Preparation and Morphological Property of $\text{Co}_3\text{O}_4/\text{Ba}_x\text{Sr}_{1-x}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ ($x=0.5-0.7$) Membranes using Starch as Binder Agent

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Abstract. $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ ($x=0.5-0.7$) or BSCF was known as promising material to prepare MIEC membrane for oxygen separation. Several modifications have been performed to improve catalytic activity of BSCF membranes. One of the promising methods was coating of the membrane with catalyst layer such as $\text{Co}_3\text{O}_4$. This work investigates the simple and effective method to coat $\text{Co}_3\text{O}_4$ layer on the surface of $\text{Ba}_x\text{Sr}_{1-x}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ ($x=0.5-0.7$) flat sheet membranes resulting $\text{Co}_3\text{O}_4$/BSCF membranes. BSCF were prepared from its initial powders by dry pressing method followed by sintering at 1150 °C for 4 hours. The resulted BSCF dense membranes were coated with $\text{Co}_3\text{O}_4$ using starch as binder agent in the form of suspension. The coating suspension consist of 62.5% w/w of starch and 37.5% w/w of $\text{Co}_3\text{O}_4$. The coating suspension was directly coated on the surface of the BSCF dense membranes followed by calcination at 800 °C for 3 hours. The surface morphology and cross section of membranes were observed using Scanning Electron Microscope (SEM) equipped with Energy Dispersive X-ray (EDX). SEM images show that the method succeeds to coat $\text{Co}_3\text{O}_4$ layer on the surface of BSCF membranes. However, the distribution of the $\text{Co}_3\text{O}_4$ was not uniform and some particles form aggregate. The particle size of the membranes was about 0.5–2.0 µm whereas the aggregate size is around 2–5 µm. The presence of $\text{Co}_3\text{O}_4$ layer was also indicated by the increasing of Co intensity in the surface of membranes as analyzed by EDX.

1. Introduction
Methane is the main gas that composed natural gas. Its abundance reaches approximately 70-90% of the natural gas composition [1]. This gas is also produce as the by product of the oil refinery [2]. Due to its abundance, methane is being potential to be developed as alternative fuel to substitute the using of oil. To increase the affectivity of the methane usage, as well as the increasing the product value, methane could be converted to be more added value product such us syngas (CO+ $\text{H}_2$). The conversion methan to be syngas could be carried out by partial oxidation of methane (POM)[3], [4]. However, POM required controllable oxygen supply.

The control of oxygen supply is crucial factor in POM. The lack of oxygen could only resulted in low yield, on the other hand, the excess of oxygen could convert methane to be $\text{CO}_2$ and $\text{H}_2\text{O}$ as product of total oxidation. This oxygen controlled supply in POM could be performed using mixed ionic and electronic conducting membranes (MIEC) [5]. This membrane could permeate oxygen in the form of...
ion resulting high selectivity, up to 100% theoretically [6]. Among MIEC membrane materials, perovskite based materials, composed of strontium-cobalt-iron (SCF) are promising material due to their high oxygen permeability [7]. Recently, the Ba$_{1-x}$Sr$_x$Co$_{1-y}$Fe$_y$O$_{3-\delta}$ (BSCF)'s are getting more interest from many researchers due to their high oxygen permeability and their excellent stability toward reducing atmosphere [8], [9]. Ghadimi et.al. reported that this increasing of oxygen permeability is caused by the decreasing of activation energy of ion diffusion through crystal lattice [10]. Moreover, Faraji et.al. reported that this material could release its oxygen ion in relatively low temperature compare to the conventional material in POM operation [11]. The selectivity of this material for CO was also excellent reaching 91.5% after addition of Ni/ZrO. The 50-60% amount of Ba in BSCF could also stabilize oxidation state on the B cation resulting higher stability in the structure[12]. BSCF membranes also exhibited good mechanical and thermal properties [13]. Despite of BSCF’s high oxygen permeability, the oxygen permeability of these membranes should still be improved to reach the commercial target. In MIEC membrane, the oxygen permeability is determined by two factors: the ionic bulk diffusion along the crystal lattice and the surface exchange reaction in the membrane surface [7]. The faster surface exchange reaction, the higher oxygen permeability. Thus, one pathway to increase the oxygen reaction is increasing the surface exchange reaction by coating the BSCF surface with catalyst. Previously, Leo at.al. used Ag for coating layer on BSCF membranes. The presence of Ag layers could indeed increase membrane’s permeability. However, the Ag particles are concentrated on the BSCF grain boundaries [14]. Leo at.al. coat the BSCF membrane using Pd nanoparticle and revealed that this coating could enhance the oxygen permeability up to 10 times at 700 °C [15]. The using of these noble metals clearly enhanced the oxygen permeability of BSCF membranes, however, this material is expensive thus make it less reliable for industrial scale.

