

Study of microstructure modification on $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF 7328) asymmetric flat membrane

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Abstract

The LSCF 7328 ($\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$) asymmetric flat membranes were successfully prepared via a phase-inversion method followed by sintering at 1200 °C. In this study, a variety of poly(ethylene glycol) (PEGs) as the pore-forming agent, with 3 wt% composition and a wide ranges of molecular weight (Mw) (200 to 8000 Da) were used to tests its' effect to the properties of LSCF membranes. The results show that the PEGs, as additives, were able to modify the pore morphology and mechanical properties of the LSCF 7328 membrane. The morphological evidence from SEM images showed that the LSCF membranes have an asymmetric configuration, comprised of sponge-like and finger-like pores which are integrated with a dense layer. The variation in average pore size is clearly seen, starting from 13.00 to 135.33 μm , following the increase in PEGs molecular weight. The LSCF membranes which were prepared using PEG additive have higher hardness (1.2 – 13.6 Hv) than the membrane with no PEG (0.2 Hv). In contrast, the porosity and pore volume of the membranes decrease with the increase of PEGs molecular weight. The decrease might be due to the formation of various closed macro-voids as the molecular weight of PEGs increases. Furthermore, the thermal expansion coefficient of the membrane with different PEGs molecular weight (ie. 400, 600, 4000 and 6000) Da posses no significant different, i.e. around $16 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$, although the membrane showed different morphology and mechanical properties.

Keywords: Asymmetric membrane, pore configuration, perovskite, inorganic membrane, poly(ethylene glycol)

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INTRODUCTION

In recent years, there has been increasing interest in improving the performance of ceramic membranes which are able to transfer oxygen ion as well as electron due to the emerging use of the membrane technology in syngas production and redox fuel cell systems. Perovskite oxides is one group of ceramic membrane materials which have attracted much attention due to its mixed ionic-electron conductor (MIEC) properties.

Perovskite oxide is usually comprised of large cations of alkaline and alkaline earth metals, surrounded by smaller transition metal cations, each of which is bridged by an oxygen anion. The large cations occupy space which is denoted as A site while the smaller transition metal cations area occupy the B sites. The atomic ratio of A and B cations and O (oxygen anion) is 1:1:3 and therefore the general formulae of perovskite oxide is ABO_3 .

Among the perovskite oxide family, LaCoO_3 based-membrane showed high oxygen permeation as firstly reported by Teraoka et al. [1]. Unfortunately, LaCoO_3 structure is unstable in a reducing atmosphere like in the case of syngas production from methane using LaCoO_3 as the catalyst. It was the reason for many researchers to partially replace the La^{3+} with Sr^{2+} and Co^{3+} with other transition metal

cation such as Fe^{3+} to improve the stability as in $\text{La}_{0.8}\text{Sr}_{0.8}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ perovskite oxide.

Generally, perovskite oxide membranes are fabricated by phase inversion method which is similar to the fabrication of polymeric membranes. Fine powder of perovskite oxide is suspended in the polymer solution and then inverse the phase from liquid to solid by immersing the suspension in a non solvent. However, the perovskite membrane requires a sintering process to burn the polymer and densify the perovskite oxide particles at a temperature greater than 1000 °C in air [2][3]. The morphology of the sintered membrane depends on factors that control the phase inversion step and sintering process. Some factors that affect the morphology of the membrane are solvent of the polymer, non-solvent as a coagulant and additives that control the phase inversion process. Their selection is based on the non-solvent precipitation value (PV) of the polymer and its solvent. When the membrane is fabricated in hollow fiber form using a spinneret, polar-nonpolar interactions of the internal and external coagulant between polymer and solvent also affects the pore configuration of the membrane [4].

As reported by Meng et al. [5], the morphology of perovskite oxide membranes can be modified by using PVP as additive and a mixture of ethanol-NMP as the non-solvent for fabrication of

$\text{La}_{0.3}\text{Sr}_{0.7}\text{Fe}_{0.7}\text{Cu}_{0.2}\text{Mo}_{0.1}\text{O}_3$ perovskite oxide membrane. The modification produced membrane with excellent activity for oxygen separation and methane conversion which is caused by regular pore morphology (finger-like pore) in the membrane. However, ethanol has a low boiling point and easy to evaporate during the phase inversion process that causing the formation of irregular micro-channels. Meanwhile, Purwanti et al. [6] also used methanol, ethanol, and propanol as an additive to modify the morphology of $\text{LaCo}_{0.8}\text{Ni}_{0.2}\text{O}_3$ and $\text{LaCo}_{0.8}\text{Cu}_{0.2}\text{O}_3$ membranes. The result showed that each membrane has irregular finger and sponge-like pores.

