

03. Effect of Dope Composition and Additive Agent on the Properties of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ Asymmetric Flat Membranes

by Silvana Dwi Nurherdiana

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Effect of Dope Composition and Additive Agent on the Properties of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ Asymmetric Flat Membranes

Silvana Dwi Nurherdiana^{1,2,*}, Mohammad Hasnan Habib², Wahyu Prasetyo Utomo², Yuly Kusumawati², Syafsir Akhlus², Hamzah Fansuri²

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¹ Department of Chemical Engineering, Faculty of Engineering, Universitas Pembangunan Nasional "Veteran"

² Jawa Timur, Jl. Raya Rungkut Madya Gunung Anyar, Surabaya, East Java, 60294, Indonesia

² Department of Chemistry, Faculty of Science and Data Analytics, Institut Teknologi Sepuluh Nopember, Kampus ITS Sukolilo, Surabaya, East Java, 60111, Indonesia

* Corresponding author

E-mail:

silvana.dwi.tk@upnjatim.a

c.id

ABSTRACT

In this study, the $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF 6428) asymmetric flat membrane was successfully fabricated using a based-phase inversion technique. The effect of different dope composition and molecular weight of polyethylene glycol (PEG) as a pore-forming agent were investigated to identify the membrane properties in term of uniformly pore configuration and the mechanical strength. The result showed that the addition of dimethyl sulfoxide (DMSO) as the solvent in varied compositions exhibits different morphology and the most uniform finger-like pores with a diameter of 22 μm were formed using 5.0 ml DMSO. Based on the uniformity of the pores, 5.0 ml DMSO was further used to study the effect of PEG addition. A highly uniform porous configuration with a pore diameter of 17 μm , less dense layer thickness, the high mechanical strength of 507.2 Hv, and good thermal expansion behavior was achieved when 0.39% PEG 8000 was added. Such PEG 8000 is promoted additive to adjust the LSCF membrane porous configuration parameter to improve oxygen permeation and catalytic performance on partial oxidation of methane.

Keywords: Inorganic membrane, LSCF membrane, pore configuration, phase inversion, flat membrane

Introduction

An inorganic membrane of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ is widely promoted as an oxygen separator and catalyst simultaneously applied at low and intermediate such as solid oxide fuel cell (SOFC) and high temperatures such as partial oxidation and oxidative coupling of methane (Teraoka *et al.*, 1988). It is also well known that the LSCF membrane with the asymmetric configuration of a finger-like and sponge-like combination offers good mechanical strength and oxygen separator which fabricated using the phase inversion method (He *et al.*, 2015).

Through the optimization of membrane performance, some modification such as the addition of polymer additive which affects the pore configuration. Also, extrusion rate, air gap, and bore liquid also affect the membrane thickness, the sintering process for membrane shrinkage control was also commonly modified (Li *et al.*, 2016; Tan *et al.*, 2011). Among the fabrication factors, the polymer additive plays an important role in pore configuration compared to the remaining factors. Any improvements have been studied, Bart *et al.* revealed the mechanism of phase inversion of polymeric membranes using acetone as an additive. The final membrane formed a denser layer with smaller

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pore due to a highly volatile even so at room temperature thus difficult to control the pore formation (Barth *et al.*, 2000).

Some studies on hydrophilic polymeric additives such as polyvinylpyrrolidone (PVP) and polyethylene glycol (PEG) were also shown in the different pore in inorganic membrane formation. The use of PVP formed the thicker top (dense) layer and macro void pore with increasing concentration up to 8% addition (Jung *et al.*, 2004). As compared to PVP, PEG seems to have more finger-like than macro void and a thinner dense layer which improves the separation and catalytic performance.

Because of this, PEG investigation was developed to observe the effect of increasing molecular weight from 400 to 20000 on its regular pore formation which can be improved the thinner top layer using 5% addition of PEG 6000 due to the highest solute separation in the polymeric membrane (Chakrabarty *et al.*, 2008).

However, the polymeric membrane exhibits a different fabrication process compared to the inorganic membrane which needs high sintering temperature which automatically affects the pore volume and configuration (Fansuri *et al.*, 2017). Thus, the investigation of the different dope solution and molecular weight of PEG is studied in this present work due to a vital part for further enhancing the uniform of pore configuration and the mechanical performance of LSCF asymmetric flat membrane as an inorganic membrane.

