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Morphological control of $La_{0.7}Sr_{0.3}Co_{0.2}Fe_{0.8}O_{3-\delta}$ and $La_{0.7}Sr_{0.3}MnO_{3-\delta}$ catalytic membrane using PEG-H_2O additive

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Abstract. Methane is the primary combustible component in non condensable part of natural gas. It is a promising source for syngas (CO and H_2) production by partial oxidation method. The conversion of methane to syngas by partial oxidation method needs a controlled amount of oxygen. Membrane which has asymmetric structure and selectively permeates oxygen can be used to supply just enough oxygen to the reaction. One pathway to the fabricate asymmetric membrane is phase inversion method with an addition of PEG to increase pore size. $La_{0.7}Sr_{0.3}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF 7328) and $La_{0.7}Sr_{0.3}MnO_{3-\delta}$ (LSM 73) powder were synthesized by solid-state method and they were characterized by XRD. The green membrane was prepared by phase inversion method. A dope solution was made by mixing LSCF 7328 or LSM 73 powder with PEG and stirred them in NMP for 24 h. PESf was then added into the dope solution and the stirring was continued to another 24 h. The resulted dope solution was degassed by immersing the solution inside and conical flask in an ultrasonic bath to remove air bubbles. The degassed mixture was then casted by spreading it on a glass surface (with a thickness of 2 mm) followed by immersion in a water bath for 24 h to coagulate the degassed mixture. Membrane morphology was characterized by Scanning Electron Microscopy (SEM) while the decomposition temperature of the polymer binder was analyzed by Thermogravimetric Analyzer (TGA). The XRD results show that phase of LSCF 7328 and LSM 73 are similar to $LaCoO_3$ and $LaMnO_3$, respectively. It indicated that the perovskite synthesis was successful. SEM micrograph of membrane cross sections show that the green membrane have finger like pores and a dense layer. Pores also appear on top and bottom surface of the membrane. Based on TGA results, the highest weight lost of green membrane at 550-600 ℃ which represents the decomposition of PESf binder.

1. Introduction

Indonesia has numerous natural resources such as natural gas which are promising to solve some problems in the energy sector. The primary hydrocarbon component in non condensable part of natural gas is methane and it can be converted to syngas as raw material to produce hydrocarbons or liquid fuels. Methane conversion to liquid fuels is known as Gas To Liquid (GTL) process which has two steps[1]. The first is methane conversion to syngas by, for example, partial oxidation [2]. The second step is Fischer tropsch reaction of the syn gas to hydrocarbons.

The conversion of methane to syngas by partial oxidation method needs a controlled amount of oxygen. If there are excessive oxygen, methane will be oxidized completely into CO_2 and H_2O, instead of partially oxidized to syn gas. In this case a membrane which selectively permeates oxygen can be used to supply just enough oxygen to the reaction. Teraoka et al reported that perovskite oxides are

