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Morphological and Physical Study of $La_{0.7}Sr_{0.3}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF 7328) Flat Membranes Modified by Polyethylene Glycol (PEG)

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ABSTRACT

The aim of this work is to study the effect of polyethylene glycol (PEG) on the modification of microstructure formation correlated with the mechanical strength properties of perovskite-based membrane in form of a flat sheet. LSCF 7328 flat membrane was potentially promoted as an oxygen separator and catalyst for partial oxidation of methane reaction at high temperature. In this study, the phase-inversion followed by sintering process was used as the membrane fabrication method using varied PEG concentration of 0.55, 1.00, and 3.00 wt% with different molecular weight, i.e., PEG 300, 600, 1500, and 4000 Da for each PEG concentration. The result of morphology observation shows that almost every membrane hasthe asymmetric structure with finger-like pores and thin dense layer. Increasing PEG concentration as well as molecular weight increases pore size and affects on porosity, pore's volume, and physical properties of membrane. The largest pore size, pore volume and porosity of the membrane after sintering were found in the addition of 3.00% PEG 4000 (Da) additive with the value of 110.45 μm, 81.34 $ml.g^{-1}$ and 120.6%, respectively. In addition, the mechanical properties of membrane were tested using the Vickers micro hardness method with the greatest value found in the addition of 3.00% PEG 1500 (Da) additive with the value of 13.58 Hv and the lowest is 3.00% PEG 4000 (Da) with the value of 1.2 Hv.

Keywords: Perovskite, membrane, PEG additive, LSCF 7328

1.0 INTRODUCTION

Membrane technology has been drawing considerable attention due to its applicability in many sectors such as gas separation [1], industry [2], water treatment [3], renewable energy [4], climate change, fuel cell development [5], etc. Teraoka *et al.* [6] successfully demonstrated the application of a perovskite oxide-based ceramic membrane for gas separation. The perovskite oxide has the ability to separate oxygen from the air due to oxygen ions diffusion in the perovskite oxide lattice. In addition to oxygen ion transfer, the membrane is also capable to conduct electron and, therefore, perovskite oxide has also been known as MIEC (Mixed Ionic and Electronic Conductivity) material [7]. With the ability to transport oxygen ions and electron at the same time, there is no need to apply current to make the perovskite oxide transfering oxygen from one side to the other when it is used as a membrane in oxygen separation. Due to its properties, perovskite oxide membranes attract many attention in the field of oxygen

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separation and reaction that require very tight control of oxygen supply such as in methane conversion to syn gas through partial oxidation method [8-9].

Perovskite oxide can be made into ceramic membrane by dry pressing [10] and phase inversion [11] method. In both methods, it is important to produce membrane with large surface area. The dry pressing method is a simple method but it is difficult to produce membrane in the form of hollow fibre, which is considered as membrane form with the highest surface area. In contrast, phase inversion can easily produce hollow fibre membrane with adjustable pore size, distribution and pore form.

Generally, phase inversion method produces membrane with two pore structures namely finger-like and sponge-like. Phase inversion-evaporation and thermal precipitation methods produce membranes that have sponge-like pores while, phase inversion-immersion precipitation produces membrane that has a mixture of finger-like and sponge like structure. Membranes that have two or more pore forms are called assymmetric membrane. Membrane with asymmetric structure has better mechanical and permeance properties than membranes with symmetric structure.

Chen *et al.* [12] reported that the addition of polyvinylpyrrolidone (PVP) into dope suspension were able to induced the formation of finger-like pores. The higher PVP loaded the larger the pore size of the resulted membranes. Polyethylene glycol (PEG) which is more hydrophilic than PVP has been used by many researchers to modify polymer membrane. Humairo *et al.* [13] and Putri *et al.* [14] successfully modified a polymeric membrane using higher PEG loading and obtained higher pore size of the membrane. However, the PEG as an additive is widely used for the study of polymer membranes. In this study, the use of PEG as an additive is evaluated in perovskite-based membrane with respect to its morphological and mechanical properties.