Research Method

In this study, the synthesized perovskite oxide of LSCF powder was prepared using a combination of the mechanochemical and solid-state method as promoted by Nurherdiana *et al.* (Nurherdiana *et al.*, 2017). Firstly, the precursors based on metal oxide and carbonate i.e., La_2O_3 , Co_3O_4 , Fe_2O_3 and Sr_2CO_3 were supplied from Merck with pa 99.99%. The precursors were then pre-treated under evaporating at 105 °C for 1 h then weighed according to the stoichiometry. The well-mixed precursor was milled then sintered and sieved up to 400 mesh.

Otherwise, the chemicals such as dimethyl sulfoxide (DMSO) with a variation of 3.7, 5, and 6 mL were also prepared as a solvent for membrane fabrication as well as an additive of polyethylene glycol (PEG) was varied in 0.23, 0.39, and 0.55% with their different average molecular weights of PEG 6000 and PEG 8000. Then polyethersulfone (PESf) and aqua DM were respectively used as polymeric binders and non-solvent.

The asymmetric membrane was fabricated using phase inversion then completed with the sintering method as described by Chi *et al.* (Chi *et al.*, 2017). The starting dope solution was prepared by mixing of different volume of DMSO, PESf, LSCF 6428 with composition as shown in Table 1. Besides, the composition in PEG addition as shown in Table 2 at room temperature for 48 h.

Table 1. Composition of the dope solution.

	Composition (wt%)		
	3.7 ml	5 ml	6 ml
LSCF 6428	63.20	52.11	43.58
DMSO	31.57	42.66	51.19
PESf	5.23	5.23	5.23
Additive	-	-	-

Thereafter, a polymeric solution was cast on the flat glass then immediately immersed in aqua DM for 24 h. The obtained green membrane was dried at room temperature for 24 h then the membrane decomposition investigation was applied using thermogravimetry analysis (TGA) at final temperature 1000 °C with an increasing rate of 10 °C.min⁻¹.

Finally, the fabricated flat membrane was sintered at adjusted decomposition temperature and characterized using a scanning electron microscope (SEM) to investigate the texture of porous configuration at the membrane surface as well as the membrane shrinkage behavior after the sintering process which was calculated using instantaneous elongation equation 1 (Möbius *et al.*, 2009).

Table 2: Additive concentration in a dope solution using 5 ml DMSO

Sample	Additive composition (wt.%)	
	PEG 6000	PEG 8000
P0	0	0
P6A	0.23	-
P6B	0.39	-
P6C	0.55	-
P8A	-	0.23
P8B	-	0.39
P8C	-	0.55

$$S (\%) = \frac{F_t - I_t}{I_t} \times 100\% \quad (1)$$

Where, S is shrinkage percentage, F_t and I_t are final and initial membrane thickness, respectively. On the other hand, the membrane pore volume was also measured. Based on the previous study, the sintered membrane was firstly weighed then immersed in water. Furthermore, the wet membrane is weighed then calculated using Equation 2 (Côrte *et al.*, 2013). Where F_m and I_m are respectively final and initial membrane mass. ρ_{water} as a water density of 1 g.cm^{-3} .

$$\text{Pore volume (ml.g}^{-1}\text{)} = \frac{F_m - I_m}{I_m \times \rho_{\text{water}}} \quad (2)$$

Also, the micro-Vickers hardness using 0.5 Kgf loading at 5 points then held for 10 s. Furthermore, thermomechanical analysis (TMA) usage was also important due to determine the membrane hardness and deformation resistance at a local point of a membrane which initiates the performance of the membrane, especially at high-temperature application. TMA analysis was operated in the range of 25-1000 °C with an increasing temperature of $10 \text{ }^\circ\text{C.min}^{-1}$ and simultaneously conducted using a load of 0.02 N (Fansuri *et al.*, 2017).