Recently, Co$_3$O$_4$ is getting interest to be used as catalyst layer on BSCF surface as its good activity toward reaction involving oxygen, both in oxygen reduction reaction (ORR) or oxygen evolution reaction (OER). Li et.al. reported that the coating of BSCF membrane using Co$_3$O$_4$ nanorod could enhance the oxygen permeability up to 11.5 times higher than unmodified BSCF membrane at 850 °C [16]. Wang et.al. reported that the coating of Co$_3$O$_4$ nanoparticle on BSCF membrane’s surface could enhance the oxygen permeability up to 4 times higher that unmodified membranes [17]. However, the methods to coat the catalyst layer on the BSCF membrane’s surface were often complex involving several steps and releasing of dangerous compounds during calcination. The precursor of Co$_3$O$_4$ was usually come from nitrate ion that release NO$_x$ during calcination that harmful for the environment. Moreover, the using of relatively complex technique such as hydrothermal requires complex procedure that could be resistant for the application on industrial scale. Due to these reasons, in this recent work, we try to propose the simple and effective way to coat Co$_3$O$_4$ layer on the BSCF xx82 membrane’s surface. The coating process was performed using Co$_3$O$_4$ particles, and starch as binder agent to bind Co$_3$O$_4$ particles in membranes surface prior to calcination. The calcination after coating process leads to formation of Co$_3$O$_4$/BSCF xx82 membranes. The morphological properties of the resulted membranes were discussed.

2. Experimental

2.1. Material

Material used for the synthesis of BSCF are barium carbonate (BaCO$_3$) p.a. 99.5%, strontium carbonate (SrCO$_3$) p.a. 99.9%, cobalt(II,III) oxide (Co$_3$O$_4$) p.a. 99.5% and iron(III) oxide (Fe$_2$O$_3$) p.a. 97%. All the reactants were purchased form Merck and were directly used without further purification. The preparation of composite membrane was carried out using starch (technical grade) purchased from Brataco chemical.

2.2. Procedure

2.2.1 Synthesis of BSCF xx82
BSCF oxides were synthesized using solid state method. All reactants were dried in the oven at 105 °C for 1 hour prior to the weighing. After drying, the reactants were placed in desiccator for cooling. The cooled reactants were then weighted according to their stoichiometric amounts. The stoichiometric amount of reactants were then mixed and were ground together in porcelain pastel and mortar for 2 hours to form a homogeneous mixture of reactants, indicated by the blending of the reactants. After grinding, the reactants were calcined at 890 °C for 2 hours. This calcination is repeated once more. The intermediate grinding for 30 minutes was applied between two calcination processes. The obtained powders were calcined again at 1000 °C for 3 hours twice by applying intermediate grinding also. The heating rate of this calcination process is 20 °C/minute. The resulted powders were characterized using X-ray diffraction (XRD) using CuKα (λ = 1.54060 Å) irradiation at 2θ of 20-90°. The obtained XRD pattern were then matched with Ba0.5Sr0.5Co0.3Fe0.2O4-δ standard obtained from Powder Diffraction File (PDF) card number 01-075-6980 published by JCPDS-International Center for Diffraction Standard 2012.