promising materials for such membrane to transfer oxygen where the oxygen flux can be controlled by modification of A and B site in ABO_3 perovskite lattice [3]. Perovskite oxides have general formula of ABO_3, where A site is occupied by a large cation such as alkaline, earth alkaline, and rare earth cation. Meanwhile B site is occupied by a smaller size cation like especially cation of transition metals [4].
Among many perovskite oxides, family of Sr^{2+} substituted $LaCoO_3$ (LSCF) and $LaMnO_3$ (LSM) attracted attention of many researchers due to their good oxygen flux. For an example, Tan et al reported the use of $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ as membrane material for oxygen separation and the result showed that the membrane has good flux and high selectivity to oxygen permeation [5]. The oxygen flux is higher when more La^{3+} was replaced by Sr^{2+}. However, at higher Sr^{2+} content, the perovskite react with CO_2 to form $Sr(CO)_3$ an reduce the oxygen flux. Therefore it is very important to limit the number of Sr^{2+} in such a way so the maximum Sr^{2+} substitution was limited to 30% $La_{0.7}Sr_{0.3}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF 7328) and $La_{0.7}Sr_{0.3}MnO_{3-\delta}$ (LSM 73). In addition to the oxygen permeation, the membrane also have good electron conductivity [6]. The combination of good oxygen and electron conductivity makes the perovskite oxide can conduct oxygen without any electrical current.
As an oxygen supplyer to partial oxidation reaction, the oxygen flux of Sr^{2+}-LSCF and -LSM is a function of the membrane's thickness. Thinner membranes will have higher oxygen flux. the In order to compensate the reduction of oxygen flux in low Sr^{2+}-LSCF and -LSM, the membrane have to be made as thin as possible. An asymmetric membrane morphology, where a thin layer of membrane is supported on a thicker and porous support, is an alternative way to improve the oxygen flux without having to modify its chemical composition.
One promising way to fabricate asymmetric perovskite based membrane by phase inversion method, and it is combined with sintering technique [7]. Phase inversion method needs polymer as binder and pore structure can modify by addition of an additive to form the pore or increase pore size. Bakeri et al using water, methanol, ethanol, glycerol and acetic acid as the additive, the result showed membrane have finger like structure except for water additive produce membrane that has sponge like structure [8]. Mohamed et al also used water as an additive, increasing amount of water into dope solution would decrease finger like and increase the thickness of dense layer [9]. The disadvantages if used liquid as the additive were possible to vaporize when mixture process. If additive vaporize before phase inversion process, the membrane has low pore size or it would obtain the dense membrane. Another pathway to solve this problem were used the polymer as additive. Polyvinyl pyrrolidone (PVP) were reported by many researchers as an excellent additive to form the pore on perovskite membrane [5]. Besides PVP, another promising polymer additive was PEG, Saljoughi et al used PEG additive for modifying morphology and membrane structure of cellulose acetate [10]. The result showed, increasing of PEG loading or molecular weight into dope solution would increase pore size. Based previous research, in this work use combination PEG and water as the additive to modify morphology and membrane structure of LSCF 7328 and LSM 73.

2. Methodology

2.1 Materials

The raw material for LSCF 7328 and LSM 73 synthesis were p.a. grade of La_2O_3 (99.5%), $SrCO_3$ (99.9%), Co_3O_4 (99.5%), Fe_2O_3 (97%) and $MnCO_3$ from Merck. The flat membrane was made by using PESf (polyethersulfone) as the binder, NMP (N-Methyl-2-pyrrolidone) as the solvent, PEG 8000 as a pore modifier and water as nonsolvent (coagulant).

2.2 Synthesis of LSCF 7328 and LSM 73

LSCF 7328 7328 and LSM 73 was synthesized by a combination of mechanochemical and solid state method according to the method that was reported by Nurherdiana et al [11]. The product was characterized by XRD Panalytical using Cu Kα (λ = 1.5406 Å) which was generated by applying 30 mA current and 40 kV of voltage. The scan rate was $1^o.min^{-1}$ and step size was 0.02^o.

2.3 Preparation and Morphological Characterization of LSCF 7328 and LSM 73 Green Membrane
The green membrane was prepared by phase inversion method. A dope solution was made by mixing LSCF 7328 or LSM 73 powder with PEG and stirred them in NMP for 24 h. PESf was then added into the dope solution and the stirring was continued to another 24 h. The resulted dope solution was degassed by immersing it in an ultrasonic bath to remove air bubbles.
The degassed mixture was then casted by spreading it on a glass surface (with a thickness of 2 mm) followed by immersion in a water bath for 24 h to coagulate the degassed mixture. After coagulation step, the resulted membrane (green membrane) was dried to remove water. The morphology of the green membrane was characterized by SEM to analyze it's morphology and TGA-DTA to examine the decomposition of PESf and other non-organic content of the membrane. Table 1 shows the chemical composition of dope solution.

