

CATALYTIC SURFACE MODIFICATION OF ALUMINA MEMBRANE FOR OXYGEN SEPARATION

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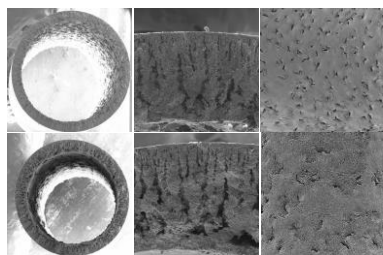
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Graphical abstract



Abstract

Two types of alumina ceramic membrane in hollow fibre shape was used in this study. Both alumina hollow fibres (AHF) were sintered at different temperatures; (a) 1350°C and (b) 1450°C. In order to improve the catalytic activity of the alumina membrane for oxygen separation purposes, surface modification of the membranes was carried out using $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-5}$ (LSCF) perovskite catalyst. LSCF was synthesised using simple Pechini sol-gel method. The evaporation time and temperature of the LSCF-sol were varied to obtain various viscosity of catalytic sol. From XRD analysis, pure LSCF perovskite structure formed at temperature at 850°C. The morphological of unmodified and surface-modified alumina hollow fibre membranes (AHF) were studied using FESEM. The effect of LSCF catalytic sol viscosity was studied and it was found that as the viscosity of the sol increases, the amount of catalyst deposited on the alumina hollow fibre were increased. Besides, the amount of catalyst deposited on 1350 AHF was found to be higher than 1450 AHF. This result is supported by the result of pore distribution data whereby 1350 AHF was observed to be more porous than 1450 AHF, with porosity percentage of 40.38% and 28.80%, respectively. Although higher viscosity of catalytic sol could lead to a high amount of catalyst deposited on the AHF substrate, there is a tendency for micro-cracks to develop. Thus, the viscosity of the catalytic sol is important to control in order to have higher oxygen permeation flux.

Keywords: Surface modification, LSCF, Alumina hollow fibre membrane, Ceramic membrane, Sintering

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1.0 INTRODUCTION

Catalyst derived from mixed ionic electronic conducting (MIEC) materials such as lanthanum strontium cobalt ferrite, $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-5}$, (LSCF [1], barium strontium cobalt ferrite,

$\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-5}$ (BSCF) [2], $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_{3-5}$ (SFC) [3] and etc. has attracted a lot of attentions in research study since it has the ability to separate oxygen from air through its ionic and electronic properties as well as oxygen pressure difference on both side of the membrane as the driving force. The very first oxygen permeable dense MIEC membrane

using LSCF was developed 28 years ago by Teraoka *et al.* [1]. Since then, many research works have been done using this material such in solid oxide fuel cells (SOFC) [4,5] oxygen permeable membrane [4,5] and methane oxidation coupling reaction [7,8,9].

The development of membrane technology using LSCF for oxygen separation can be considered as potential replacement to conventional method like cryogenic distillation and pressure swing adsorption since it can reduce cost, energy and more adapting to green technology and sustainable approach. Recently, much effort has been devoted in the search for new materials for surface modification on LSCF perovskite membrane. Table 1 shows some research works on surface modification of LSCF hollow fibre membrane. However, LSCF is still remains as one of the best perovskite catalyst and many research shown LSCF can produce high oxygen permeation flux and better stability [10,11,5]. Therefore, LSCF was chosen in this work as catalyst for surface modification on alumina ceramic membrane.

Table 1 Surface modification of LSCF hollow fibre membrane

Membrane material	Surface modification materials	Ref.
LSCF	H ₂ SO ₄	[12]
LSCF	Palladium	[13]
LSCF	LSCF	[14]
LSCF	Silver	[14]
Acid etched-LSCF	LSC	[15]
LSCF	BSCN	[16]

The uses of alumina ceramic membrane as a substrate to the deposition of MIEC materials is still considered in early stage since there are a small number of researchers work on this [17,18,19,20,21,22]. Due to the inert property of the alumina substrates, catalytic surface modification is required for oxygen separation. On the other hand, the special feature such as finger-like pores on the inner surface of the membrane provides larger surface area for catalyst deposition as compared to dense and disc shape permeable membrane. Figure 1 illustrates the catalyst deposition in the finger-like pores of a ceramic membrane.

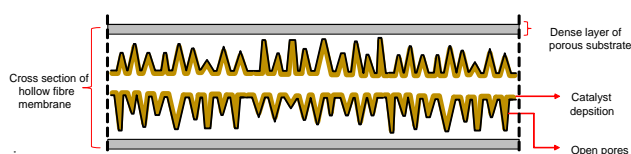


Figure 1 Illustration of deposited LSCF catalyst on porous substrate

From our previous work [23], it is known that the viscosity of the catalytic sol plays an important role in deposition properties since less viscous sol could infiltrate better through the membrane and higher viscosity sol will leads to non-homogenous deposition and micro-cracks on the membrane surface [24]. Thus, the aim of this work was to synthesis different viscosity of LSCF catalyst and investigate its effect on the surface modification of alumina hollow fibre membrane (AHF) sintered at different temperature.