2.0 METHODS

2.1 Materials

Powders of metal oxides and carbonates from Merck were used in the preparation of LSCF. The metal oxides and carbonates were La_2O_3 (99.5%), Co_3O_4 (99.5%) and Fe_2O_3 (97%). Polyethersulfone (PESf) as polymer binder, N-methyl-2-pyrrolidone (NMP) as a solvent and water as a non solvent (coagulant) were used in the preparation of suspension for membrane preparation by phase inversion method while polyethylene glycol (PEG) with different molecular weight (300; 600; 1500 and 4000 Da was used as the additive to the suspension.

2.2 Synthesis of LSCF 7328 Powder

LSCF 7328 was synthesized using solid-state method which was reported by Nurherdiana *et al.* [15]. All metal oxides (La_2O_3, Co_3O_4 and Fe_2O_3) and carbonate ($SrCO_3$) at stoichiometric composition to make LSCF 7328 were ground until homogen using a porcelain mortar and pastle. The mixture was then calcined in a furnace at 890 ^oC for 2 h followed by calcination at 1000 ^oC for another 2 h. In both steps, the temperature was increased at a rate of 3 $^oC.min^{-1}$.

The resulted LSCF 7328 was ground into fine powder and characterized by X-ray diffraction method using Cu-Kα X-ray (λ =

Table 1 Composition of dope suspension

LSCF 7328 (wt%)	PESf (wt%)	NMP (wt%)	PEG Additive (wt%)	PEG Molecular weight (Da)	Membrane code
52.10	6.70	41.20	0.00	-	A0
51.55			0.55	300	B1
51.10			1.00		B2
49.10			3.00		B3
51.55			0.55	600	C1
51.10			1.00		C2
49.10			3.00		C3
51.55			0.55	1500	D1
51.10			1.00		D2
49.10			3.00		D3
51.55			0.55	4000	E1
51.10			1.00		E2
49.10			3.00		E3

1.5406 Å) generated at 30 mA and 40 kV. Scan rate of all diffraction analyses were set at 1°min^{-1}).

2.3 Preparation of LSCF 7328 Membrane

Membrane of LSCF 7328 was prepared by phase inversion method, followed by sintering. The powder of LSCF 7328, PEG and NMP were mixed and stirred for 24 h in a closed conical flask. The PESf was then added gradually into the stirred suspension and stirred continuously for another 24 hours. The resulted dope suspension was then casted on a glass plate and then immersed in water for 24 hours. When the suspension on the glass plate was immersed in water, the suspension was coagulated and it called as green membrane.

The green membrane was dried and then calcined to decompose all organic content (solvent, PESf and PEG), followed by sintering process to densify the membrane. The composition of the dope suspension is shown in Table 1 while temperature program for calcination and sintering of green membrane is given in Figure 1.

The obtained membrane was characterized by Scanning Electron Microscopy (SEM Zeiss EVO MA-10) for to characterize its' morphology and thermomechanical analysis (TMA) to characterize its' thermal expansion coefficient (TEC). In addition to morphology and TEC, the membrane was also characterized using Vickers Microhardness tester (Mitutoyo-HM-2000) to characterize its hardness.

2.4 The Measurment of Membrane Porosity and Pore Volume

The membrane porosity and pore volume were determinate using liquid adsorption method and calculated using equation 1 while equation 2 for pore volume of each variation with three-time repeatition for the average value. Water was used as the adsorbate. The sintered membrane was firstly weighed as the dry weight (W_d) then immersed in water at 80-100 ^{o}C for 30 minutes which weighed as the wet weight (W_w). The measurement:

$$\text{Porosity (\%)} = \frac{W_w - W_d}{W_d} \times 100\% \qquad (1)$$

$$\text{Porosity (mL. g}^{-1}\text{)} = \frac{W_w - W_d}{W_d \times \rho_{water}} \times 100\% \qquad (2)$$