In an effort to modify polymeric membrane pores using phase inversion method, Humairo et al. [7] reported that the increasing amount of poly(ethylene glycol) (PEG) additive in dope solution (a solution of polymer which will be inverted into solid membrane) produced larger pore size of PVDF/TiO₂ polymer membrane. Other studies using a variety of molecular weight of PEG additive to modify pore morphology of polymeric membrane showed an increasing pore size at increasing PEG molecular weight [8]-[10]. The additive effect may be different in the case of perovskite oxide membranes since at the end of the process, the membrane must go through a high temperature decomposition and sintering processes to solidify the membrane that may alter the pore morphology.

In an attempt to gain deeper information of the effect of PEG additive to a perovskite membrane morphology, a concentration variation of some small PEG additives were used and reported [11]. However, the results only show that the best morphology was achieved when 3 wt% PEG additive was used. Different molecular weight of some small PEG molecular weight was not shown a clear effect. It becomes the main motivation in this report to study the effect of wider molecular weight of PEG additives to the morphology of perovskite oxide membranes.

In the present study, $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF 7328) fine powder was chosen as the materials to make a perovskite oxide membrane and different molecular weight of PEG from 200 to 8000 Da were used as additives in the membrane preparation, followed by a sintering process at 1200 °C. The morphological and physical properties of the resulted membranes are discussed in terms of pore form and morphology, thermomechanical properties and hardness.

METHOD

Materials

Lanthanum (III) oxide (La_2O_3) p.a 99.5%, strontium carbonate (SrCO_3) p.a 99.0%, cobalt oxide (Co_3O_4) p.a 99.5%, iron (III) oxide (Fe_2O_3) p.a 97% from Merck were used as the raw materials to synthesize LSCF 7328 powder using solid state method following the report of Nurherdiana et al. [12]. poly(ether sulfones) (PESf) was used as the polymer binder and *n*-methyl-2-pyrrolidone (NMP) p.a 99.5% as a solvent. Tap water was used as a coagulant (non solvent) in the phase-inversion process. A wide range of poly(ethylene glycol) (PEG) was used as pore modifying additive, starting from 200 to 8000 Da.

Preparation of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ flat membrane

An asymmetric LSCF flat membrane was prepared by tape-casting phase inversion method followed by sintering at high temperature, following the procedure of Iqbal et al. [13]. The detailed dope composition is described in Table 1.

Firstly, the NMP solvent was put in a screw cap conical flask and stirred by a magnetic stirrer. PEG and LSCF powder were gradually added to the solvent. After 24 h of stirring, PESf, as a polymer binder, was added into the mixture and then the stirring was continued for another 24 h to achieve highly homogeneous dope suspension. The resulting dope suspension was then casted on a glass plate and flattened to a thickness of 1 mm and then immediately immersed into a coagulant bath (water) for 24 h to solidify. The resulted membrane precursor was then heated at 550 °C for 1 h to decompose the PESf and PEG. After that, the furnace temperature was increased to 1200 °C and hold for 4 h to sinter the membrane. All the heating processes were carried out with temperature increase of 3 °C.min⁻¹.

Table 1 Dope composition for membrane preparation.

Composition (wt %)				Mw of PEG	Membrane code
PESf	NMP	PEG	LSCF 7328		
		-	52.1	-	P1
				200	P2
				300	P3
				400	P4
				600	P5
6.7	41.2	3	49.1	1000	P6
				1500	P7
				4000	P8
				6000	P9
				8000	P10

Membrane characterization

Microstructure of the precursor and sintered membranes were characterized using scanning electron microscopy (SEM) ZEISS EVO MA-10. A carbon tape was used to stick the membrane on an aluminum stub and AuPd coating was applied by sputtering for 1 h to increase the conductivity.

Thermal expansion coefficient (TEC) and hardness of LSCF 7328 membrane were determined by the Thermomechanical Analyzer/TMA (Metler Toledo TMA/SDTA) and Micro Vickers Hardness Tester (MITUTOYO HM-2000 type 211), respectively. TMA analysis was carried out from 25 to 1000 °C with heating rate of 10 °C.min⁻¹ and a 0.02 N load. Micro Vickers Hardness tests were carried out using a loaded force of 0.5 Kgf for 10 s at 5 different points on the surface of the membrane. Analysis of Variance (ANOVA) and t-Test were used to assess the data.