2.0 METHODOLOGY

2.1 Preparation of LSCF Catalyst

The LSCF catalyst was prepared by using Pechini sol-gel technique [25]. Figure 2 illustrates the flow process of preparation of LSCF catalytic sol. Firstly, stoichiometric amount of lanthanum nitrate hexahydrate, La(NO₃)₃.6H₂O (99.99% Merck), strontium nitrate, Sr(NO₃)₂ (99.99%, Merck), cobalt nitrate hexahydrate, Co(NO₃)₂.6H₂O (ChemAR, System Chemicals), and iron (III) nitrate nonahydrate, Fe(NO₃)₃.9H₂O (R&M Chemicals) were mixed and stirred in distilled water. Chelating agent, citric acid, C₆H₈O₇ (99.99% Merck), and polymerization agent, ethylene glycol, C₂H₆O₂ (99.99% Merck) were added to the metal nitrates solution with molar ratio of ethylene glycol to citric acid to metal nitrates is 9:3:1. The mixed solution was stirred and heated at 80°C for 5 hours to encourage polyesterification. The heated solution was divided into four samples for further heated in the oven to form a sol-gel solution of LSCF catalyst. The samples mark as sample A with no heating while sample B and C were heated at 70°C for 17 and 41 hours respectively to gain different viscosity. At constant evaporation time of 17 hours, sample D was heated at 90°C.

To study the effect of calcination temperature towards the formation of pure perovskite phase of MIEC materials, the heated catalytic sol was calcined in the furnace at temperature of 750°C for 4 hours dwelling time using heating and cooling rate of 2°C/min. The same steps were repeated for calcination temperature at 850 and 950°C. The calcined powder was further characterised using XRD.

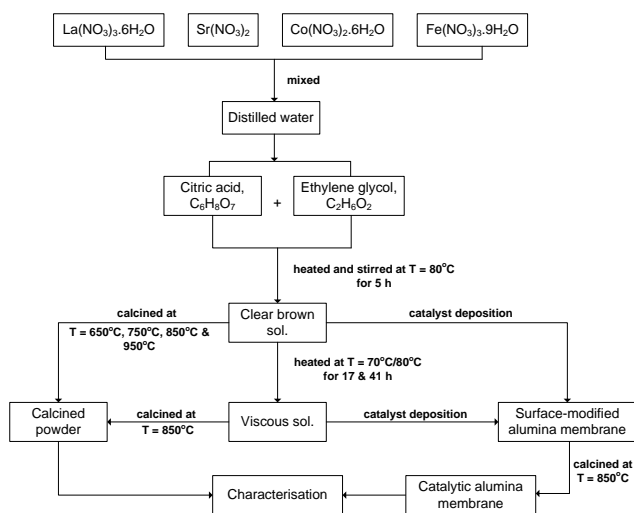


Figure 2 Flow process of preparation of LSCF catalytic solution

2.2 Catalyst Deposition on Alumina Hollow Fibre Membrane

The alumina hollow fibre (AHF) membrane was prepared by using phase inversion/sintering technique with composition of 55 wt% alumina powder, 0.38 wt% arlacel, 39.12 wt% dimethyl sulfoxide (DMSO) and 5.5 wt% polyethersulfone (PESf). The hollow fibers were sintered at two different temperatures; 1350°C and 1450°C for 4 hours to study the effects of porosity. The samples sintered at 1350°C and 1450°C were labelled as 1350 AHF and 1450 AHF, respectively.

The prepared catalytic sol (A, B, C and D) was deposited onto alumina membranes surface by using vacuum-assisted technique to enhance the deposition of catalyst into the pores [23]. The experimental setup for catalyst deposition is shown in Figure 3. Firstly, the unmodified AHF membranes were wrapped with PTFE tape on the outer surface followed by vacuumed for several hours before catalyst deposition in order to remove air inside the lumen of the hollow fibres. Then, the tube containing vacuumed AHF membranes were filled with LSCF catalytic sol by opening the suction valve till all the AHF was fully immersed in the solution. The vacuum process was continued for one hour. After that, the surface-modified AHFs membrane were dried in air vertically for 24 hours and only after that the calcination process was conducted at temperature of 850°C for 4 hours to activate the catalytic effect of the oxygen permeable membrane.