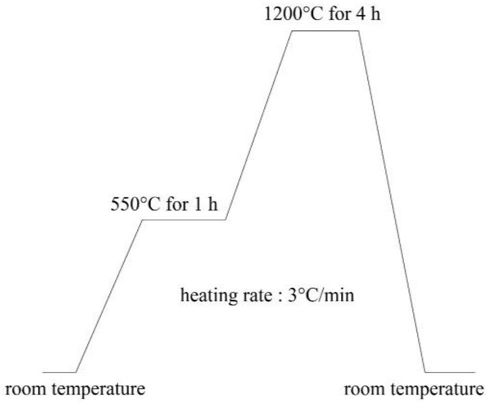


Figure 1 Temperature profile on the calcination and sintering process during the preparation of LSCF 7328 flat membranes

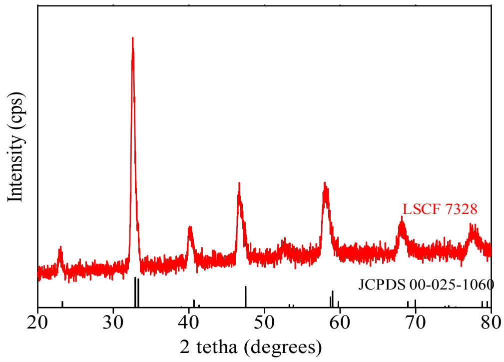


Figure 2 XRD of synthesized LSCF7328

Each measurement was repeated three time to get the average value. In this experiment, water was used as the adsorbate. The sintered membrane was firstly weighed as the dry weight (W_d) then immersed in a warm water at 80-100 °C for 30 minutes. After immersion, the membrane was weighed as the wet weight (W_w).

3.0 RESULTS AND DISCUSSION

3.1 The Synthesis of LSCF 7328 Powder

LSCF 7328 was successfully synthesized using solid-state method as reported by Nurherdiana *et al* [13]. The diffractogram of LSCF 7328 was shown in Figure 2. Based on the result, the diffractogram of LSCF 7328 has the similar peak with $LaCoO_3$ (JCPDS no. 00-025-1060) as standard which exhibits LSCF 7328 as perovskite structure. The specific diffraction peaks of LSCF 7328 were 22.9; 32.4; 39.90; 46.53; 52.56; 58.4; 67.9; and 72.27°.

As reported by Iqbal *et al.* [10-11], the specific peak of LSCF 7328 was shifted to lower of 2θ as consequence of partial substitution La^{3+} with Sr^{2+} and Co^{3+} with Fe^{3+} which caused increasing interplanar distance.

3.2 Morphology of LSCF 7328 Membrane

Asymmetric flat membrane of LSCF 7328 was prepared by phase inversion method. The asymmetric membrane has thin-dense layer (sponge-like), self supported with porous layer (finger-like). The formation of finger-like can be controlled using additive. This study successfully investigated the effect of additive addition of varied molecular weight and concentration on the morphological and mechanical properties of the membrane.

The membrane was prepared by phase inversion-immersion precipitation method. This method changes liquid (dope solution) to solid phase (membrane) [16]. This occurs because of the exchange between polymer solvents (NMP) and non-solvent (water). The solvent (NMP) diffuses out of the polymer solution and water as non-solvent as well as the coagulant enters the dope solution [11]. This process causes the coagulation and pore formation of the membrane. When the solvent exits, the polymer concentration increases and the subsequent process leads to the solidification of greenbody of the membrane which is called phase inversion.

The morphology of membrane is shown in Table 2. The cross-section figure shows that the membrane without PEG addition has thicker sponge-like pores. On the contrary, the membrane with PEG addition shows more porous with finger-like pores formed on the cross-section of membranes. Generally, the increasing of PEG molecular weight and its concentration gives larger pore to the membrane.

Based on the previous study, there are two types of pore structure of membrane which are sponge-like and finger-like structure, where sponge-like structure has lower mechanical strength as compared to the finger-like structure [9]. The finger-like pores formation indicates that the PEG addition into dope solution reduce the diffusion and exchange rate between solvent (NMP) and nonsolvent (water). It is due to PEG has better solubility into water then it is easily diffuse from the membrane into non-solvent and leaves finger-like pores on membrane [17].