Result and Discussion

LSCF 6428 was chosen due to its superiority of separator and catalyst usage simultaneously. As a separator, the LSCF structure has an oxygen vacancy lattice that can separate oxygen from the air. The oxygen from the air will fill the lattice in the form of oxygen ions which will then react with methane to form syngas and reduce the formation of CO_2 . The LSCF 6428 was synthesized using a solid-state method due to it is relatively easy to do, green synthesis and the yield is close to the desired amount of the product.

In this study, the crystallinity is particularly important because it affects the oxygen diffusion through the oxygen vacancy lattice in the structure. To determine the crystallinity of the formed phase, x-ray diffraction analysis is applied, which the result is shown in Figure 1.

The diffractogram shows the peaks of 2θ at 32.3° ; 39.9° ; 47.0° ; 57.5° ; 68.0° and 77.0° with high crystallinity. Besides, the shifting 2θ to a lower value indicates a change of lattice parameter on increasing interatomic distance due to the La^{3+} substitution by Sr^{2+} which has a greater ionic radius (Nurherdiana *et al.*, 2017).

A Thermogravimetry study was also required to determine the decomposition behavior of the membrane. Based on Figure 2a, both of PEG addition thermogram shows weight decreasing at 250-450 °C, indicating the occurrence of solvent and PEG decomposition. Subsequently, at 500-550 °C also shows weight decreasing which indicates the decomposition of PESf (Abate *et al.*, 2006). Furthermore, at 800-850 °C is the reaction of partial reoxidation of LSCF which is reduced when PEG or PESf decomposition occurs to CO_2 and H_2O simultaneously. According to the previous data, the sintering process needs to be applied gradually, thus the reactions which during the process such as PEG and PESf decomposition occur without destroying the membrane configuration as shown in Figure 2b.

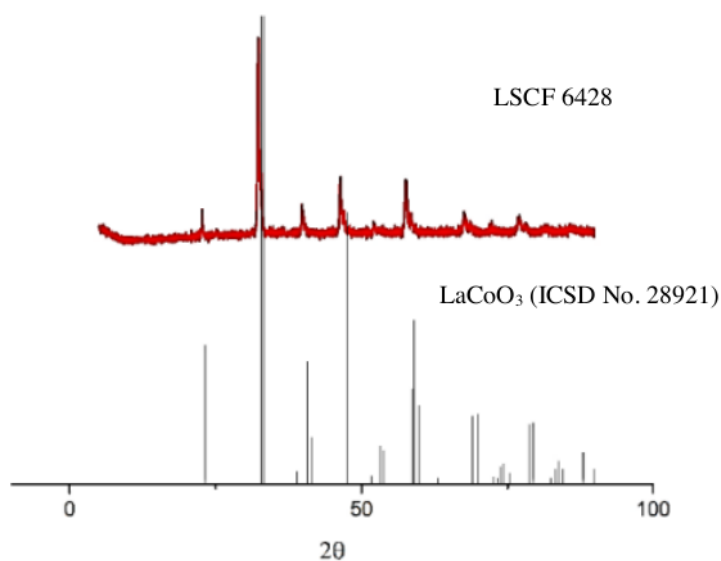
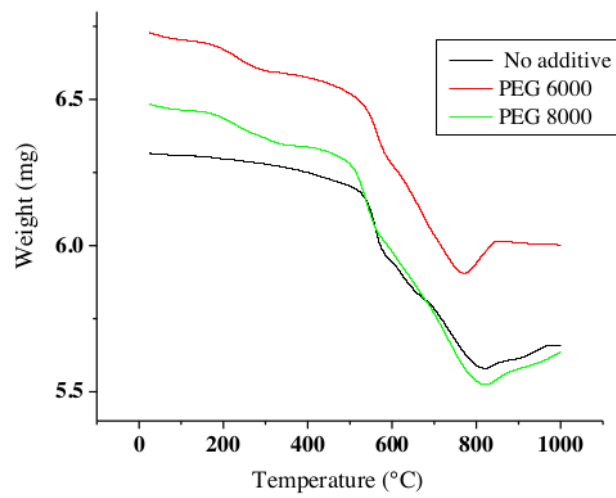