Figure 3 Vacuum deposition setup for catalyst deposition

2.3 Characterisation

The crystallite structure of calcined LSCF powder was determined by X-ray diffractometer (XRD) (D/Max 2200/PC, Rigaku, Japan) using Cu-K α radiation source with step scanning ranging from 10° to 80° and scanning rate of 5°/min. The voltage and current used for the scanning is 40 kV and 40 mA respectively. The morphological of the unmodified and surface-modified AHF membranes were viewed using field-emission scanning electron microscopy (FESEM) (Zeiss Supra 35 VP, Germany). The viscosity of the heated LSCF sol was measured using viscometer (LV DV-II, Brookfield, USA). The pore size distribution and porosity percentage of unmodified alumina membrane was analysed using mercury porosimetry (IV 9510, Micromeritic Autopore, USA).

3.0 RESULTS AND DISCUSSION

3.1 Morphological Study of Unmodified and Surface-modified Alumina Hollow Fibre Membrane

Figure 4 shows SEM images of unmodified alumina hollow fibre membrane sintered at different temperature; 1350°C and 1450°C. Generally, both fibres were porous and has finger-like pores on the top and bottom of the wall section. As the sintering temperature increases, the total surface area and porosity of the fibres decreases from 40.38% to 28.8% (Table 2). From the SEM images shown in Figure 4(b) and 4(e), the thickness of 1350 AHF and 1450 AHF was ~0.24 mm and ~0.44 mm respectively. It was found that the thickness of the membrane was lower for the fibre that was sintered at higher temperature. This is because the effect of elevated temperature exerted during sintering process made the hollow fibre shrunk. According to Zydorczak *et al.* [10] thinner membrane will produces higher oxygen permeation flux. It is because at elevated operation temperature during separation activity the ionic bulk diffusion across the membrane wall becomes a rate-limiting step. Thus, it is believed that by reducing the

membrane thickness can overcome the problem and produce high oxygen permeation flux compared to thick membrane.

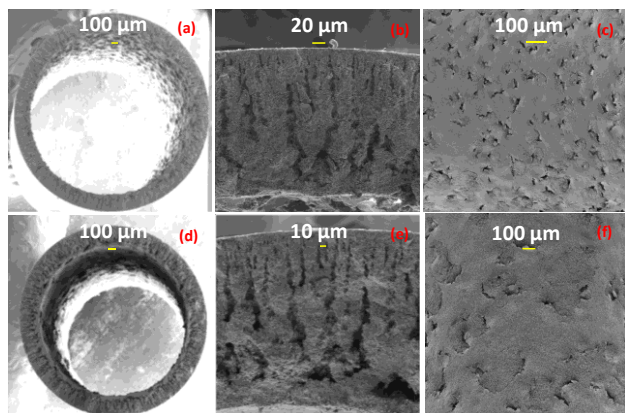


Figure 4 SEM images of unmodified AHF at different sintering temperature; (a-c) 1350°C and (d-f) 1450°C where (a & d) cross-section, (b & e) wall section and (c & f) inner surface

Pore size distribution data for both alumina fibres was shown in Figure 5. For fibre sintered at 1350°C, the data shows broad pore size distribution at peak of approximately 0.183 nm which represent the broad opening of the finger-like pores at the inner surface of the fibre. While, for 1450 fibre, it has narrower pore distribution and intrusion intensity indicates that it has few small opening finger-like pores at approximately 0.227 nm. This results were consistent with work by Kingsbury [17], in which at elevated sintering temperature, more pores will be eliminated and thus, the final porosity decreases. In this work, highly porous substrate is needed in order to deposit large amount of catalyst and since 1350 AHF provide large pore size distribution, it is suitable to be used as the substrate for further investigation in this study

Table 2 Total surface area and porosity percentage of alumina hollow fibre membrane

Alumina hollow fibre	Porosity (%)
1350 AHF	40.38
1450 AHF	28.80

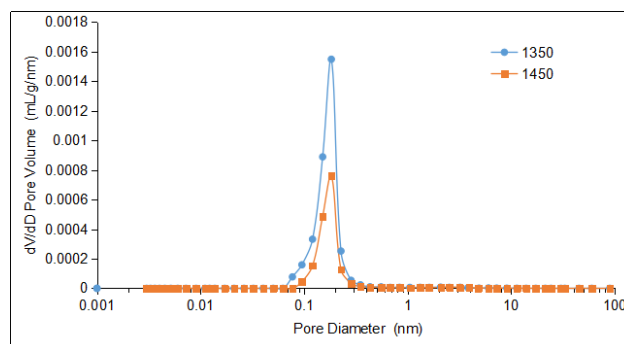


Figure 5 Pore size distribution of unmodified alumina hollow fibre membranes

3.2 $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) Catalyst

Figure 6 shows the XRD patterns of LSCF powder calcined at 650°C, 750°C, 850°C and 950°C. At 850°C, pure perovskite structure starts to develop. At 650°C, strontium carbonate (SrCO_3) and strontium oxide (SrO) peak (in the circle) obviously can be seen but as the calcination temperature increases, the peak no longer appeared as it undergoes decomposition [24]. The increasing of peak intensity with higher calcination temperature indicates that larger crystalline particles of LSCF was formed after calcination process [10].