2.2.2 Preparation of Co3O4/BSCF xx82

The Co3O4/BSCF xx82 membranes were prepared by coating the starch-Co3O4 suspension to the surface of BSCF xx82 dense flat sheet membranes. For this purpose, the procedure is consisted of two steps. The first step is preparation of BSCF xx83 dense membrane. In this step, BSCF xx82 powders were sieved using 400 mesh sieve. The BSCF particles passing the sieve (particle size ~400 mesh) were used for flat sheet membranes. Each BSCF xx82 with particle size ~400 mesh were weighed for 1 g. The powders were then placed into 13 mm mold. The powders were pressed into pellets with pressure of 4 tons. The pressing was handled for 15 minutes. The obtained pellets were then sintered at 1150 °C for 4 hours. This sintering process is carried out using heating rate of 3 °C/minute. The shrinkage of flat sheet membrane was calculated using Equation 1.

\[
\text{Shrinkage (\%) = } \frac{V_i - V_f}{V_i} \times 100\%
\]

were \(V_i\) is initial volume before and \(V_f\) is final volume after sintering. The density of flat sheet membrane was examined physically using water droplet test. The surface of membrane was observed using Scanning Electron Microscope (SEM) with 20kv accelerating voltage and Secondary Electron (SE) imaging.

The second step is coating the flat sheet membrane using starch-Co3O4 suspension. Prior to the coating process, the suspension is prepared by mixing 0.3 g starch with 2 mL water. The mixture was stirred to form starch suspension. After forming suspension, 3 mL of hot water was added and the stirring is continued to form starch gel. After obtaining gel, 0.3 g Co3O4 was added to the starch gel, and the stirring is continued on the hotplate to form homogeneous starch-Co3O4 suspension. The starch-Co3O4 suspension was then coated to the one surface of the each of BSCF xx82 membranes. The coated membranes were let dried overnight. After getting dried, the membranes were calcined at 800 °C for 3 hours with heating rate of 3 °C/minute to remove the starch. This process yielded Co3O4/BSCF xx82 composite membranes, i.e. Co3O4/BSCF 5582, Co3O4/BSCF 6482 and Co3O4/BSCF 7382 respectively. The membrane’s surface and cross section is examined using SEM equipped with Energy Dispersive X Ray (EDX).

3. Result and Discussion

3.1 Synthesis of BSCF xx82

BSCF 5582, BSCF 6482 and BSCF 7382 were synthesized using solid state method. This method could produce material with high yield as well as high crystallinity. The reactants used in this work are in the form of carbonate and oxide with high purity. The selection of this reactant type is based on the property of the material. Previously, Aliyatulmuna et.al. had synthesized La1-xSrxC0.3Fe0.2O4-δ (LSCF) by solid state method using nitrate compound, i.e. strontium nitrate (Sr(NO3)2). This compound is hygroscopic thus during the weighing, the compound may adsorp water vapor from the air resulting in
the inappropriate amount of strontium. As the result, the resulted LSCF contained impurity [18]. For making sure the amount of reactants, all of the reactants were dried in oven prior to weighing. After weighing, all of reactants were mixed, ground together and then calcined at 890 °C. This calcination step is aimed to form perovskite as reported by Maulidah [19] who state that the cobalt based perovskites were formed in the calcination temperature of 880 °C. The next calcination step at 1000 °C is the optimization of the perovskite formation process as well as increasing BSCF crystallinity. Each calcination step is repeated twice, with intermediate grinding between calcination. This intermediate grinding is aimed to reduce the particles sizes and to form new contact area between the particles that can enhance the reaction [20].

