

The Compatibility of NiO, CeO₂ and NiO-CeO₂ as a Coating on La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ}, La_{0.7}Sr_{0.3}Co_{0.2}Fe_{0.8}O_{3-δ} and La_{0.7}Sr_{0.3}Mn_{0.3}O_{3-δ} Ceramic Membranes and Their Mechanical Properties

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Abstract. Metal oxides and perovskites have got tremendous attention as a good catalyst for partial oxidation of methane (POM). In the present work, the materials were cast into a double layer planar membrane using the dry pressing method in order to enhance its' catalytic activity. Unfortunately, the majority of metal oxides and perovskites have different thermal expansion coefficient (TEC). Therefore, this work was aimed to study the compatibility between catalyst metal oxides (NiO, CeO₂) and perovskite oxides La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} (LSCF 6428), La_{0.7}Sr_{0.3}Co_{0.2}Fe_{0.8}O_{3-δ} (LSCF 7328) and La_{0.7}Sr_{0.3}MnO_{3-δ} (LSM 73) when they were made as double layer membranes. The result shows that the density and volume shrinkage of LSCF 7328 was the highest, followed by LSM 73 and LSCF 6428. It was also found that the trends of hardness and density in the perovskites and metal oxides follows their thermal expansion trends. According to thermomechanical analysis (TMA) results, TEC of LSCF 6428, LSCF 7328, LSM 73, NiO-CeO₂, NiO and CeO₂ were 22.16; 9.31; 10.14; 12.21; 20.86 and 21.11 ppm/°C, respectively. From the TEC data, Large differences in TEC cause the delamination of NiO, CeO and mixtures of NiO-CeO₂ from perovskite surface except those who were prepared using amylum as a binder in the preparation of double layer membranes.

Keywords. Ceramic membrane, mechanical properties, perovskite oxide, and partial oxidation of methane.

1. Introduction

POM reaction is a promising way to convert methane to syngas (a mixture of H₂ and CO). By the Fischer-Tropsch reaction, the syngas can be converted to liquid fuels and other hydrocarbons [1]. However, a successful POM reaction needs a controlled supply of oxygen. If there is too much oxygen in the reaction, the results will be CO₂ and H₂O rather than syngas. The use of an oxygen transport membrane is a promising way to supply a controlled amount of oxygen to the partial oxidation of methane reaction in order to improve the selectivity of the reaction.

The use of mix ionic and electronic conducting (MIEC) membrane to control oxygen supply has been reported by many researchers. Scott *et al* [2] reported that La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} (LSCF 6428)



could be used as an oxygen transport membrane with excellent stability on POM at high temperature (500 to 900) °C. Schlehner *et al* [3] added that LSCF 6428 membrane is active for POM reaction during 3000 h operation and it shows good catalytic activity. Another lanthanum-based oxygen transport membrane, i.e. $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_{3-\delta}$ (LSM 73), has also been reported to have good ion stability at oxidant environment [4]. However, lanthanum-based perovskite oxide oxygen transport membranes generally have low oxygen permeation flux.

One method that can be used to increase the oxygen permeation of lanthanum-based perovskite membranes is by combining it with a noble metal catalyst. Yacou *et al* [5] reported that LSCF membrane covered by Pd catalyst have an improved oxygen flux. The addition of Ir and Rh on Al_2O_3 membrane surface also showed good catalytic activity on POM reaction [6]. The drawback of using noble metals as a catalyst is their high price.

Several transition metals have been reported to have comparable activity to the noble metals. Nickel has been widely known as a cheaper alternative to noble metal as an oxidative catalyst. It has also reported being active and highly stable in methane oxidation reaction [7]. Another promising material is CeO_2 which also has good activity in a POM reaction due to its high specific area [8]. In addition, both catalysts have an ability to reduce carbon deposition during POM reaction which led to increasing methane conversion and syngas selectivity on POM reaction.

One concern in using nickel and cerium catalyst to improve oxygen permeation of lanthanum-based perovskite membranes is that they react with the perovskite to produce another phase at a high temperature. The POM reaction is normally carried out at high temperature (between 500 °C and 900 °C). Both catalysts might also incompatible with the membrane when they are applied as a thin layer catalyst on the surface of the membrane. Therefore, the compatibility between the catalyst with lanthanum-based perovskite membrane is an interesting subject to be studied. This paper reports our study on the compatibility study of both catalysts as a thin layer coating to the surface of LSCF dan LSM membranes.