Table 1. Composition of Dope Solution

LSCF 7328 (wt%)	LSM 73 (wt%)	PESf (wt%)	NMP (wt%)	Additive (wt%)		Code
				PEG	H_2O	
52.1	-	6.7	41.2	-	-	A1
47.1	-	6.7	41.2	3.5	1.5	B1
47.1	-	6.7	41.2	4	1	C1
47.1	-	6.7	41.2	4.5	0.5	D1
47.1	-	6.7	41.2	5	-	E1
-	52.1	6.7	41.2	-	-	A2
-	47.1	6.7	41.2	3.5	1.5	B2
-	47.1	6.7	41.2	4	1	C2
-	47.1	6.7	41.2	4.5	0.5	D2
-	47.1	6.7	41.2	5	-	E2

3. Result and discussion
LSCF 7328 and LSM 73 were synthesized using a combination of mechanochemical and solid state method. The X-ray diffractogram (XRD) of the resulted perovskites are shown in Figure 1 and 2. The figure shows that diffractogram of LSCF 7328 is similar to $LaCoO_3$ (JCPDS 00-025-1060) while diffractogram of LSM 73 is similar to $LaMnO_3$ (JCPDS 00-035-1353). The similarities shows that the synthesis procedure successfully produce LSCF 7328 and LSM 73. In addition to the crystal structure, the diffractograms also shows that there is no impurities in the resulted perovskite.

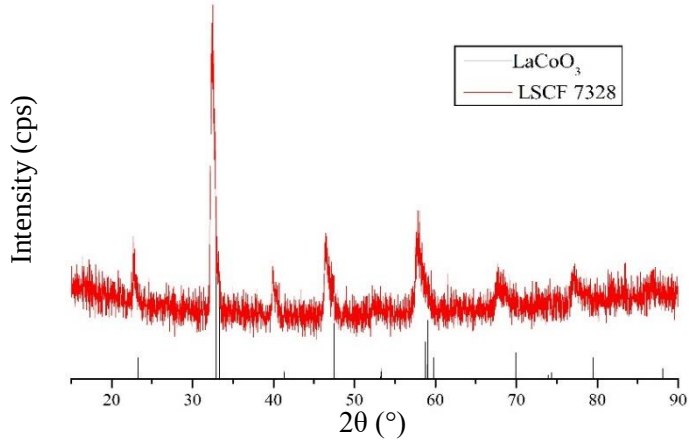


Figure 1. XRD Pattern of LSCF 7328

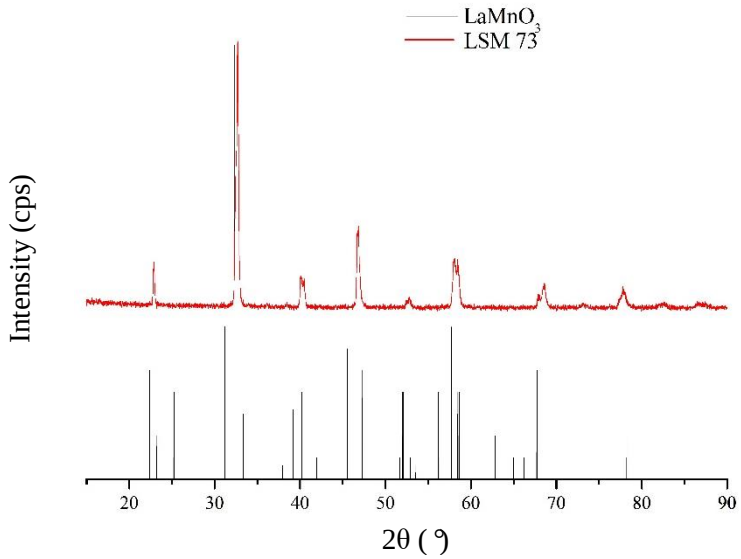


Figure 2. XRD Pattern of LSM 73

Further examination of diffractogram in Figure 1 revealed that specific diffraction peaks of LSCF 7328 was shifted to lower of 2θ. The partial substitution of Co^{3+} with a slightly larger Fe^{3+} and partial substitution of La^{3+} (1.5 Å) with larger Sr^{2+} (1.58 Å) cation makes the unit cell size larger than $LaCoO_3$. The increase of unit cell size also increase the interplanar distances of the perovskite crystal which was indicated by the shifts of all peaks to lower 2θ [1].

Phase inversion method was used to prepare LSCF 7328 and LSM 73 membranes. The advantage of the method is pore structure and size can be modified by modifying the diffusion rate of solvent (J1) and nonsolvent (J2). When J1=J2 the resulted membrane pores will be sponge like while when J2>J1 the pores will be finger like [12]. Figure 3 shows the mechanism of pore formation as a function of diffusion rate of solvent and nonsolvent.