The yielded powders from synthesis process were then characterized using XRD to confirm the formation of perovskite oxide [18], [21]. The XRD patterns of the three samples (BSCF 5582, BSCF 6482 and BSCF 7382) were then compared to the BSCF 5582 standard pattern from PDF Card 01-075-6980. The comparison of XRD patterns form the three samples with the standard is shown in Figure 1. Figure 1 shows that the three samples possess good accordance with the standard pattern as shown in the presence of BSCF 5582 characteristic peaks around 31, 45 and 55° in all samples. This confirms the formation of perovskite structure in all samples. The three samples were also have good intensity indicating that the samples possess high crystallinity. This high crystallinity is quite important in application of this material as oxygen membrane separation because the high crystallinity could reduce the resistance of oxygen ion diffusion due to grain boundary of the particles during permeation process. This XRD result also suggest that the three BSCF’s could be proceed further for preparing Co$_3$O$_4$/BSCF xx82 membranes.

![Figure 1. XRD patterns of three samples](image)

**Figure 1. XRD patterns of three samples a) BSCF 5582, b) BSCF 6482 and c) BSCF 7382**

### 3.2 Preparation BSCF Dense Membrane

Preparation of Co$_3$O$_4$/BSCF membrane was carried out by dry pressing method from the initial BSCF powders to form dense membrane followed by coating of one side of the dense flat membrane using starch-Co$_3$O$_4$ suspension. The calcination is then carried out to the coated flat BSCF membrane to remove the starch binder. This process began with the preparation of green membranes from BSCF xx82 powders. This step was carried out by pressing 1 g of each BSCF xx82 powders with pressure of 5 tons followed by sintering process at 1150 °C for 4 hours at heating rate of 3 °C/minute [13]. The temperature of 1150 °C is the suitable temperature for the BSCF type membrane as in higher temperature, the BSCF will be melted due to the presence of Ba$^{2+}$ that could be role as flux in solid solution. This flux species could decrease the melting point of the solid materials. On the other hand, the lower temperature could not produce
the dense membranes because the sintering of the BSCF particles is not optimally yet. This could lead to the presence of pores in the membrane. The pores in BSCF membrane lead to the reducing of membrane’s ability to separate oxygen gas. In BSCF membrane separation system, the oxygen should be separated in the form of oxygen ions, not oxygen molecules, by diffusion of these ions via oxygen vacancies that exist in the BSCF crystal lattice [9]. The presence of pores lead to the diffusion of oxygen in the form of oxygen molecules and will be risky also to pass the other gas molecule via the membranes pore. This process could reduce the BSCF membrane’s selectivity toward oxygen. During the sintering process, the particles of BSCF xx82 membranes were sintered. This process made the physical change on the membrane before and after sintering. Before sintering, in general, the physical appearance of BSCF xx82 is brittle black disc solid. After sintering, the color of the membrane changed to lighter color similar to shiny silver as shown in Figure 2. This changing indicates that the BSCF xx82 particles were sintered producing the dense membrane [18].

![Figure 2](image_url)

**Figure 2.** Membranes of a) BSCF 5582, b) BSCF 6482 and c) BSCF 7382. Upper side: before sintering, down side: after sintering at 1150 °C

The densification of the membranes could also be indicated by the reduction of membrane’s dimension before and after sintering. Before sintering, the BSCF xx82 membranes posses similar dimension i.e.12.7 mm in diameter and 2.2-2.4 mm in thickness. These dimensions are varied after sintering. Based on this dimensional changing, the shrinkage of membranes could be calculated as shown in Table 1. Based on data in Table 1, the shrinkage of the membranes reaches 30-40% from its initial volume. This indicates that sintering of the particles is successfully occurred, where the BSCF xx82 particles were melted and bound each other removing the space between the particles. The highest shrinkage is exhibited by BSCF 6482 membrane, followed by BSCF 5582 and BSCF 7382. This result is in good accordance with the previous report [13]. This shrinkage could also be influenced by the membrane’s morphology.