2. Materials and methods

2.1. Materials

The materials that were used in this research follows those reported by Nurherdiana *et al* [9] ie: using p.a. grade of La_2O_3 (Merck, 99.5 %), SrCO_3 (Merck, 99.9 %), Co_3O_4 (Merck, 99.5 %), Fe_2O_3 (Merck, 97 %) and MnCO_3 (Merck, 99.9 %) as precursors and methanol. Powders of p.a grade NiO (Aldrich, 99 %) and CeO_2 (Merck) without further treatment were used as the catalyst.

2.2. Method

A stoichiometric amount of La_2O_3 , SrCO_3 , Co_3O_4 , Fe_2O_3 and MnCO_3 powders were ball milled for 2 h at 200 rpm using methanol as a dispersant. After milling, the methanol was separated by decantation and then the slurry was dried at 100 °C for 2 h and then calcined at 1000 °C for 2 h with a heating rate of 3 °C·min⁻¹. The resulted perovskite was then characterized by X-ray diffraction (XRD) method using Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$) which was generated by applying 30 mA of current and 40 kV of Voltage. Powders of NiO (Aldrich, 99 %) and CeO_2 (Merck) were used as the catalyst without further treatment.

The perovskites were made into single and double layer ceramic membranes by the dry pressing method. For single layer membranes, 0.93 g of perovskite powder was cast into a disc-shape green membrane (diameter = 13 mm) by applying 8-ton pressure for 15 min. The double layer membrane was made with the same method as the single layer with two variations of catalyst layer application procedure. The first was made by consecutive pressing. In this method, 0.93 g of perovskite powder was cast by applying 4 t of pressure. After that, a powder catalyst was added on the top of the casted disk and then pressed again with 8 t of pressure. The other was made exactly the same as the single layer disk-shaped membrane. However, after the casting of the membrane, a suspension of catalyst powder in an amylum solution was coated on the surface of the membrane.

All green membranes were initially calcined at 800 °C. After 3 h at 800 °C, the temperature of the furnace was increased to 1250 °C and held at the temperature for 2 h. In both heating procedure, the temperature of the furnace was increased at a rate of 3 °C·min⁻¹. The morphology and membrane composition were characterized by SEM-EDX. The hardness of the membranes was measured by Vicker's microhardness method while thermal expansion coefficient was measured by a thermomechanical analyzer (TMA).

3. Results and discussion

La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} (LSCF 6428), La_{0.7}Sr_{0.3}Co_{0.2}Fe_{0.8}O_{3-δ} (LSCF 7328) and La_{0.7}Sr_{0.3}MnO_{3-δ} (LSM 73) were successfully synthesized by solid state method. The color of oxides and carbonates mixtures were changed from brown and light brown to black and dark blue after calcination for LSCF and LSM, respectively. The color change is a clear indication that the precursors reacted together during calcination process to form a new phase.

XRD analysis result of the LSCF and LSM product is shown in Figure 1. The diffractograms of LSCF 6428, LSCF 7328, and LSM 73 are similar to JCPDS No 089-1268 (LSCF 7337). The results indicate that LSCF 6428, LSCF 7328, and LSM 73 have the same crystal structure to LSCF 7337 which is a perovskite oxide. The sharpness of all peaks and flat background indicated that the perovskites are highly crystalline. The diffractograms also show no other peaks except perovskite which indicate that there are no impurities in the resulted perovskites. Therefore, it can be concluded that the solid state method was successful when it was used to produce the perovskites.

Powders of NiO and CeO₂ were also characterized by XRD and the result shows a specific peak of NiO appearing at 2θ = (37.23°, 43.28°, 62.83°, 75.38°, and 79.36°) as well as CeO₂ with its characteristic 2θ at (28.54°, 33.08°, 47.49°, 56.35°, 59.09°, 69.42°, 76.70°, and 79.07°). As in the perovskite case, diffractograms of NiO and CeO₂ show no impurities.

