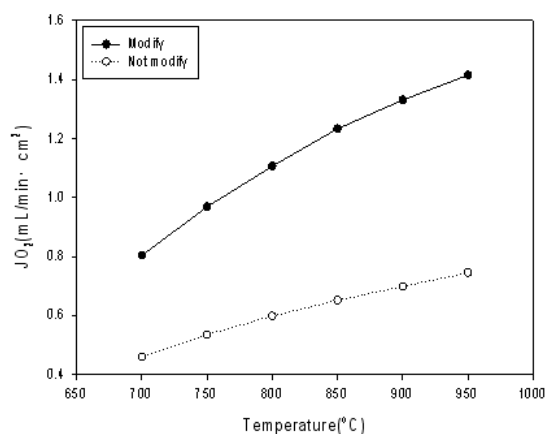


**Figure 5:** Oxygen permeation flux of according to surface modification

Fig. 5 shows oxygen permeation flux of BSCF-5582 according to surface modification. Oxygen permeation flux was increased as temperature increased irrespective of membrane modification. In the case of modified membrane, it reached  $1.4 \text{ ml/cm}^2\cdot\text{min}$  at  $950^\circ\text{C}$  exposed to flowing air ( $P_{\text{H}_2}=0.21 \text{ atm}$ , feed side of membrane) and helium ( $P_{\text{I}}=10^{-5} \text{ atm}$  permeated side of membrane). Though the membrane thickness is same ( $1.0 \text{ mm}$ ), the permeation fluxes of modified membrane were higher than those of non-modified membrane. In addition, the increasing rate is higher in high temperature region. It indicates that surface reaction is more dominant in higher temperature region. It means that in higher temperature over  $850^\circ\text{C}$ , surface reaction is rate exterminating step.

### 3.3 Membrane Stability

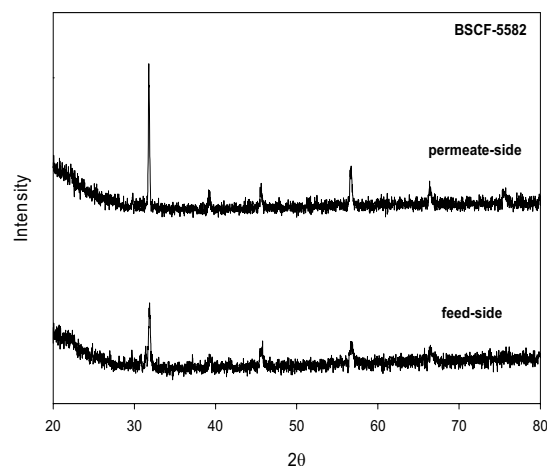
XRD, SEM and EDX analysis were conducted to evaluate the stability of membrane after permeation test.

Fig. 6 shows the results of XRD for modified and non-modified membranes respectively. No additional peak in XRD is in Fig. 6 for modified and non-modified membranes. It was known that all the membrane was stable after at least 100 hr permeation test.

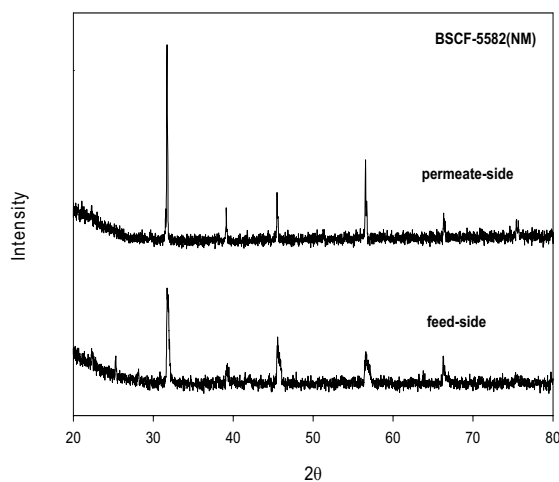
Fig. 7 shows the SEM images of modified and non-modified membranes after permeation test. In the case of modified membrane, the surface has no crack though grain boundary is not clear due to surface modification. In the case of non-modified membrane, the images of permeation side and feed side before permeation test are almost similar to the image of Fig. 7 (d). However, the SEM image of the feed-side surface is totally different from Fig. 7 (d). It looks like swollen forms. In comparison of SEM images of Fig. 7 (c) and (d), it is clear that the feed side is more important for non-modified membrane.

EDS mapping results of non-modified permeate-side is shown in Fig. 8. Fig. 8 (a)

is mapping area and Fig. 8 (b) and (c) are element mapping results about all metals and Sr and oxygen respectively. From these results, the swollen part might be Barium oxide. The reason why barium is rich in swollen part mainly is not clear until now. But it is evidence that surface reaction is important for BSCF-5582 membrane.