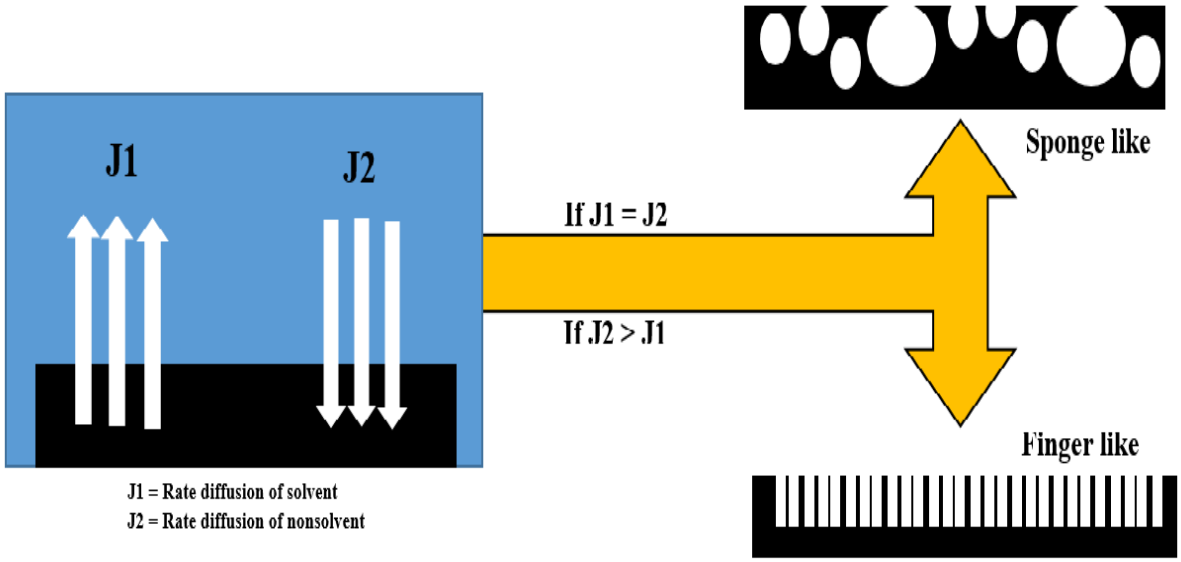
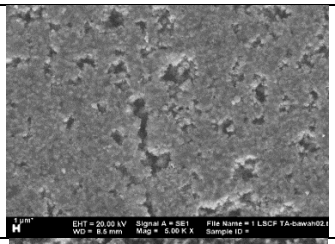
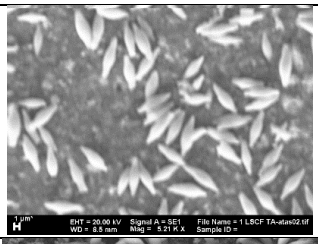
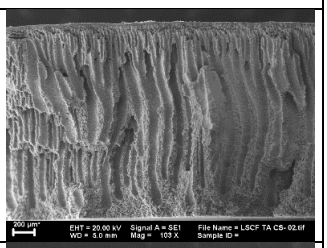
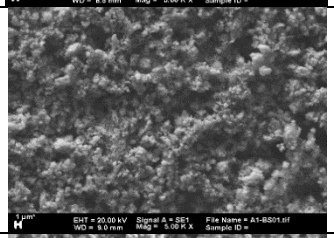
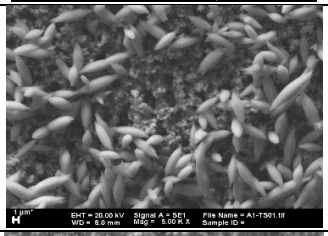
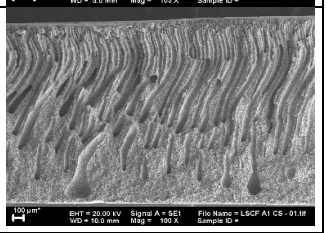
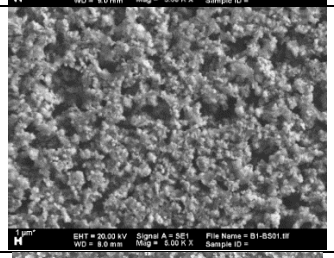