For further analysis, the percentage of porosity (P) and pore volume of the LSCF membranes were evaluated using liquid adsorption technique and calculated using Equation 1 and 2, respectively. The dried membrane was firstly weight (W_d) before immersed in hot water for 30 min and the wet membrane was weight as W_w after immersion.

$$P (\%) = \frac{W_w - W_d}{W_d} \times 100\% \quad (1)$$

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

RESULTS AND DISCUSSION

Morphological study of LSCF 7328 flat membranes

The LSCF 7328 flat membranes were successfully fabricated by using the tape-casting method which includes a phase-inversion process followed by sintering at 1200 °C for 4 h. This method is a cost-effective way due to simple equipment needs. Micro-channels of finger-like and sponge-like pores were generally formed in a single step of membrane fabrication as a result of the phase-inversion process where a diffusive exchange of water molecules in coagulant bath and NMP in the dope suspension was occurred and coagulate the polymer [13].

The morphology and microstructure of the LSCF 7328 flat membranes are shown in Fig. 1.

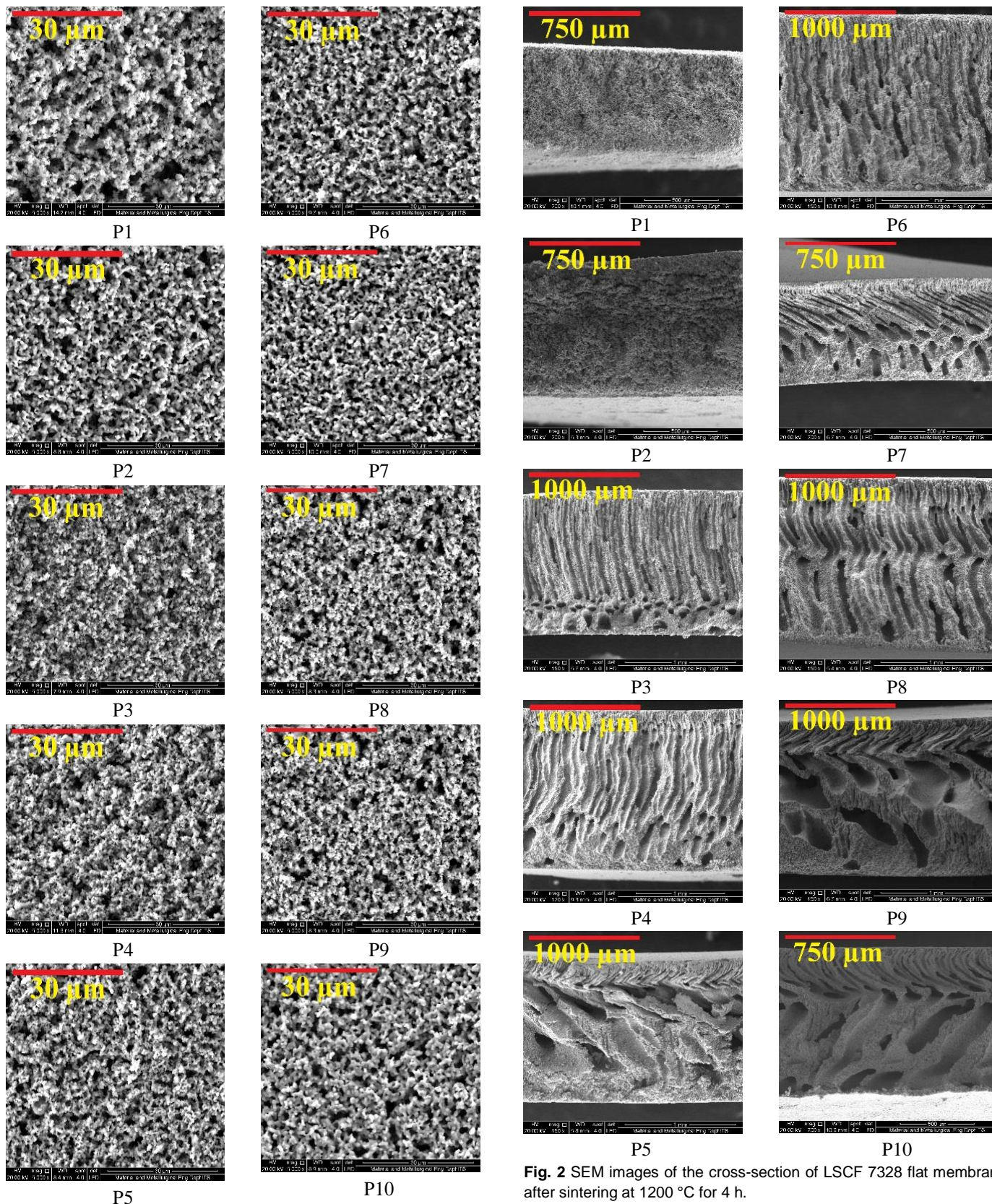


Fig. 1 SEM images of the top surface of LSCF 7328 flat membranes after sintering at 1200 °C for 4 h.

Effect of PEG additive can be seen in the figure where the surface pores of P1 membrane, which was prepared with no PEG additive, are larger than the remaining membranes. However, the increase of PEG molecular weight (Mw) shows no clear differences to the surface pore size.

In contrast to surface morphology, a clear differences are shown on the membrane cross-section as in Fig. 2.

Fig. 2 SEM images of the cross-section of LSCF 7328 flat membranes after sintering at 1200 °C for 4 h.