For further details, the top layer of membrane cross section was also investigated using SEM. SEM images show that pores formation on their top surface was caused by the effect of non-solvent and PEG diffusion through the membrane. As seen in SEM images, the increasing molecular weight and concentration of PEG reduce the thickness of dense layer. For membrane application, the thicker the dense layer the better the performance of the membrane for oxygen separation and catalyst for partial oxidation of methane (POM) to syngas production.

Investigation about average pore size of membranes was carried out through analyzing the cross-section SEM images of the membranes. As can be seen in Figure 3a, pore size follows the concentration and molecular weight of PEG although there is an anomaly for 3.00 wt% of PEG 1500. The largest pore is about 110 μm which is shown by 3 wt% of PEG 4000 addition. However, the membrane pores have poor regularity compared to PEG additive with lower molecular weight.

Membrane pores were formed during phase separation or exchange of solvent and nonsolvent. High molecular weight PEG diffuse slower to the non solvent due to its higher viscosity, resulting in the formation of finger-like pores with poor regularity. The results is similar to the reports by Aminudin *et al*. [18] who found that PEG aditive causing the formation of finger-like pores that are bigger and longer in the membrane. However, porosity of membranes is fluctuative. In addition, as can be seen in Figure 3b, the porosity of membrane with 3 wt% of PEG 4000 additive reached up to 122% which is much larger than those reported by other literatures [3,17].

Increasing amount of PEG increase the membrane's pore size due to the increase in the viscosity of dope solution. Higher viscosity reduce the thermodynamic stability of mixture that leads to solidification process [18]. It is a consequence of diffusion of solvent and nonsolvent during the solidification process. Due to the existence of PEG in the dope solution, the diffusion rate of water (nonsolvent) is faster than NMP (solvent) and the membrane have finger-like structure. The size of finger-like structure increase as well as increasing PEG concentration .

In addition to pore size and porosity, pore volume is also affected by PEG addition. Figure 3c shows the pore volume of all membranes and it is shown that the highest pore volume

Table 2 Morphology of LSCF 7328 flat membrane at different composition of PEG as an additive