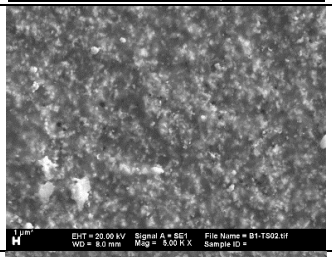
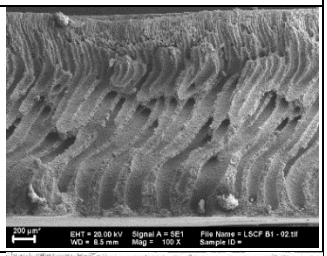
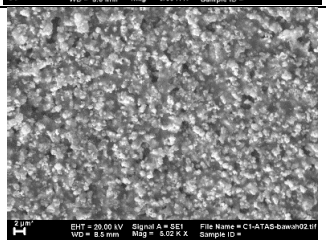
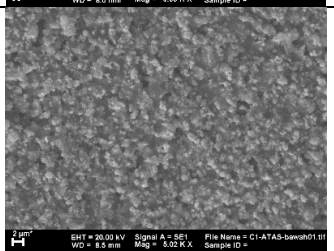
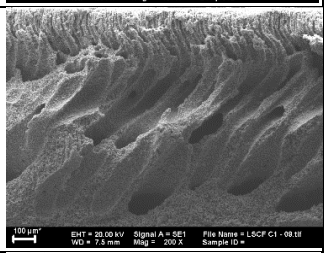
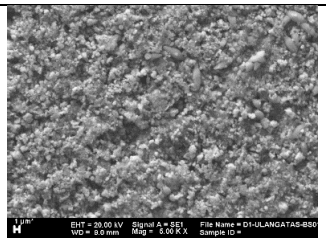
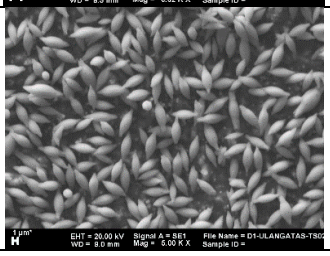
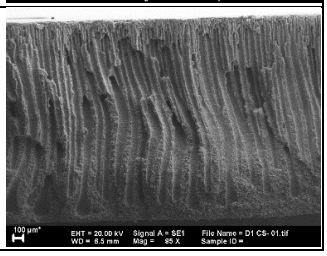