P1 membrane only has sponge like pores while the others have a mixture of finger and sponge like pores with asymmetrical structure. The pore morphology represents a low exchange diffusion rate between solvent (NMP) and non-solvent (water). In addition, higher PEG Mw produce larger diameter of finger like pores. However, when the PEGs Mw is too high, macro-voids are formed inside the membrane.

A linear PEG polymer, as represented in Fig. 3, is a hydrophilic polymer. It is soluble in both water (non solvent) and NMP (solvent) and is responsible to its polar chemical interaction with water (coagulant) and the formation of asymmetric geometry. It indicates that

the PEG in freshly formed (nascent) membrane can be self-assembled with water in coagulant bath to form the interconnection. This phenomenon increase the inflow rate of water diffusion through the nascent membrane as reported by Xie et al [14]. As a consequent, the existence of PEG forms a longer pore (finger-like) during the phase-inversion process which will then be refined through the sintering process. As the PEG molecular weight increases, the pore getting longer. It is, therefore, that makes the finger-like pore of P3 membrane is longer than P1 and P2 membranes. However, as the molecular weight of PEG increase further to a very high molecular weight, they respond differently in the exchange diffusion. Longer chain length alter the self assembly of PEG in water due to their tends to folded, causing the formation of voids. This is proven by membrane P2 until P10 in the figure which produces more macro-voids and reduces the finger-like pore regularity.

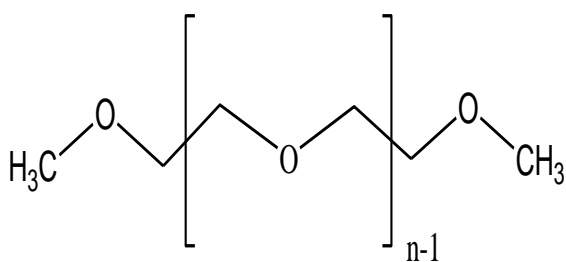


Fig. 3 Molecular structure of a single poly(ethylene glycol) (PEGs) chain.

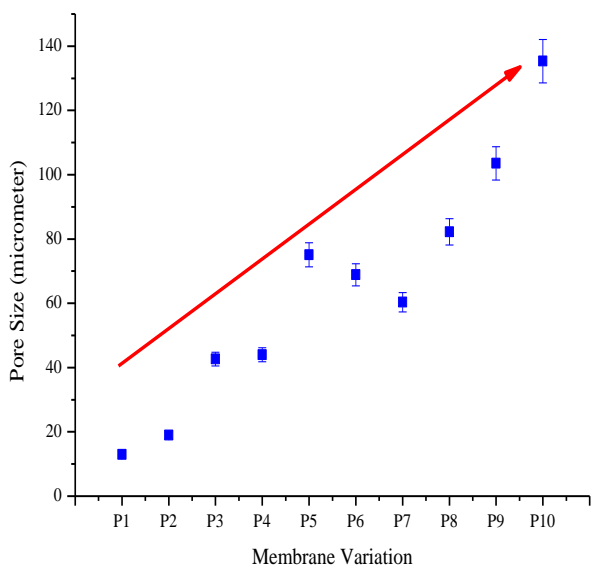


Fig. 4 Pore size of LSCF 7328 flat membranes.