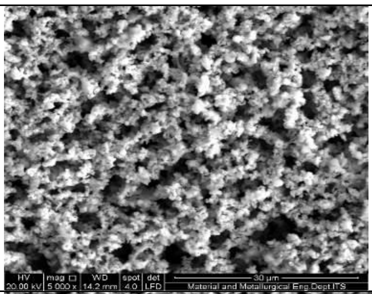
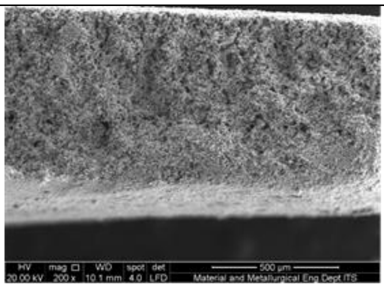
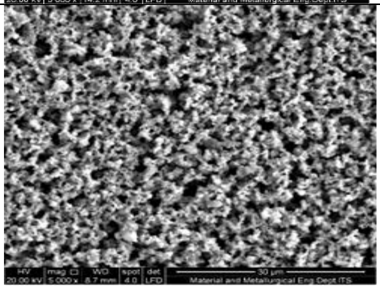
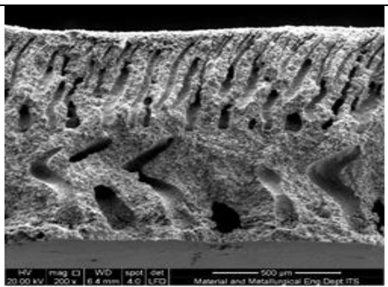
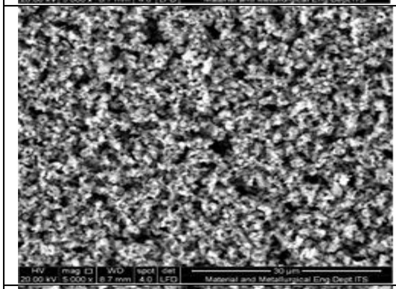
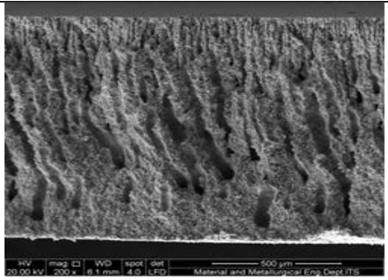
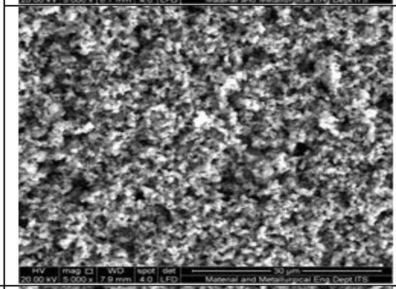
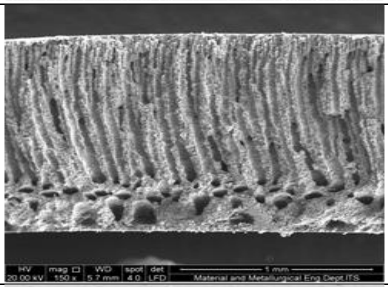
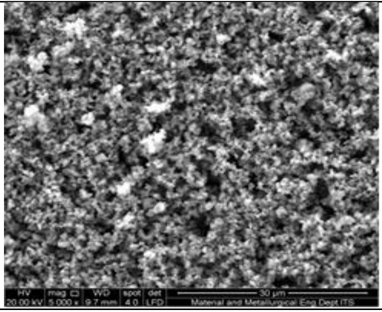
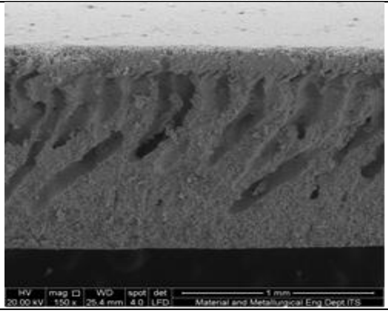
PEG (wt%)	PEG (Da)	Top Surface	Cross Section
0	Without additive		
0.55	300		
1.00			
3.00			
0.55	600		

Table 2 Morphology of LSCF 7328 flat membrane at different composition of PEG as an additive (Continue)