Figure 3. Pore formation mechanism

Table 2 and 3 show SEM Micrographs of LSCF 7328 and LSM 73 membrane with different loading of additive. In Table 2, it is shown that increasing PEG concentration in the dope solution gradually

increase pore size of the membrane and each membrane has finger like pores. Membranes with finger like pores have better mechanical strenght than sponge like pores. It is also shown that each LSCF 7328 membrane has a thin layer of dense membrane on the top of membrane cross section.
In addition to the cross section, the top and bottom surface of the membrane was also identified by SEM micrograph. The top and bottom part of LSCF 7328 membrane have some small size pores which was probably formed during the diffusion of PEG into nonsolvent. The small pores, especially on the dense surface, may be reduced during the sintering process which will increase the densification of LSCF 7328 membrane [7].

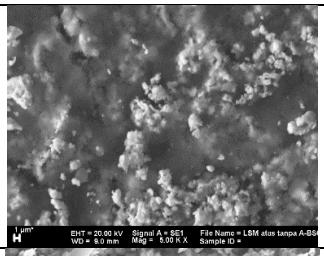
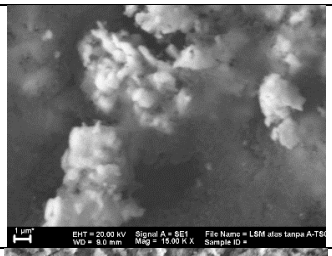
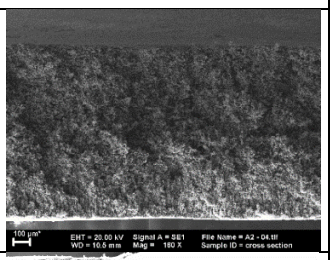
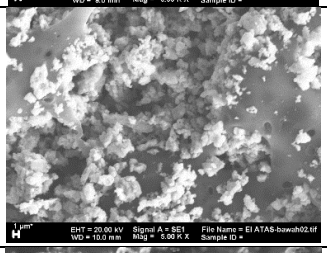
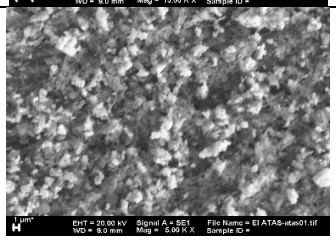
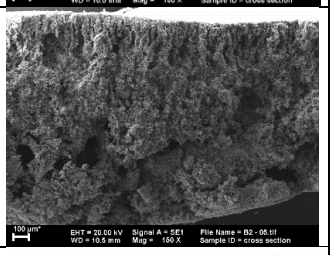
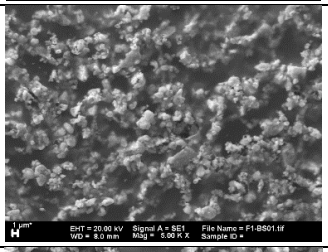
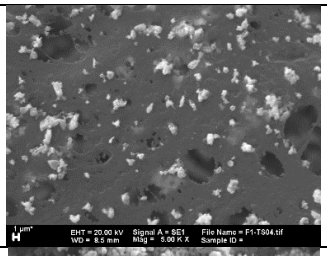
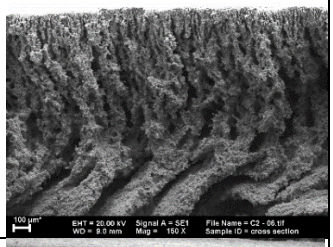
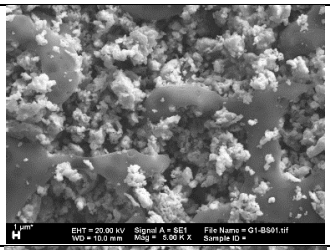
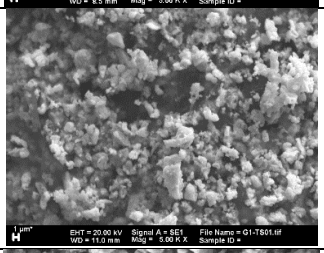
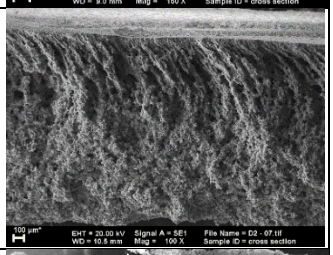
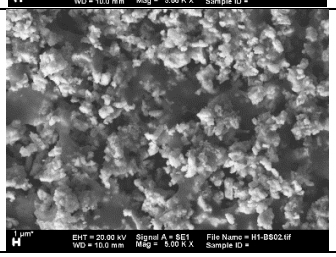
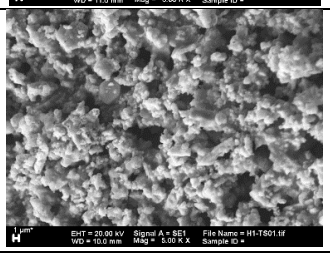
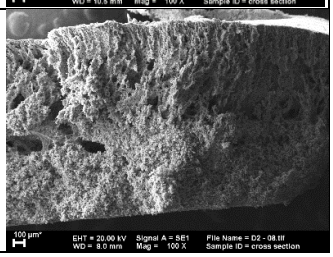
Table 2. SEM Micrograph of LSCF 7328 Green Membranes

Sample Code	Bottom Surface	Top Surface	Cross Section
A1			
B1			
C1			
D1			
E1			

When comparing the pores on LSCF 7328 and LSM 73 membranes, the LSM 73 has less regular pores than LSCF 7328. It indicates that each powder has its own characteristic and properties which affect the pore formation during phase inversion process. Top and bottom surface of LSM 73 membrane showed the similar result to LSCF 7328 membrane where some small pores are observed. LSM 73

membrane also shows thicker dense layer than LSCF 7328. The thickness of dense layer will have effect on its oxygen flux and ultimately to the catalytic activity on partial oxidation of methane (POM) reaction [1]. Membranes with thicker layer of then dense part will have lower oxygen flux.