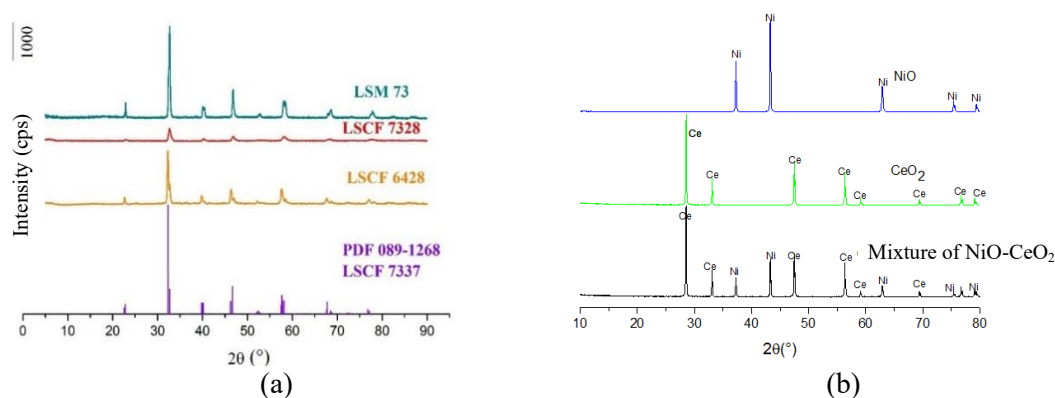


Figure 1. Diffraction pattern of: (a) perovskites and (b) the catalyst

The resulted single layer membrane is shown in Figure 2. Due to shrinkage, the shape of the membranes is slightly distorted from their original shape before sintering. All single layer membrane is dense which is confirmed by water drop test method that has been reported elsewhere [10]. A drop of water was put on the surface of the membrane and if the membrane is dense then the water drop stays unchanged for a long time. In this research, the drop was stayed undispersed. When the membrane is porous, the water drop will disperse quickly.

Figure 3 shows the TMA results of the single layer membranes. The TEC (Thermal Expansion Coefficient) of LSCF 6428, LSCF 7328, LSM 73, NiO-CeO₂, NiO and CeO₂ are (22.16, 9.31, 10.14, 12.21, 20.86 and 21.11) ppm·°C⁻¹, respectively. The TEC of LSCF 6428 is the highest of all perovskites. However, its TEC is at the same order of magnitude as the catalysts (NiO and CeO₂) while LSCF 7328 and LSM 73 are one order lower. Based the TEC, the catalyst seems to be

compatible only with LSCF 6428. However, when NiO and CeO₂ are mixed together, the mixture will be compatible with LSCF 7328 and LSM.



Figure 2. Single layer membrane of (a) LSCF 6428, (b) LSCF 7328, (c) LSM 73, (d) NiO, (e) CeO₂, (f) NiO-CeO₂ and (g) example of drop water test result

Huang *et al* [11] reported that there are two things which affect the expansion of perovskite material. The first is repulsion force among cations or anions in the crystal structure of perovskites. When the temperature increase, the bonding in the structure is weakened and the repulsive force becomes more dominant which make the cations and anions are pushed away from their original position. The second is the reduction of cations, especially the transition metal, to maintain the charge balance in the crystal structure due to the loss of oxygen at high temperature. The size of reduced transition metal cations are larger than the size of the oxidized one, thus it led to the increase in the size of the crystals' unit cell. The second cause of thermal expansion is called chemical expansion [12]. For that reason, there is a possibility that LSCF 6428 is easier to be reduced by heating at high temperature than LSCF 7328 and LSM. NiO and CeO₂ are also easily reduced but when they are mixed together, they become more difficult to be reduced.