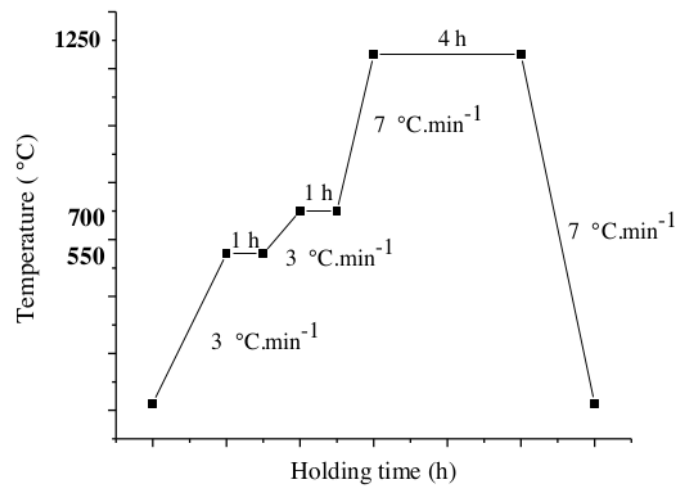
Figure 1. X-Ray diffraction patterns of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (-) and LaCoO_3 as a standard data (-).

After the sintering process, a microscopy identification is required to understand the membrane morphology. From the SEM image in Figure 3, asymmetric membranes are successfully prepared by the phase inversion method in different solvent volumes which produce finger-like and sponge-like. Based on the previous study, the finger-like contributes to the bulk diffusion of oxygen which passes through the membrane.

Whereas, the thinner sponge-like reveals the improvement of the oxygen permeability from the air. Different pore configuration on green membranes with no additive is shown while the dope solution concentration is varied. The uniformity of pore size and configuration is indicated on the use of 5.0 ml DMSO. However, the resulting sponge-like layer is still thick, thus it may lead to reducing the membrane performance by decreasing the ability of oxygen pass through the membrane.



(a)



(b)

Figure 2. TGA plot of LSCF 6428 asymmetric flat membrane (a) and graph of the sintering process (b)

Therefore, an additive is added to regulate the formation of membrane pore. However, not all types of polymer additive can be used as an additive due to some polymers are hydrophilic and hydrophobic.

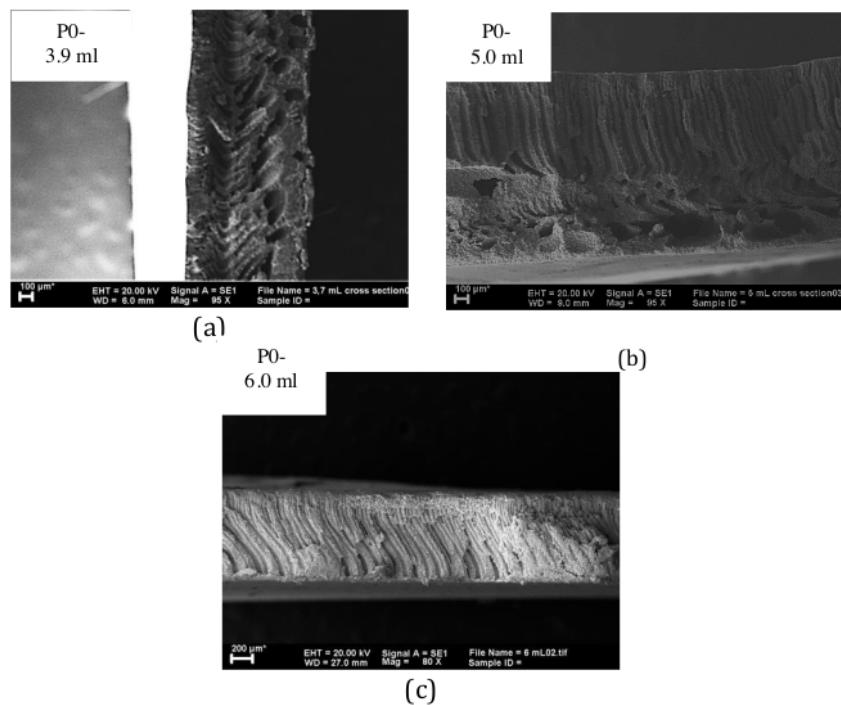


Figure 3. SEM image of the LSCF 6428 with different DMSO volumes of 3.7 ml (a), 5 ml (b), and 6 ml (c).