| BSCF membrane | Diameter (mm) | Thickness (mm) | Volume (mm³) | Shrinkage (%) |
|---------------|--------------|---------------|--------------|---------------|
|               | Initial | Final | Initial | Final | Initial | Final |               |
| 5582          | 12.9     | 11.6   | 2.2    | 1.7    | 287.4 | 181.1 | 37.0          |
| 6482          | 12.7     | 11.6   | 2.4    | 1.7    | 383.9 | 278.5 | 40.9          |
| 7382          | 12.7     | 11.7   | 2.2    | 1.7    | 181.1 | 182.7 | 34.4          |
Previously, Utomo et.al. reported that \( \text{Ba}^{2+} \) could be acted as flux, a species that lower the melting temperature of the solid material. The increasing of \( \text{Ba}^{2+} \) amount lead to the higher decreasing of melting point of the materials thus the materials would be easier to be softened in lower temperature. Also, the particles will be easier to join. As the result, the whole materials would become denser as the particles join together and the pores were removed [22]. The dimension (volume) of the material will be reduced tremendously. This makes the BSCF 6482 posses higher shrinkage than BSCF 5582 because BSCF 6482 posses higher amount of \( \text{Ba}^{2+} \) in its A-site compare to BSCF 5582. However, the membrane sintering also causes the reduction of B-site cation that release oxygen gas [13]. As mentioned before, the higher amount of \( \text{Ba}^{2+} \), the softer membrane material during sintering process. In this case, BSCF 7382 posses highest amount of \( \text{Ba}^{2+} \). Due to the softening of the membrane particles, the oxygen gas released by the reduction of B-site cation is easier to suppress the BSCF 7382 particles resulting larger pore volume in the membrane’s body. The formation of larger pore in the membrane’s body would expand the membranes volume in BSCF 7382 thus the shrinkage would be reduced as can be seen from shrinkage data in Table 1. To physically test the density of membranes, the water is dropped on the top surface of the membranes. If the membrane could resist the water droplet on its surface without absorbing it, thus the membrane was dense. This method is usually called water droplet test. The result of this water droplet test is shown in Figure 3. Figure 3 clearly shows that the water is resisted on the membrane’s surface. This indicates that the membrane is dense as no pore in the membrane that could absorb the water due to capillarity. However, in dense membrane, the pores may still exist, as indicated by the different in shrinkage value. However, in the dense membrane, the pores that generally exist are the isolated pores, meaning that the pores are not connected between each others thus could not provide the pathways to water to be absorb in the body of membrane via pores.

![Figure 3. Water droplet test for BSCF xx82 membranes](image)

(a) BSCF 5582, (b) BSCF 6482 and (c) BSCF 7382

SEM analysis was then carried out to the surface of the membrane to confirm the density in the membrane’s surface. The SEM images of the three membrane’s surface were shown in Figure 4. Figure 4 shows that all membrane’s surfaces were dense with clear grain boundary. However, the there are several points in the surface of BSCF 6482 as indicated by the rectangular line. EDX analysis of this point revealed that these points contain calcium that is not used in this experiment. The presence of calcium is predicted as impurity coming from ruins of firebrick in the furnace during sintering process. The calcium is one of the element that compose firebrick on furnace [23]. The result of the shrinkage calculation, water droplet test and SEM images show that the dense membrane was ready to be processed for coating with starch-Co\(_3\)O\(_4\) suspension.
3.3 Preparation and characterization of Co$_3$O$_4$/BSCF xx82

The resulted BSCF membranes were then coated with starch-Co$_3$O$_4$ suspension. The starch- Co$_3$O$_4$ suspension was coated in one surface of the membrane and then aged for 24 hours. In this work, after coating the BSCF xx82 membrane’s surface with starch-Co$_3$O$_4$ suspension, the coated membranes were then calcined at 800 °C. In this process, the starch would begin to decompose at 700 °C left the Co$_3$O$_4$ particles in the membrane’s surface. The BSCF xx82 and Co$_3$O$_4$ particles were then partially sintered forming deposit of Co$_3$O$_4$ in the surface of BSCF xx82 membrane forming Co$_3$O$_4$/BSCF xx82 composite membranes.