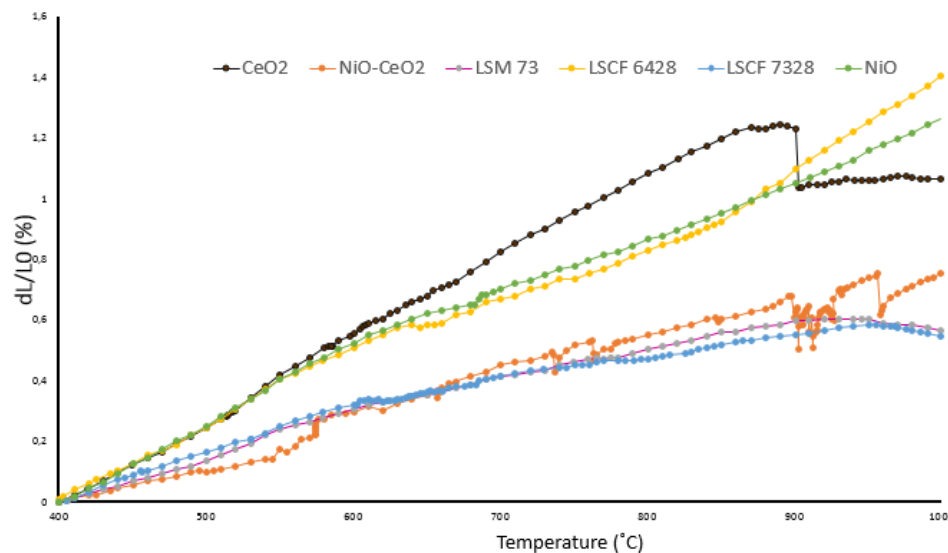


Figure 3. Thermal expansion of single layer membranes

Vicker's microhardness test results of membranes are shown in Figure 4. It is apparent that LSCF 7328 is the hardest among all perovskite's membranes. When it is compared to the trend in TEC, the hardness of membranes are more likely related to their microstructure as shown by SEM micrographs of their cross-section in Figure 5. The density of LSCF 7328 is appeared to be the highest one and therefore it is the hardest membrane. On the other hand, although LSCF 6428 is appeared to be more porous than the LSM, its' hardness is higher. The similar results are also supported by Mobius *et al*.

[13] who reported that the densification of LSM membrane was 92 % while LSCF 7328 and LSCF 6428 membranes were 95 % and 94 %, respectively although they were sintered at slightly different temperature.

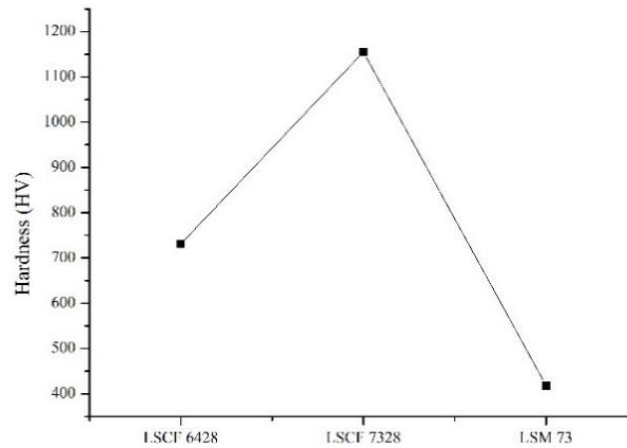


Figure 4. Hardness of single layer membranes

Meanwhile, the SEM images of the cross-section of NiO, CeO₂ and NiO-CeO₂ membranes show that the membranes are not as dense as the perovskite membranes. The porous catalyst membranes might be caused by lower sintering temperature that was applied to the membranes in this research. Some references reported that in order to make dense NiO, CeO₂ and NiO-CeO₂ membranes, the sintering temperature must be between 1400 °C and 1600 °C [14, 15].

Figure 5 shows the cross-section of double layer membranes. The figure shows that the catalyst (NiO, CeO₂ and NiO-CeO₂) were successfully coated on the surface of perovskite membrane. In the figure, the dense layer represents the perovskite part while the catalyst is represented by porous phase or particles on the surface of the perovskite membranes and it is shown more clearly by the element mapping using SEM-EDX as in Figure 6.

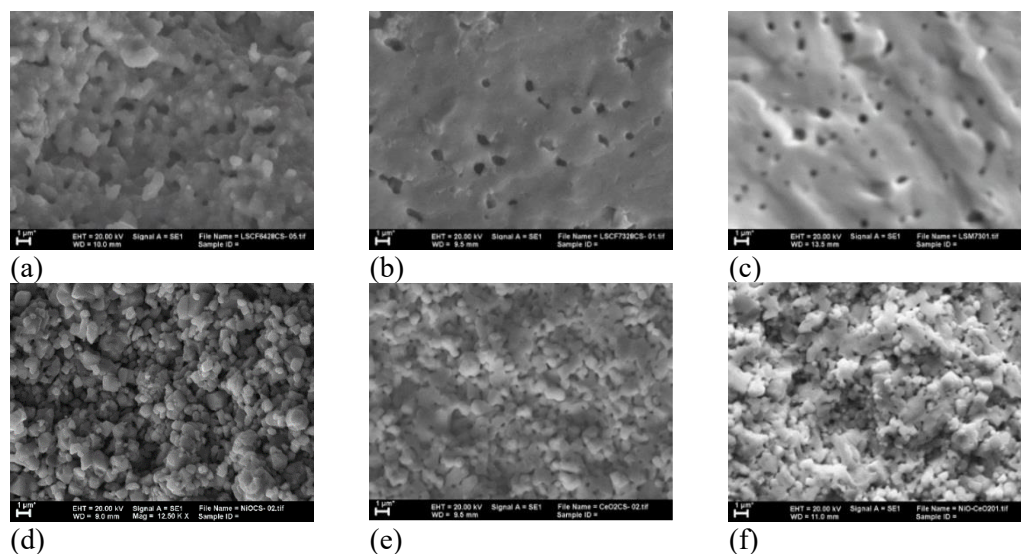


Figure 5. Cross section of single layer membrane (a) LSCF 6428, (b) LSCF 7328, (c) LSM 73, (d) NiO, (e) CeO₂ and (f) NiO-CeO₂

Nickel (Ni) might be diffused into perovskite membranes due to its' similarity to cobalt during the sintering process at high temperature. Although the diffusion of Ni and Ce into LSCF membranes was relatively very small, the diffusion reached all area of membranes as shown in Figure 6.d.