PEG is a good type of hydrophilic polymer that has a molar mass of $18.02+44.05n \text{ g.mol}^{-1}$ and its molecular formula as shown in Figure 4. The value of n shows the length of the polymer chain corresponding to the molecular weight (Chakrabarty *et al.*, 2008).

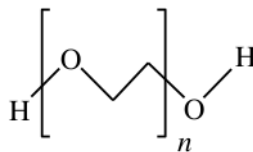


Figure 4. The molecular structure of polyethylene glycol (PEG)

Figure 5 also shows a different pore membrane configuration between no additive and PEG 6000 addition. A higher concentration of PEG up to 0.55 wt% increases the uniform of finger-like pores. Also, the use of PEG 6000 and 8000 produce different membrane morphology. This is because PEG 8000 is more readily soluble in a polymer solution and increases the viscosity of the dope solution, thus it forms a more regular membrane morphology compared to PEG 6000 as shown in Figure 6. Moreover, the hydrophilic properties possessed unstable the phase separation dope solution due to PEG has a stronger interaction with water as described by Chakrabarty *et al.* (Chakrabarty *et al.*, 2008). Generally, the pore formation is initiated by contact between the dope solution which has a greater viscosity with a non-solvent or coagulant agent (Othman *et al.*, 2014).

Also, the greater concentration of PEG (in the same molecular weight) into the dope solution forms asymmetric membranes with an increasingly thinner size and smaller pore diameter. This is due to the increasing concentration of PEG additives will increase the viscosity thus the rate of compaction of the dope solution decreases. Therefore, there is sufficient time for the rearrangement of the dope solution to form pores before the membrane is solidified (Lalia *et al.*, 2013).

Furthermore, the membrane after the sintering process still retains the asymmetric structure with values as shown in Figure 7. It appears that the membranes with no additive and membranes with the addition of PEG 6000 and 8000 still have the same morphological structure trends as before sintering. The addition of PEG 8000 with different concentrations showed similar changes in shrinkage percentage compared to PEG 6000 usage.

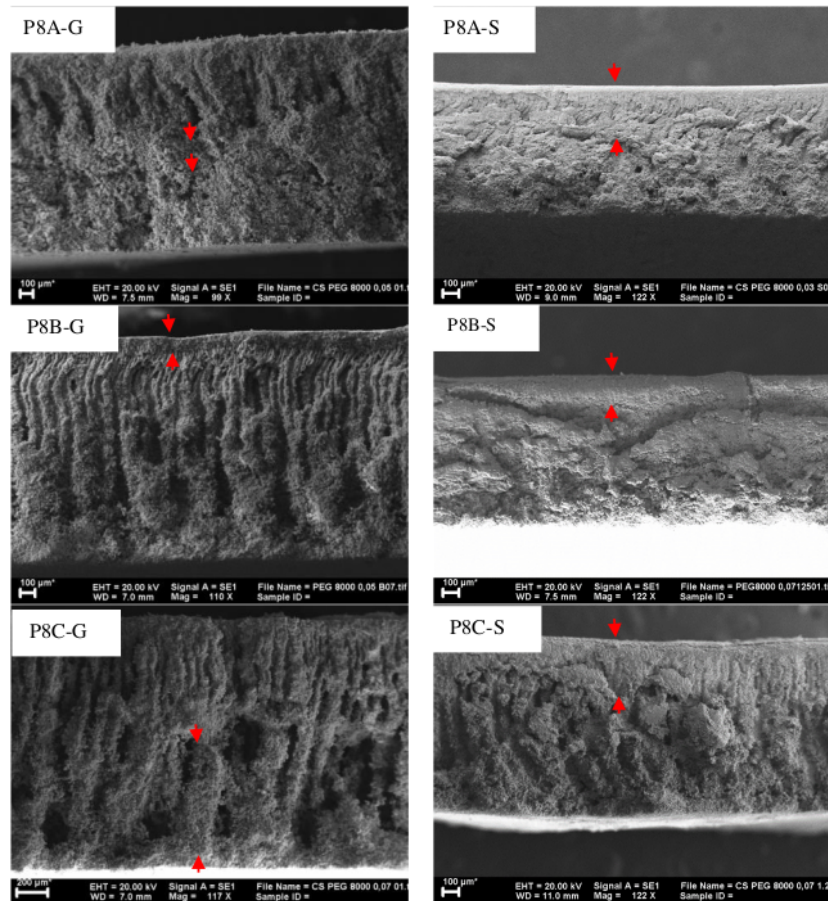


Figure 6. SEM image of LSCF 6428 asymmetric flat membrane with PEG 8000 addition (G: Green membrane, S: Sintered membrane).