Scanning Electron Microscope (SEM) was then used to investigate the surface of BSCF membranes after calcination. The surface morphology of the three composite membranes was shown in Figure 5. Figure 5 shows that the Co$_3$O$_4$ particles were successfully coated to the surface of BSCF xx82 membranes. This confirms that the coating method using starch as binder agent succeeds to coat Co$_3$O$_4$ layer in the BSCF xx82 surface. However, the dispersion of Co$_3$O$_4$ particles was not perfectly uniform indicated by the presence of BSCF surface that does not coated by the Co$_3$O$_4$ particles as pointed by the arrow sign. Also, it seems that the Co$_3$O$_4$ particles form aggregate [24]. To further analyze the Co$_3$O$_4$ particle’s shape and size, as well as the aggregate size, the analysis was conducted to the BSCF 5582 as representative sample. The SEM image of Co$_3$O$_4$ coating in BSCF 5582 is shown in Figure 6.
Figure 6 shows that the Co$_3$O$_4$ particles have firm angles [25]. These particles are bound each other forming aggregate. The measurement of this particles size revealed that the size of the particle is around 0.5-2.0 µm. The aggregate size (as shown in dash square sign as example) is varied from 2-5 µm. This shows that the particles size as well as the aggregate is larger than the previous result as reported by Wang et.al [17] and Chen et.al [16]. Wang et.al. succeeded to coat Co$_3$O$_4$ nanoparticle on the surface of BSCF membrane. The mean particle size was about 100 nm in diameter and 20 µm in thickness. Whereas, Li et.al. succeeded to coat Co$_3$O$_4$ nanorod on the surface of BSCF. The particle size of this nanorod was about 100 nm in diameter and 2 µm in length. Both reports succeeded to coat a nano-sized Co$_3$O$_4$ particles in the BSCF membrane which can not be achieved in this work. This phenomenon is mainly caused by the initial reactant of Co$_3$O$_4$ layer. Wang et.al. and Li et.al. used Co(NO$_3$)$_2$•6H$_2$O as starting material to form Co$_3$O$_4$. Despite of difference coating method (using hydrothermal and dip coating method), the starting material was dissolved in the certain solvent to form solution. The Co$_3$O$_4$ particles were formed during calcination of BSCF surface coated with solution containing cobalt ion. The heating under air atmosphere creating the Co$_3$O$_4$ that coated on the BSCF surface. This process allow to the formation of Co$_3$O$_4$ particles from the smallest size to the larger one when the cobalt ion in the solution contact with oxygen in the air to form Co$_3$O$_4$. The Co$_3$O$_4$ particles then grew along with time and temperature (bottom-up process). This process is different with this recent work. In our works, the Co$_3$O$_4$ layer is composed form the initial Co$_3$O$_4$ powders. The Co$_3$O$_4$ particles had been existed prior to coating process. Thus, the smallest particle in the Co$_3$O$_4$ layer would be as big as the initial Co$_3$O$_4$ powder/particles size. Furthermore, the calcination process could also initiate the sintering process between the Co$_3$O$_4$ particles forming larger particles and/or aggregate as can be seen in Figure 6. This phenomenon occurs in the three samples.

The SEM analysis was then continued to the cross section of the three Co$_3$O$_4$/BSCF xx82 membranes to convince the coating of Co$_3$O$_4$ particles on the surface of BSCF xx82 membranes. The SEM images completed with membrane’s mapping using EDX were shown in Figure 7. It can bee seen form Figure 6 that there is strict border between BSFF xx82 surface with Co$_3$O$_4$ layer. The BSCF membranes exhibit excellent density form its cross section. Several pores appear on the membrane’s body, however, the amount of pore is minor compare to the whole membranes body. Beside that, the pores are isolated which means that the pore can not become the pathway for oxygen molecules to diffuse. The Co$_3$O$_4$ particles were indicated by the irregular particle coated on the surface of the membranes. The thickness of this layer is about 2-10 µm. The mapping using EDX in the cross section exhibits the increasing intensity of Co element confirming the presence of Co$_3$O$_4$. 
Figure 7. Mapping images of membrane’s cross section of a) Co$_3$O$_4$/BSCF 5582, b) Co$_3$O$_4$/BSCF 6482 and c) Co$_3$O$_4$/BSCF 7382