Table 3. SEM Micrograph of LSM 73 Green Membranes

Sample Code	Bottom Surface	Top Surface	Cross Section
A2			
B2			
C2			
D2			
E2			

TGA analysis results of LSCF 7328 (LSCF-5) and LSM 73 (LSM-5) green membranes are shown in Figure 4. It is apparent that the highest lost weight of both green membranes occurs at around 550-600 ℃. Tan et al reported that the wight lost at 550-600 ℃ is due to the decompotion of PESf. The weight lost at higher temperature might be due to thermal reduction of perovskites where some of their structural oxygen escape from the perovskites, leaving some oxygen vacancies. The reduction might be happening because the TGA analysis was carried in nitrogen atmoshpere that makes the oxygen partial pressure in the surrounding atmosphere was very low, similar to the reduction of titanate provskites that was reported by Rodenbücher et al. [13].

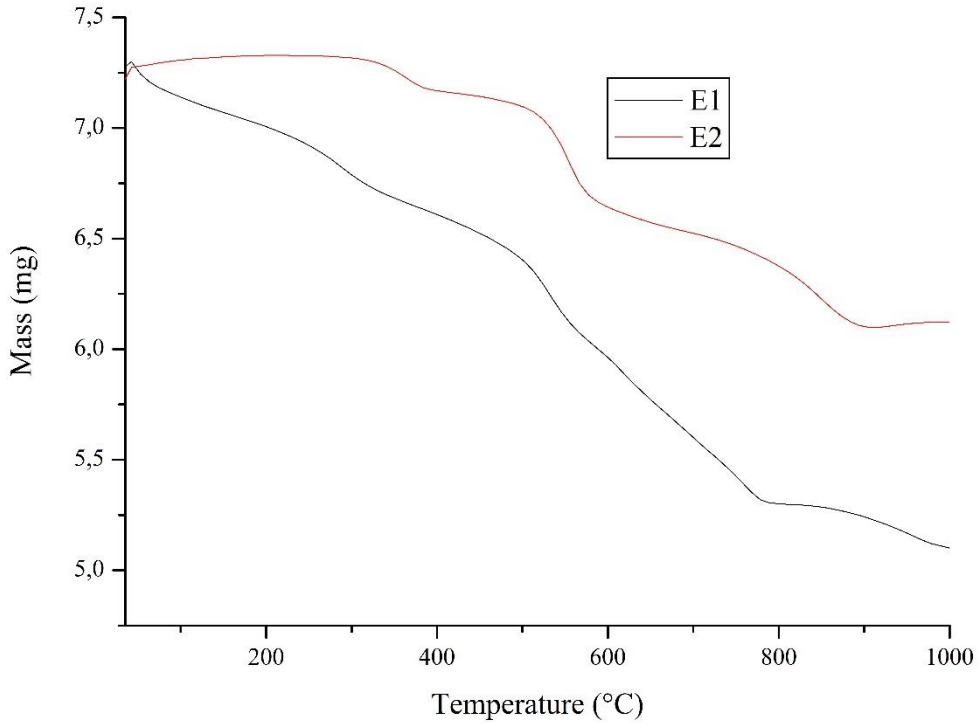


Figure 4. TGA Curve of LSCF 7328 (E1) and LSM 73 (E2) Green Membranes

4. Conclusion

LSCF 7328 and LSM 73 were successfully synthesized by solid state method. LSCF 7328 and LSM 73 has a similar structure with $LaCoO_3$ and $LaMnO_3$, respectively. Partial substitution to the lower size of ion caused shifted peak to the lower 2θ. Then, fabrication of each membrane use PEG-H_2O additive by phase inversion method obtained membrane that has finger like structure of their pores and thin dense layer. The higher PEG loading lead to increasing pore size of finger like and some pore with small size appear on the bottom and top surface of the membrane. Thermogravimetric analyzer result exhibit decomposition of PESf binder around 550-600 ℃ and increasing temperature would increase densification of LSCF 7328 and LSM 73 particle.

5. References

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