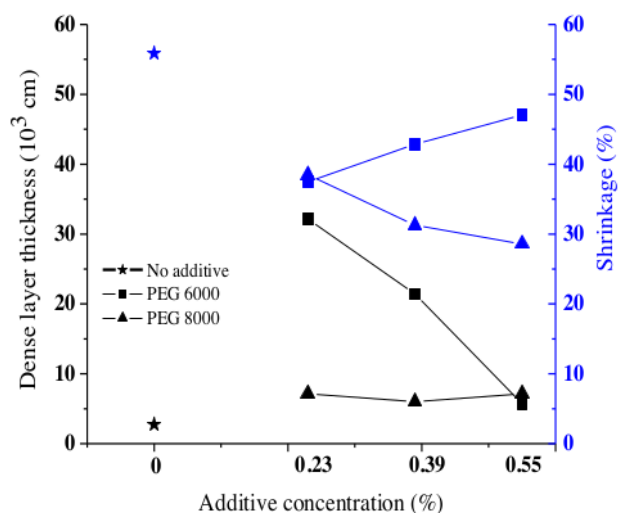


Figure 7. The effect of PEG addition to dense layer thickness and membrane shrinkage.

Mechanical properties were studied in detail in form of pore volume, hardness, and thermal expansion behavior. Figure 8 exhibits the result of pore volume and membrane hardness in different PEG addition. The membranes with no PEG addition have a smaller pore volume than the remaining membranes. Furthermore, the membrane with PEG 6000 produces a larger pore volume compared to the PEG 8000 usage. Sintered membranes are tested for hardness using micro Vickers hardness.

The test was performed to determine the mechanical strength of the membrane which the result is shown in Figure 8. The hardness graph illustrates that the P0 membrane has a hardness value of 278.9-488.9 Hv. Whereas, the P6A, P6B, and P6C have a varying hardness value respectively of 412.1-673.3 Hv, 121.3-310.0 Hv, and 348.9-562.6 Hv. While P8A, P8B, and P8C have a higher value than the remaining membranes of 412.5-591.9 Hv, 412.5-591.9 Hv, and 297.6-598 Hv, respectively. Thus, the value of the difference was tested using the ANOVA test which shows that $F_{\text{calculated}}$ value of 6.3156 is higher than F_{critical} value of 2.4453, indicating that PEG addition significantly affects the differences of membrane hardness value.

Based on the resulting data of the hardness test is known that membrane hardness is inversely proportional to the pore volume of the membrane. A larger pore volume affects a smaller hardness value. This is caused by a larger pore volume has a large vacuum area inside the membrane thus reducing the mechanical strength of the asymmetric membranes.

Also, the sintered membrane has been measured the thermal expansion behavior using TMA to determine the thermal expansion coefficient (TEC) of the varied membrane which is shown in Figure 9. The TEC of the membrane is influenced by chemical and physical factors. In this work, the chemical factors do not affect the value of the measured membrane due to all membranes are made of the same material (LSCF 6428 perovskite oxide).

Hence, the value of TEC is only influenced by physical factors such as membrane morphology. Based on the results showed that the membrane P8A-C and P0 has a linear TEC value which compared the fluctuating value of P6A-C. Moreover, the P8A-C value of TEC is inversely proportional to the increasing of PEG 8000 concentration which is affected by the asymmetric membrane morphology.