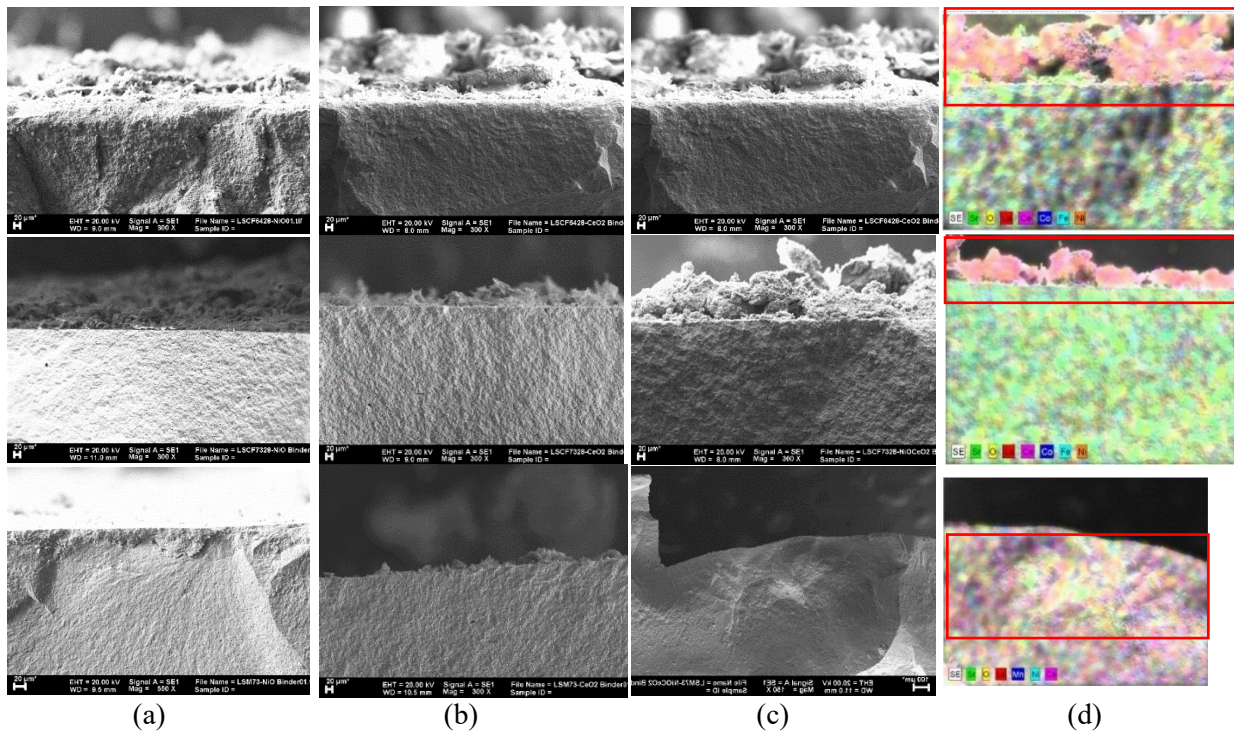


Figure 6. Cross section of double layer membranes (top to bottom : LSCF 6428, LSCF 7328, LSM 73) coated by: (a) NiO, (b) CeO₂ (c) NiO-CeO₂; (d) elemental mapping by SEM-EDX

The visual appearances of double layer membranes after sintering process are shown in Figure 7. The figure shows that NiO, CeO₂, NiO-CeO₂ was successfully coated on the perovskite surfaces. However, the color of the catalyst was turned into black which means that the catalyst might be reacted with perovskites. In addition to the reaction, the coating also made the surface of the membrane become rougher compared to the membrane before sintering. The roughness might be caused by the decomposition of amylum as a binder that was used to apply the catalyst layer on the top of the perovskite membranes.