4. Conclusion

The Co$_3$O$_4$ particles are successfully coated to the surface of BSCF xx82 using starch as binder agent. This coating process forms composite membranes of Co$_3$O$_4$/BSCF 5582, Co$_3$O$_4$/BSCF 6482 and Co$_3$O$_4$/BSCF 7382. The different composition of membranes body leads to the difference of the membranes shrinkage. BSFF 5582 exhibits the highest shrinkage. However, the observation using SEM revealed that all membranes are dense. The Co$_3$O$_4$ particles are distributed irregularly and the particles form aggregates. The particle size of the Co$_3$O$_4$ varied from 0.5-2.0 µm whereas the aggregate size is around 5-10 µm. The Co$_3$O$_4$ layers were thin enough with thickness of 2-10 µm. This result indicates that the coating of Co3O4 layers using starch as binder gent could be potential and effective method to fabricate Co$_3$O$_4$/BSCF xx82 composite membranes.

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6. References

[1] V J Ferreira 2013 Development of Nanostructured Catalysts for The Oxidative Coupling of Methane Doctoral Thesis, Porto, Portugal
[2] C F Zuhra 2003 Penyulingan, Pemrosesan dan Penggunaan Minyak Bumi
[3] Z Shao, G Xiong, H Dong, W Yang, and L Lin 2001 Synthesis, oxygen permeation study and membrane performance of a Ba0.5Sr0.5Co0.8Fe0.2O3-δ oxygen-permeable dense ceramic reactor for partial oxidation of methane to syngas p. 20
[4] H Luo et al 2010 Performance of a ceramic membrane reactor with high oxygen flux Ta-containing perovskite for the partial oxidation of methane to syngas Journal of Membrane Science vol. 350 no. 1–2, pp. 154–160
[5] Z Shao, H Dong, G Xiong, Y Cong, and W Yang 2001 Performance of a mixed-conducting ceramic membrane reactor with high oxygen permeability for methane conversion Journal of Membrane Science vol. 183 no. 2, pp. 181–192
[6] W Chen, N Nauels, H J M Bouwmeester, A Nijmeijer, and L Winnubst 2015 An accurate way to determine the ionic conductivity of mixed ionic–electronic conducting (MIEC) ceramics,” *Journal of the European Ceramic Society* vol. 35 no. 11, pp. 3075–3083

[7] J Sunarso *et al* 2008 Mixed ionic–electronic conducting (MIEC) ceramic-based membranes for oxygen separation *Journal of Membrane Science* vol. 320 no. 1–2, pp. 13–41

[8] S Baumann *et al* 2010 Influence of sintering conditions on microstructure and oxygen permeation of Ba0.5Sr0.5Co0.8Fe0.2O3−δ (BSCF) oxygen transport membranes *Journal of Membrane Science* vol. 359 no. 1–2, pp. 102–109

[9] A Behrouzifar, A A Asadi, T Mohammadi, and A Pak 2012 Experimental investigation and mathematical modeling of oxygen permeation through dense Ba0.5Sr0.5Co0.8Fe0.2O3−δ (BSCF) perovskite-type ceramic membranes *Ceramics International* vol. 38 no. 6, pp. 4797–4811

[10] A Ghadimi, M A Alaee, A Behrouzifar, A A Asadi, and T Mohammadi 2011 Oxygen permeation of BaxSr1−xCo0.8Fe0.2O3−δ perovskite-type membrane: Experimental and modeling *Desalination* vol. 270 no. 1–3, pp. 64–75