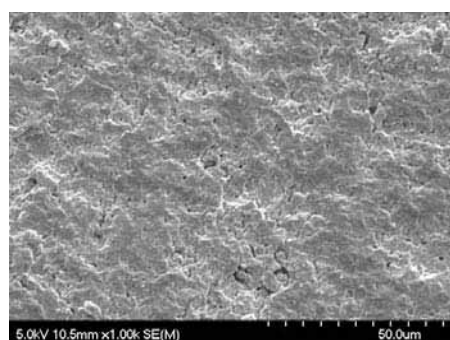


(a) Modified membrane

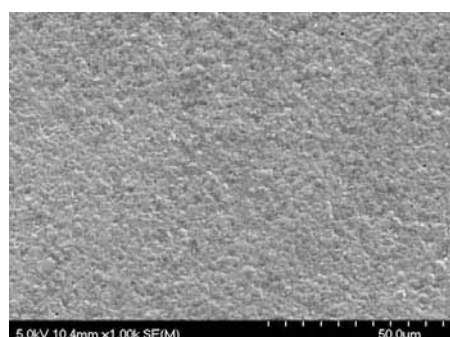


(b) Non-modified membrane

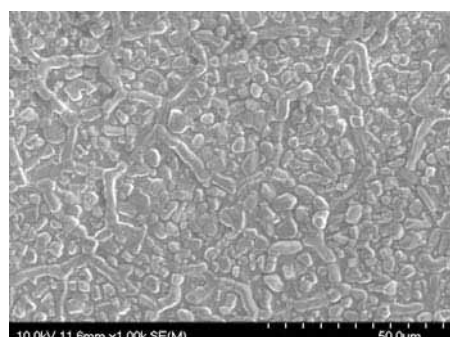
**Figure 6:** XRD patterns for modified and non-modified membranes respectively after permeation test.



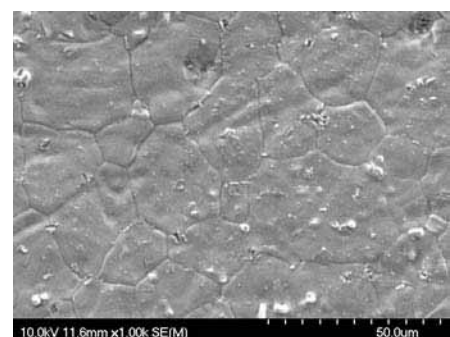
(a)



(b)

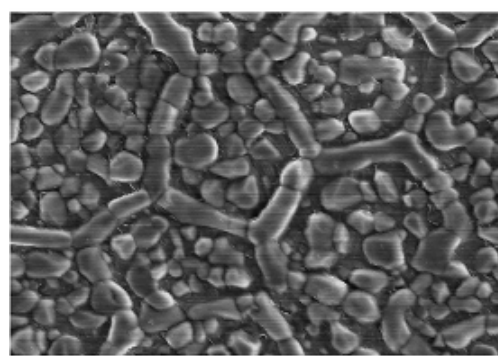


(c)

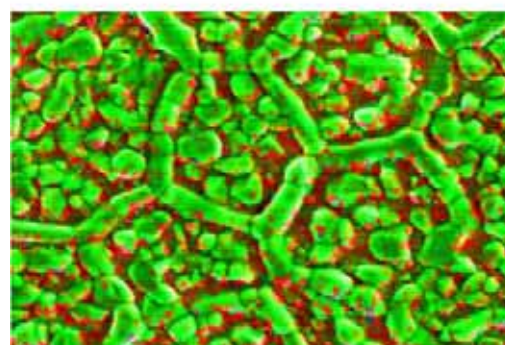


(d)

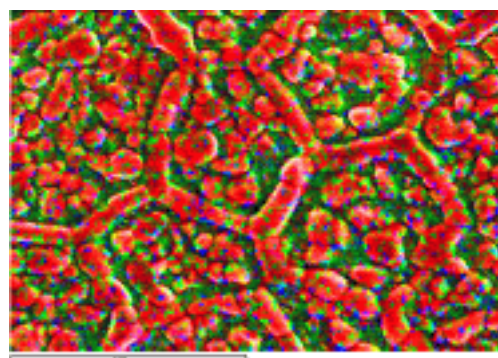
**Figure 7:** SEM images of membrane surfaces after permeation test; (a) modified feed-side (b) modified permeate-side (c) non-modified feed-side and (d) non-modified permeate-side.



(a)



(b)



(c)

**Figure 8:** EDS mapping images of non-modified membrane surfaces after permeation test; (a) mapping area of feed-side surface; (b) mapping results of Oxygen (green) and Sr (red); (c) mapping results of Ba (red), Sr (green), Co (blue) and Fe (black)

#### 4. CONCLUSION

Peovskite type ceramic oxides  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ , (BSCF-5582) was

synthesized by polymerized complex method. The characterization results showed that the oxides prepared possessed perovskite structure without secondary phase in narrow sintering temperature region between 1000 and 1100 °C.

The oxygen flux of  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$  membrane increased with increasing temperature and decreasing thickness, and the oxygen permeation flux through 1.0 mm membrane with modified surface exposed to flowing air ( $P_{\text{H}_2} = 0.21$  atm) and helium ( $P_{\text{I}} = 10^{-5}$  atm) was ca. 1.4 ml/cm<sup>2</sup>·min at 950 °C. In comparison of permeations between modified and non-modified membrane, it is known that the surface reaction is rate exterminating step for oxygen permeation of BSCF-5582 membrane.

Perovskite structure and phase for all membranes in XRD results did not change even after permeation test of 100 hr but barium diffusion into feed-side surface of non-modified membrane occurred to form swollen parts. Low oxygen permeation flux of non-modified membrane might be originated from low surface adsorption and barium surface diffusion in feed side.

## ACKNOWLEDGEMENT

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