Figure 7. Double layer after sintering process: (a) NiO/Perovskite (b) CeO₂/Perovskite (c) NiO-CeO₂/Perovskite

4. Conclusions

Thermal expansion coefficient (TEC) of perovskites and catalyst material is an indicator of the compatibility of the catalyst with La-based perovskite membranes, especially when the coating

process was applied to form double layer membranes. TEC values of LSCF 6428, LSCF 7328, LSM 73, NiO, CeO₂, NiO-CeO₂ are (22.16, 9.31, 10.14, 12.21, 20.86, and 21.11) ppm·°C⁻¹, respectively. The different of TEC might be caused by the reduction of the oxidation state of the transition metal cations and the porosity of the membranes. The different order of magnitude in TEC of the membranes and the catalyst may cause delamination or cracking of the coats. Hence, the coated catalyst on the surface of perovskite membrane using amylum as a binder has fabricated successfully to form a double layer planar membrane.

Acknowledgments

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References

- [1] Meng B, Zhang H, Zhao Z, Wang X, Jin Y, and Liu S 2015 A novel LaGa_{0.65}Mg_{0.15}Ni_{0.20}O_{3-δ} perovskite catalyst with high performance for the partial oxidation of methane to syngas *Catal. Today* **259** 388–392
- [2] Scott S P, Mantzavinos D, Hartley A, Sahibzada M, and Metcalfe I S 2002 Reactivity of LSCF perovskites *Solid State Ionics* **152–153** 777–781
- [3] Schlehuber D, Wessel E, Singheiser L, and Markus T 2010 Long-term operation of a La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ}-membrane for oxygen separation *J. Membrane Sci.* **351** 16–20
- [4] Zhang Q, Nakagawa T, and Saito F 2000 Mechanochemical synthesis of La_{0.7}Sr_{0.3}MnO₃ by grinding constituent oxides *J. Alloy Compd.* **308** 121–125
- [5] Yacou C, Sunarso J, Lin C X C, Smart S, Liu S, and da Costa J C D 2011 Palladium surface modified La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} hollow fibres for oxygen separation *J. Membrane Sci.* **380** 223–231
- [6] Mark M F and Maier W F 1996 CO₂-Reforming of Methane on Supported Rh and Ir Catalysts *J. Catal.* **164** 122–130
- [7] Colomer M T and Kilner J A 2015 Effect of sintering time on structural, microstructural and chemical composition of Ni-doped lanthanum gallate perovskites *J. Solid State Chem.* **228** 167–173
- [8] Bulfin B, Lowe A J, Keogh K A, Murphy B E, Lubben O, Krasnikov S A, and Shvets I V 2013 Analytical Model of CeO₂ Oxidation and Reduction *J. Phys. Chem C* **117** 24129–24137
- [9] Nurherdiana S D, Sholichah N, Iqbal R M, Sahasrikirana M S, Utomo W P, Akhlus S, Nurlina and Fansuri H 2017 Preparation of La_{0.7}Sr_{0.3}Co_{0.2}Fe_{0.8}O_{3-δ} (LSCF 7328) by Combination of Mechanochemical and Solid State Reaction *Key Eng. Mat.* **744** 399–403
- [10] Fansuri H *et al* 2017 Preparation of dense Ba_xSr_{1-x}Co_{0.8}Fe_{0.2}O₃ membranes: Effect of Ba²⁺ substituents and sintering method to the density, hardness and thermal expansion coefficient *Adv. Mat. Lett.* **8** 799–806
- [11] Huang B X *et al* 2010 Mechanical aspects of ferro-elastic behavior and phase composition of La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} *J. Membrane Sci.* **349** 183–184
- [12] Perry N H, Kim J J, Bishop S R, and Tuller H L 2015 Strongly coupled thermal and chemical expansion in the perovskite oxide system Sr(Ti,Fe)O_{3-α} *J. Mater. Chem. A* **3** 3602–3611
- [13] Möbius A, Henriques D, and Markus T 2009 Sintering behaviour of La_{1-x}Sr_xCo_{0.2}Fe_{0.8}O_{3-δ} (0.3 ≤ x ≤ 0.8) mixed conducting materials *J Eur Ceram Soc* **29** 2831–2839
- [14] Batista R and Muccillo E 2011 Densification and grain growth of 8YSZ containing NiO *Ceram. Int* **37** 1047–1053
- [15] Lipińska-Chwałek M, Schulze-Küppers F, and Malzbender J 2015 Mechanical properties of pure and doped cerium oxide *J. Eur. Ceram. Soc.* **35** 1539–1547