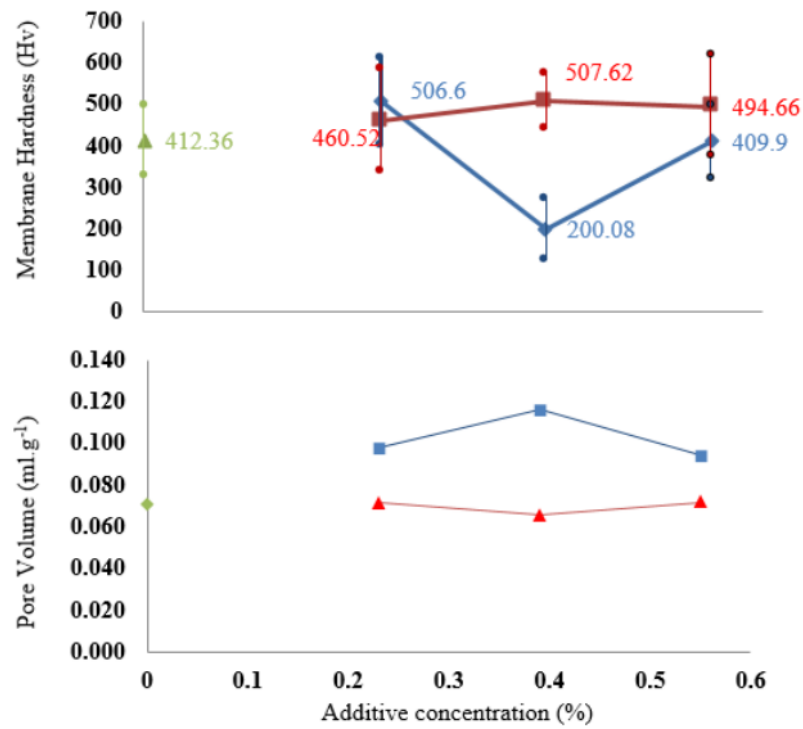


Figure 8. The pore volume and membrane hardness measurement of fabricated membranes after sintering process.

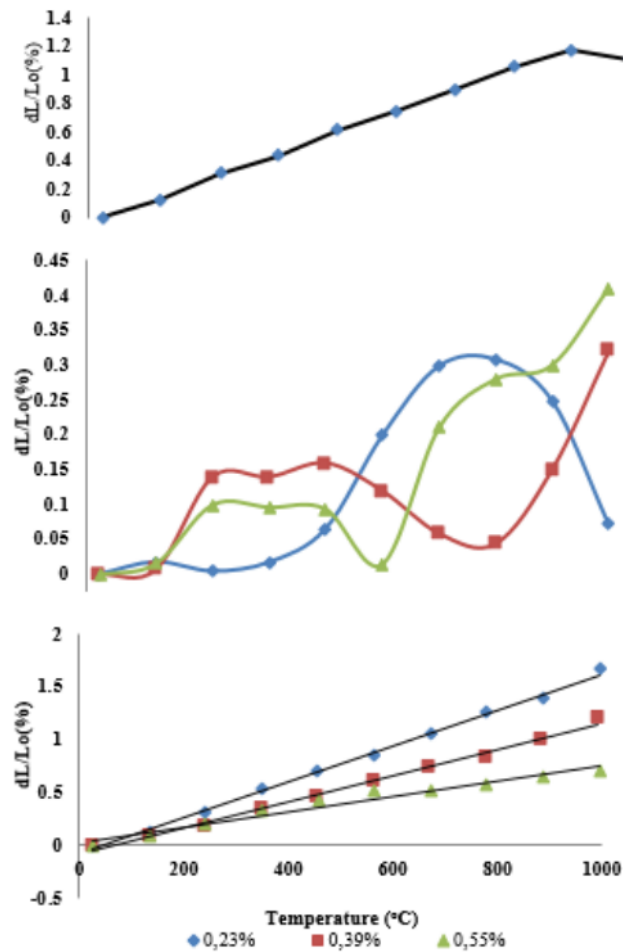


Figure 9. Thermal expansion behavior of sintered LSCF 6428 asymmetric flat membrane.

Conclusion

It can be concluded that the different dope solution produces different membrane configurations and a highly uniform pore configuration has been produced using PEG 8000 as an additive, as well as the dense layer thickness is decreased by increasing PEG concentration. Besides, a membrane with higher pore volume affects low mechanical strength and different thermal expansion coefficient caused by the pore volume distribution.