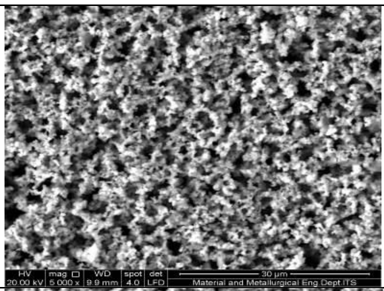
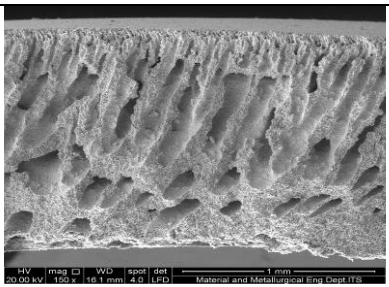
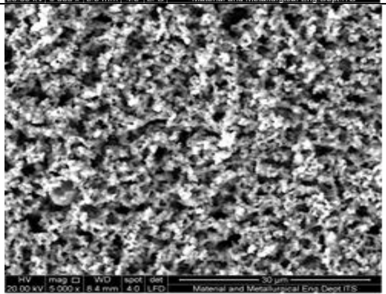
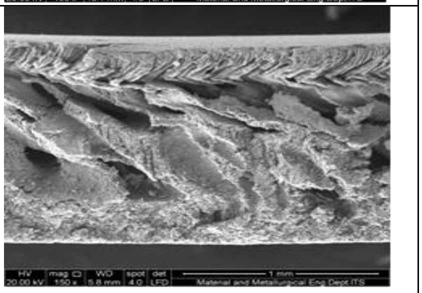
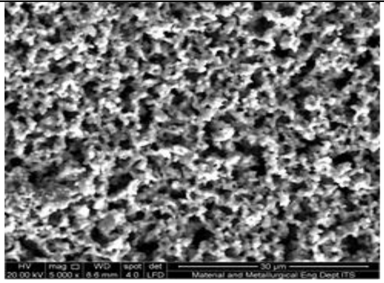
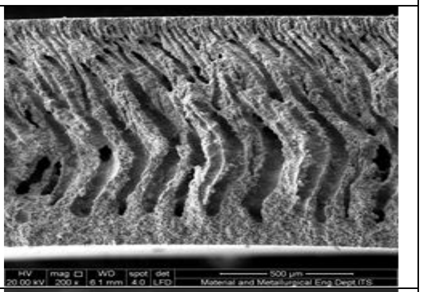
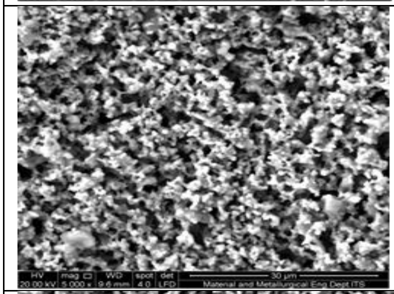
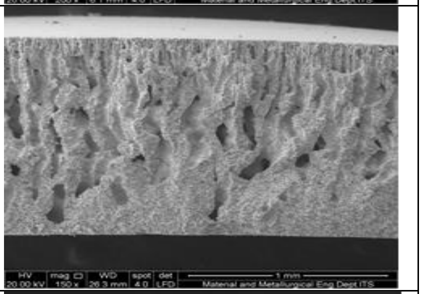
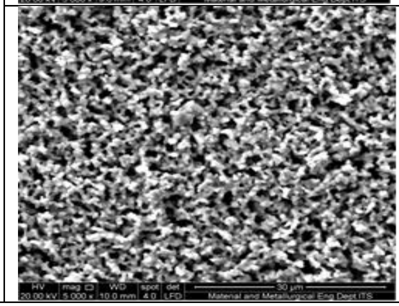
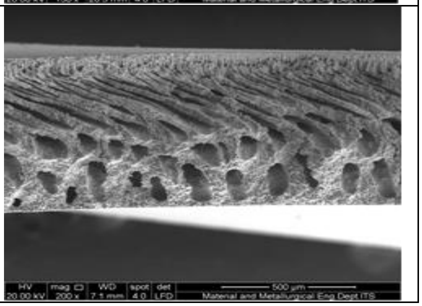
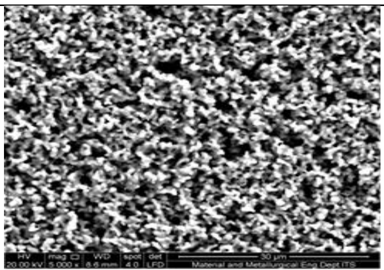
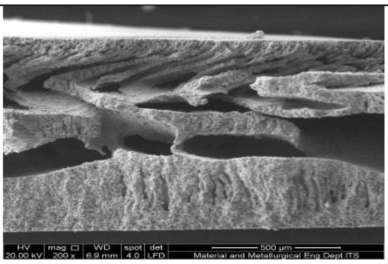
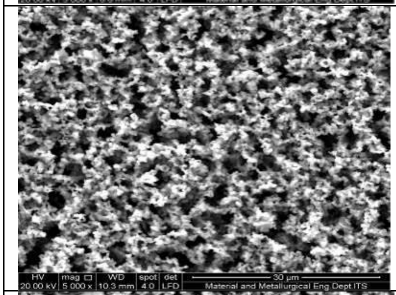
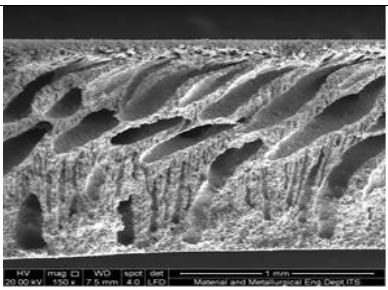
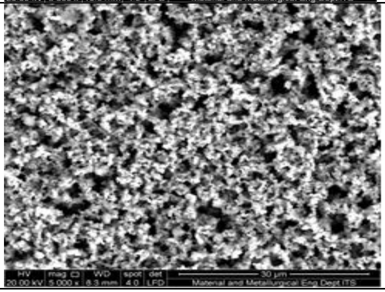
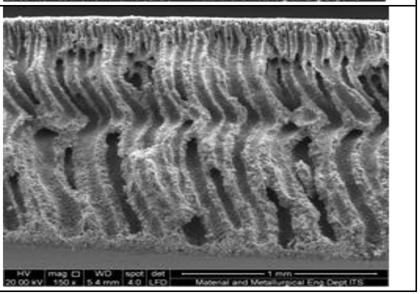
1.00	600		
3.00			
0.55	1500		
1.00			
3.00			