Further analysis of pore size and other properties which related to pores such as porosity and pore volume was also examined by using the liquid absorption method. The results is shown in Fig. 4 where the higher Mw of PEGs dramatically increase the pore size of the membrane from 13.00 μm for P1 to 135.33 μm for P10. The results is in agreement with previous report [9] which explained that the higher Mw of PEG produce the larger pore size in the polymeric membrane.

In contrast to the average pore size, the effect of PEG to porosity and pore volume showed a different trend. The increase of PEG Mw tends to decrease the porosity and pore volume as shown in Fig. 5 and 6, respectively, although some anomalies are apparent at P8 for porosity and P8 and P9 for pore volume.

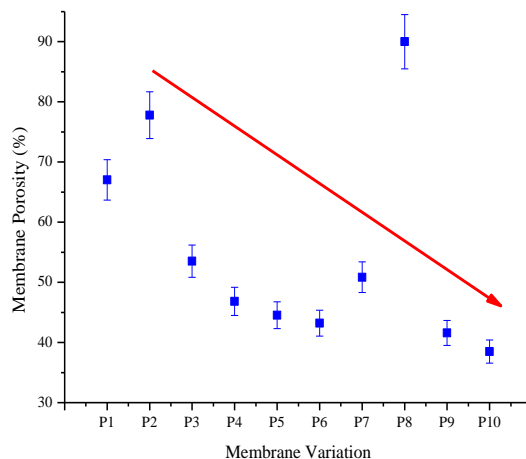


Fig. 5 Porosity of LSCF 7328 flat membranes.

The addition of PEG 8000 Da (membrane P10) produced the lowest porosity and pore volume. The possible caused are: (i) the presence of hydrophobic PEG inhibits the water inflow that caused different pore size distribution and/or (ii) low interconnection membrane pores/closed pores in the middle (barrier layer) of the membranes as shown in the cross-section images. As a result, closed macro-voids were formed in the membranes and the volume of the voids increases at the increase of PEGs Mw. The closed voids were inaccessible by the water that was used to probe the porosity and pore volume of the membranes.

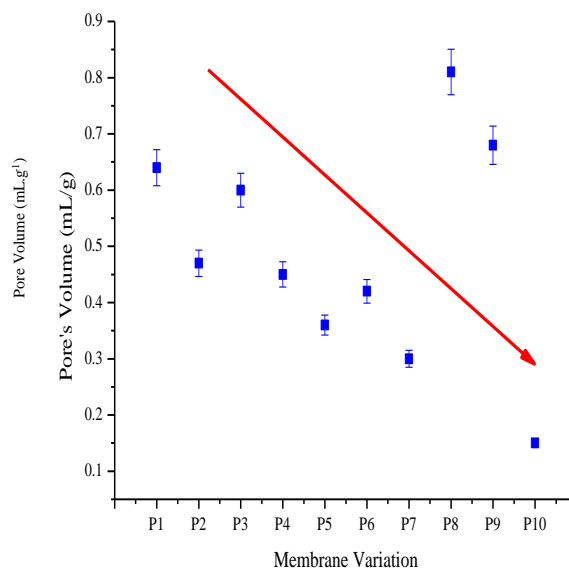


Fig. 6 Pore volume of LSCF 7328 flat membranes.

Physical properties of LSCF 7328 flat membranes

The membrane hardness, which were examined by Micro Vickers Hardness tester, is strongly affected by the membrane pore configuration, such as pore shape and regularity. As can be seen in Fig. 7, the hardness of LSCF 7328 flat membranes is varied i.e 0.2 Hv for P1 membrane with no PEG and between 1.2 and 13.6 Hv for P2 to P10 membranes with PEG additive. An analysis of variance (ANOVA) test (Table 2) shows a significant difference between membranes with and without PEG in their preparation.