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References

- Teraoka, Y., Zhang, H. M., Okamoto, K., & Yamazoe, N. (1988). Mixed ionic-electronic conductivity of $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ perovskite-type oxides. *Mater. Res. Bull.*, 23(1), 51–58.
- He, W., Liu, J. J., Chen, C.S., & Ni, M. (2015). Oxygen permeation modeling for $\text{Zr}_{0.84}\text{Y}_{0.16}\text{O}_{1.92}-\text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.3}\text{Fe}_{0.5}\text{O}_{3-\delta}$ asymmetric membrane made by phase-inversion. *J. Memb. Sci.*, 491, 81–98.
- Li, L., Mingliang, C., Yangchao, D., & Xinfu, D. (2016). A low-cost alumina-mullite composite hollow fiber ceramic membrane fabricated via phase-inversion and sintering method. *J. Eur. Ceram. Soc.*, 36(8), 1–10.
- Tan, X., Nan, L., Bo, M., Shaomin, L. (2011). Morphology control of the perovskite hollow fibre membranes for oxygen separation using different bore fluids. *J. Memb. Sci.* 378(1-2), 308–318.
- Barth, C., Goncalves, M. C., Pires, A. T. N., Roeder, J., & Wolf, B. A. (2000). Asymmetric polysulfone and polyethersulfone membranes: effects of thermodynamic conditions during formation on their performance. *J. Memb. Sci.*, 169(2), 287–299.
- Jung, B., Bokyung, K., Joon, K. Y., & Hee-Woo, R. (2004). Effect of molecular weight of polymeric additives on formation, permeation properties and hypochlorite treatment of asymmetric polyacrylonitrile membranes. *J. Memb. Sci.*, 243(1-2), 45–57.
- Chakrabarty, B., Ghoshal, A. K., & Purkait, M. K. (2008). Effect of molecular weight of PEG on membrane morphology and transport properties. *J. Memb. Sci.* 309(1-2), 209–221.
- Fansuri, H., Muhammad, I. S., Shofiyullah, R., & Alfia, M. (2017). Preparation of dense $\text{Ba}_x\text{Sr}_{1-x}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$ membranes: Effect of Ba^{2+} substituents and sintering method to the density, hardness and thermal expansion coefficient of the membranes. *Adv. Mater. Lett.* 8(7), 799–806.
- Nurherdiana, S. D., Nikmatin, S., Rendy, M. I., & Mutya, S. S. (2017). Preparation of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF 7328) by combination of Mechanochemical and Solid State Reaction. *Key Eng. Mater.*, 744, 399–403.
- Chi, Y., Tao, L., Bo, W., Zhenao, W., & Kang, L. (2017). Morphology, performance and stability of multi-bore capillary $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ oxygen transport membranes. *J. Memb. Sci.* 529, 224–233.
- Möbius, A., Henriques, D., & Torsten, M. (2009). Sintering behaviour of $\text{La}_{1-x}\text{Sr}_x\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ ($0.3 \leq x \leq 0.8$) mixed conducting materials. *J. Eur. Ceram. Soc.*, 29(13), 2831–2839.
- Côrte, R. V. Conceição, L., & Souza, M. M. (2013). Structural and electrical properties of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.5}\text{Fe}_{0.5}\text{O}_3$ powders synthesized by solid state reaction. *Ceram. Int.* 39(7), 7975–7982.
- Abate, L., Blanco, G., Cicala, G., Recca, A., Cicala, G., La-Spina, R., & Restuccia, C. L. (2006). Thermal and rheological behaviour of some random aromatic polyethersulfone/polyetherethersulfone copolymers. *Polym Degrad Stab.*, 91(4), 924–930.
- Othman, N. H., Wu, Z., & Li, K. (2014). A micro-structured $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ hollow fibre membrane reactor for oxidative coupling of methane. *J. Memb. Sci.* 468, 31–41.
- Lalia, B. S., Victor, K., Raed, H., & Nidal, H., (2013). A review on membrane fabrication: Structure, properties and performance relationship. *Desalination* 326, 77–95.

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