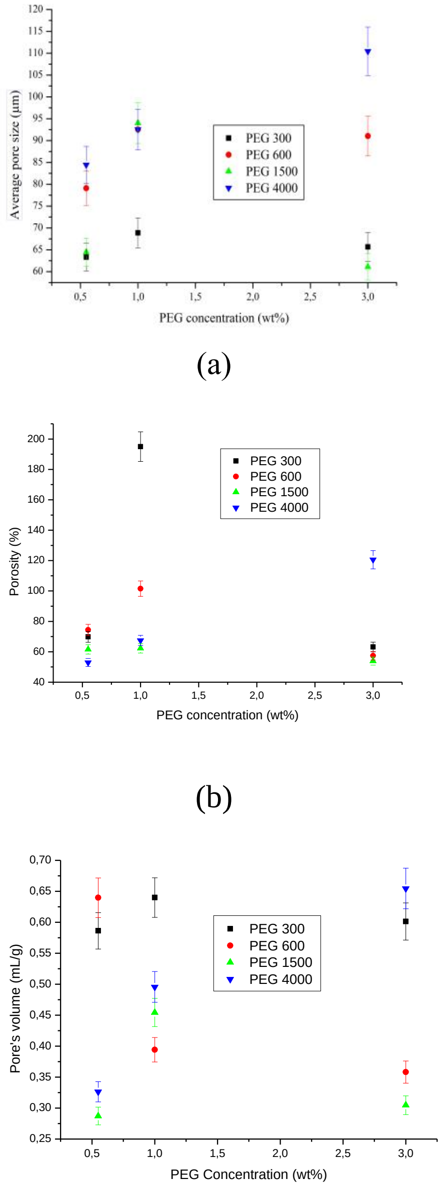
Table 2 Morphology of LSCF 7328 flat membrane at different composition of PEG as an additive (Continue)

0.55	4000		
1.00			
3.00			

(0.67 mL.g^{-1}) is achieved by 3.00 wt% PEG 4000 Da additive. Theoretically, pore volume follows the trend of pore size as a function of PEG concentration and molecular weight. However, the result shows that the trend is scattered although the higest one still belong to the highest concentration and molecular weight (3.00 wt% and 4000 Da). of porosity and pore volume measurement was not like the similar trend with the average pore size of membranes. It was caused by the incomplete water filling in the precursor membrane space.