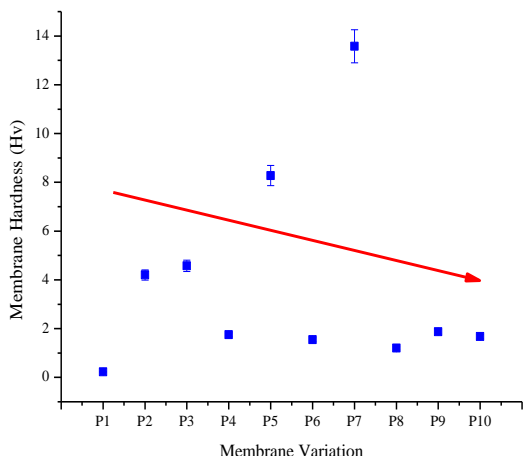


Fig. 7 Vickers hardness value of LSCF 7328 flat membranes.

Table 2 ANOVA result of hardness.

Source of variation	Sum of square (SS)	Degree of freedom (df)	Mean square (MS)	F-Stat	P-value	F _{crit}
Between groups	613.13	9	68.13	80.26	1.6x10 ⁻¹⁸	2.22
Within groups	25.465	30	0.849			
Total	638.59	39				

In addition to ANOVA, a t-Test was also used to evaluate the data and the results is presented in Table 3 shows a significant hardness different when using PEG 400 and 4000 Da and PEG 600 and 6000 Da.

Table 3 t-Test result of PEGs 400 and 4000 and PEGs 600 and 6000 Da hardness.

	PEGs 400 & 4000 Da	PEGs 600 & 6000 Da
t Stat	3.667	37.210
P(T<=t) one-tail	5.25.10 ⁻³	2.13.10 ⁻⁵
t Critical one-tail	1.943	2.353
P(T<=t) two-tail	0.010	4.27.10 ⁻⁵
t Critical two-tail	2.447	3.182

The ANOVA and t-test results reveals that the hardness is inversely proportional to the pore size but directly proportional to porosity and pore volume. It is also shown that macro-void is the weakest point on the membrane. Interestingly, P7 membrane has the highest hardness value as compared to the remaining membranes. This might be due to the pores form, where the finger like pores has irregular direction in the membrane. However, further studies need to be carried out to get a better understanding on how the pore structure and configuration relates to the strength of the membrane. Nevertheless, this result is similar to those reported by Tan and Liu [15].

The last properties that was examined is thermal expansion coefficient (TEC). The TEC was measured from room temperature to 1000 °C by a TMA and shown in Fig. 8. The thermal expansion coefficient of LSCF 7328 flat membranes as a function of temperature with different molecular weight of PEG is given in Table 4. Although the pore size of the membrane are apparently different, no significant different on the TEC value of all membranes (around 16 ppm or 1.6 x 10⁻⁵ °C⁻¹) which was also confirmed by the report of Coble and Kingery [16].

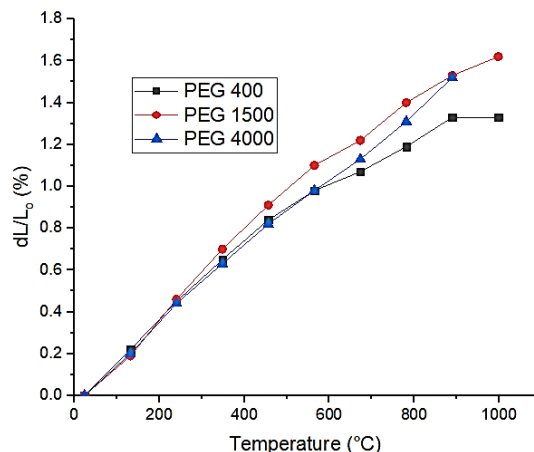


Fig. 8 Thermal expansion curve of LSCF 7328 flat membranes.

Table 4 Thermal expansion coefficient (TEC) of the membranes.

Temperature (°C)	TEC (10 ⁻⁶ .°C ⁻¹)		
	P4	P7	P8
23.52	19.35	-7.51	2.86
131.78	20.06	17.25	18.71
240.04	20.94	21.25	20.23
348.3	19.89	21.55	19.26
456.56	19.42	21.06	18.94
564.82	18.13	20.35	18.14
673.08	16.41	18.84	17.36
781.34	15.7	18.56	17.3
889.6	15.32	17.68	17.51
997.86	13.6	16.65	17.39

CONCLUSION

The flat LSCF 7328 membranes were successfully prepared using tape-casting of phase inversion method, followed by a sintering at 1200 °C. The use of PEG as an additive with a wide range of molecular weights in the preparation, produced LSCF membranes with asymmetrical pore configuration where dense layer was integrated with porous, finger-like layers. The average pore size increases when the PEGs molecular wight increase. However, the PEG addition produced membranes with smaller surface porosity with no differentiable size as increasing PEGs molecular weights. It is believed that the trend in pore size ia a result of water inflow mechanisms through the nascent membranes that can be caused by the hydrophilic characteristic of each PEG.