[11] S Faraji, K J Nordheden, and S M Stagg-Williams 2010 A comparative study of Ba0.5Sr0.5Co0.8Fe0.2Ox (BSCF) and SrFeCo0.5Ox (SFC) ceramic membranes used for syngas production *Applied Catalysis B: Environmental* vol. 99 no. 1, pp. 118–126

[12] S Tanasescu *et al* 2013 Effects of A-site composition and oxygen nonstoichiometry on the thermodynamic stability of compounds in the Ba–Sr–Co–Fe–O system *Journal of Solid State Chemistry* vol. 200, pp. 354–362

[13] H Fansuri *et al* 2017 Preparation of dense BaxSr1-xCo0.8Fe0.2O3 membranes: Effect of Ba2+ substituents and sintering method to the density, hardness and thermal expansion coefficient of the membranes *Advanced Materials Letters* vol. 8 no. 7, pp. 799–806

[14] A Leo, S Liu, and J C Diniz da Costa 2009 The enhancement of oxygen flux on Ba0.5Sr0.5Co0.8Fe0.2O3−δ (BSCF) hollow fibers using silver surface modification *Journal of Membrane Science* vol. 340 no. 1, pp. 148–153

[15] A Leo, S Smart, S Liu, and J C Diniz da Costa 2011 High performance perovskite hollow fibres for oxygen separation *Journal of Membrane Science* vol. 368 no. 1, pp. 64–68

[16] S Li, J Cheng, Y Gan, P Li, X Zhang and Y Wang 2015 Enhancing the oxygen permeation rate of Ba0.5Sr0.5Co0.8Fe0.2O3−δ membranes by surface loading Co3O4 nanorod catalysts *Surface and Coatings Technology* vol. 276 pp. 47–54

[17] Y Wang, J Cheng, M Huang, M Liu, M Li, and C Xu 2017 Effects of surface modification with Co 3 O 4 nanoparticles on the oxygen permeability of Ba 0.5 Sr 0.5 Co 0.8 Fe 0.2 O 3−δ membranes *Applied Surface Science* vol. 416 pp. 574–580

[18] A Aliyatulmuna, W P Utomo, H Fansuri, and I K Murwani 2017 Thermal Expansion, Microhardness and Oxygen Permeation of La1-xSrxCo0.8Fe0.2O3-δ Membranes *Asian Journal of Chemistry* vol. 29 no. 10, pp. 2191–2196

[19] N Maulidah 2010 Sintesis dan Karakterisasi Oksida Perovskit La1-xSrxCo1-yFeO3-δ (0,0≤x,y≤0,5) Dengan Metode Solid-State Surabaya, Undergraduate Thesis, Institut Teknologi Sepuluh Nopember

[20] A R West, 1987 *Solid State Chemistry and Its Applications* John Wiley & Sons

[21] A B Pambudi, R Kurniawati, A Iryani, and D Hartanto 2018 Effect of calcination temperature in the synthesis of carbon doped TiO2 without external carbon source *AIP Conference Proceedings* vol. 2049 no. 1, p. 020074

[22] W P Utomo 2014 *Kajian Permeabilitas Ion Oksigen Pada Membran Rapat Asimetris La0,7Sr0,3Co0,8Fe0,2O3-δ (LSCF 7382), SrCo0,8Fe0,2O3-δ (SCF 182) dan Ba0,5Sr0,5Co0,8Fe0,2O3-δ (BSCF 5582)* Surabaya, Thesis, Institut Teknologi Sepuluh Nopember

[23] S Lukin and G A Serova *Certain Properties Of Calcium-Oxide Refractories* p. 14
[24] C H Yulianti et al 2014 Synthesis of CaOZnO Nanoparticles Catalyst and Its Application in Transesterification of Refined Palm Oil,” Bulletin of Chemical Reaction Engineering & Catalysis vol. 9 no. 2, pp. 100–110

[25] S C Zi et al 2016 New method to synthesize mesoporous titania by photodegradation of surfactant template Solid State Sciences vol. 52, pp. 83–91