3.3 Physical Properties LSCF 7328 Membranes

Physical properties of LSCF 7328 membranes was observed using Vickers microhardness test and Thermomechanical Analyzer (TMA) to determine the hardness and thermal expansion properties of LSCF 7328 membranes, respectively. The hardness is shown in Figure 4 while the thermal expansion coefficient is shown in Figure 5. As consequence of higher average pore size (more than 180 µm), PEG 4000 produced membrane with the lowest hardness properties, especially at 3.00 wt% of PEG concentration. Larger diameter of finger-like pores weaken the hardness of membrane. This indicates that membrane morphology or structure have direct influence on physical and mechanical properties of perovskite membrane as reported by Tan *et al*. [9]



(a)

(b)

(c)

Figure 3 LSCF 7328 Membrane: (a) average pore size, (b) porosity, and (c) pore's volume

The thermal expansion properties of membrane is shown in Figure 5. As it is a function of temperature, higher temperature automatically increase the length of membrane due to heat expansion properties [19]. The highest membrane expansion is shown by 1.00 wt% PEG 1500 Da addition. The SEM cross section images in Table 2 shows that the membrane has thicker-dense layer compared to porous layer. The membrane composed of particles LSCF 7328 with better density which lead to increased length as consequence of heat expansion. On the other hand, other membranes with more porous have the lower value of dL/L_0. The thermal expansion properties is also described as thermal expansion coefficient (TEC) value as shown in Table 3.

The highest TEC value of membrane reaches up to 19.55 ppm.K^{-1} and the lowest TEC value is 11.42 ppm.K^{-1}. The denser membrane has the higher TEC compared to the others which have more spaces (pores). In spite of the all membranes were fabricated from the same material, physical properties of membrane was influenced by another factor such as membrane structure or morphology [9].

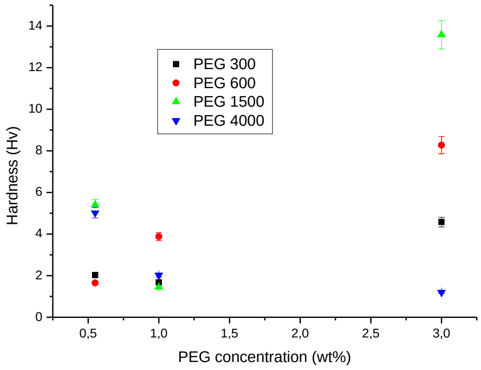


Figure 4 The hardness of LSCF 7328 membranes

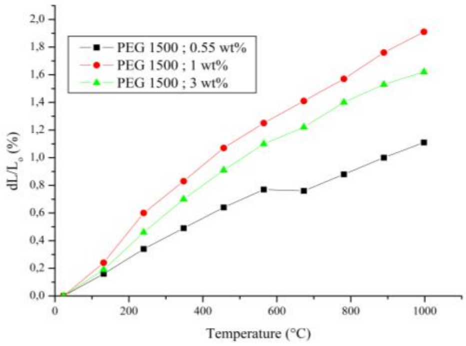


Figure 5 The thermal expansion cure of LSCF 7328 membranes

Table 3 Thermal expansion coeficient (TEC) of LSCF 7328 membranes

PEG 1500 Da (wt%)	TEC (ppm.K^{-1})
0.55	11.42
1.00	19.55
3.00	16.65

4.0 CONCLUSION

LSCF 7328 asymmetric membrane was successfully prepared by phase inversion method, followed by sintering. Asymmetric structure can be designed using PEG as an additive and it has other function as pores-forming agent. Generally, the membranes has two layers, namely dense layer which is supported by porous layer with finger-like pores.

Increasing PEG concentration leads to the higher pore size formation, which is also confirmed by cross section images. Morphology of the membranes influenced the physical as well as mechanical properties. Higher pore size of the membrane causing the decrease in hardness value due to the increasing of empty space and thus lower particle density. It is the reason why the membrane was not strong enough to hold the indentation during examination.

The thermal expansion of membrane is one of important properties which needs deepinvestigation. From TMA examination result, it can be concluded that the membrane structure is influenced by thermal expansion properties as well as TEC values, the higher particle density of membranes lead to increasing TEC value and percentage of membrane expansion. The highest TEC of membranes of 19.55 ppm.°C^{-1} is achieved using 1 wt% PEG = 1500 Da. On the other hand, the lowest TEC value of 11.2 ppm.°C^{-1} is achieved when using 0.55 wt% PEG 1500 Da.

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