A high Mw (in thousand Da) formed membranes with more macrovoids and non-interconnected pores due to the increase of hydrophobic properties of longer chained PEG. As a result, the porosity and pore volume, which were tested by water absorption method, decreases when PEG molecular weight increased.

The same trend was also apparent on membrane hardness. Higher Mw of PEGs produced membranes with lower hardness although all membranes with PEG have higher hardness (1.2 to 13.6 Hv) than the membrane with no PEG (0.2 Hv). However, it seems that thermal expansion coefficient which is about 16 ppm (1.6 x 10⁻⁵ °C⁻¹) was merely depend only on the properties of LSCF 7328, regardless its membrane morphology.

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REFERENCES

- [1] Y. Teraoka, H. M. Zhang, K. Okamoto, N. Yamazoe. *Mater. Res. Bull.* 23, 1, (1988), 51-58.
- [2] P. van de Witte, P. J. Dijkstra, J. W. A. van den Berg, J. Feijen, *J. Memb. Sci.* 117, 1-2, (1996), 1-31.
- [3] S. Mansur, M. H. D. Othman, A. F. Ismail, M. N. Z. Abidin, N. Said, P. S. Goh, H. Hasbullah, S. H. S. A. Kadir, F. Kamal. *Mal. J. Fund. Appl. Sci.* 14, 3, (2018), 343-347.
- [4] D. Wang, K. Li, W. K. Teo. *J. Membr. Sci.* 176, (2000), 147-158.
- [5] B. Meng, H. Zhang, J. Qin, X. Tan, R. Ran, S. Liu. *Sep. Purif. Technol.* 147, (2015), 406-413.
- [6] E. P. Setyaningsih, M. Machfudzoh, W. P. Utomo, H. Fansuri. *Indones. J. Chem.* 16, 1, (2016), 20-24.
- [7] F. Y. Humairo, C. S. Ong, N. Widiastuti, A. F. Ismail, S. A. Putri, J. Jafar. IPTEK J. Proceedings series, PVDF/TiO₂/PEG hollow fiber membrane for oily wastewater treatment at various concentration of oily wastewater. *The 1st International Seminar on Science and Technology*, 5 August 2015, Surabaya, Indonesia, 2015, p. B208-57 – B208-58.
- [8] E. Saljoughi, M. Amirilargani, T. Mohammadi. *DES.* 262 1-3, (2010) 72-78.
- [9] B. Chakrabarty, A. K. Ghoshal, M. K. Purkait. *J. Memb. Sci.* 309 1-2, (2008), 209-221.
- [10] J. H. Kim, K. H. Lee. *J. Memb. Sci.* 138 2, (1998) 1533-1563.
- [11] A. M. Ilham, N. Khoiroh, S. Jovita, R. M. Iqbal, L. Harmelia, S. D. Nurherdiana, W. P. Utomo, H. Fansuri. *J. Appl. Memb. Sci. Technol.* 22 2, (2018), 119-130.
- [12] S. D. Nurherdiana, N. Sholichah, R. M. Iqbal, M. S. Sahasrikirana, W. P. Utomo, S. Akhlus, Nurlina, H. Fansuri. *Key. Eng. Mater.* 744, 3, (2017), 399-403.
- [13] R. M. Iqbal, S. D. Nurherdiana, D. Hartanto, M. H. D. Othman, H. Fansuri. *IOP Conf. Ser.: Mater. Sci. Eng.*, morphological control of La_{0.7}Sr_{0.3}Co_{0.2}Fe_{0.8}O_{3-δ} and La_{0.7}Sr_{0.3}MnO_{3-δ} catalytic membrane using peg-h₂o additive. *International Conference on Materials Engineering and Applications*, 14-16 January 2018, Bali, Indonesia, 2018, 348,1-8.
- [14] L. Xie, K. Y. Chan, N. Quirke. *Langmuir* 33, 42 (2017) 11746-11753.
- [15] X. Tan, S. Liu. *J. Memb. Sci.* 378, (2011) 308-318.
- [16] R. L. Coble, W. D. Kingery. *J. Am. Ceram. Soc.* 39, 11 (1956) 377-385.