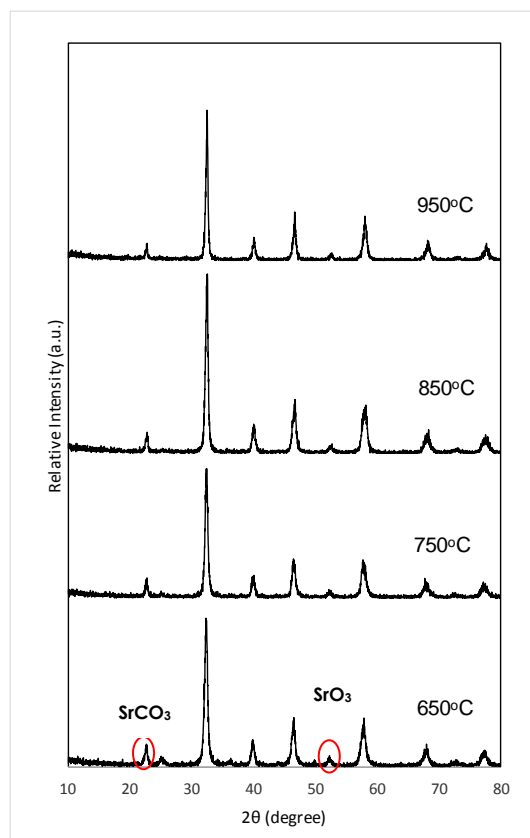


Figure 6 XRD patterns of calcined LSCF catalyst at different temperature

3.3 Effect of Viscosity on Surface-modified Alumina Hollow Fibre Membrane

The viscosity of LSCF catalytic sol evaporated at different temperature and time are shown in Figure 7 and Table 3. At constant evaporation temperature, the viscosity of the sol increases as the heating time increases. The same trend also applied at constant evaporation time and increasing heating temperature. According to Jin *et al.* [24], all the viscosity value in Table 2 are in the range of suitable viscosity for catalyst deposition. Viscosity below 5 cp causes the catalyst infiltrate into the pores thus promotes to the formation of holes or cracks. Meanwhile, for the viscosity that above 80 cp causes non-homogeneously deposition of catalyst onto membrane and tends to produce cracks after calcination.

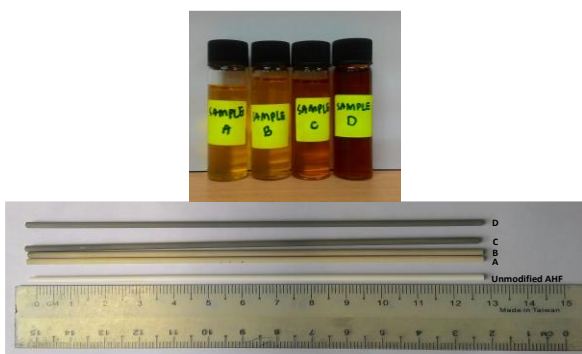


Figure 7 Surface-modified 1350 AHF using different viscosity of LSCF catalytic sol

Table 3 Viscosity of LSCF catalytic sol.

Sample	Evaporation parameter		Viscosity (cp)
	Temperature (°C)	Time (h)	
A	Room temp.	0	7.71
B	70	17	9.00
C	70	41	10.30
D	90	17	13.30

The amount of catalyst deposited was determined by weighing the initial weight of bare (unmodified) membrane and the final weight of the surface-modified membrane after calcination process. The difference value of weight measured is the total amount of catalyst deposited. By referring to Figure 8, the amount of catalyst deposited onto both of the ceramic alumina membranes significantly increased as the LSCF catalytic sol becomes more viscous due to the increasing of evaporation temperature and time. The amount of catalyst deposited on 1450 AHF membranes were significantly lower (<70%) than 1350 AHF membranes, this result indicates that the porosity of the substrate plays an important role in determining the amount of catalyst deposited.

As the sintering temperature applied on 1450 AHF membrane was higher, thus made the pores becomes smaller and reduce the porosity of the membrane, a small amount of catalyst deposited on membranes might not enhance the oxygen permeation flux during the oxygen permeation test. Thus, appropriate viscosity of catalytic sol should be used in order to obtain sufficient oxygen permeation activity.

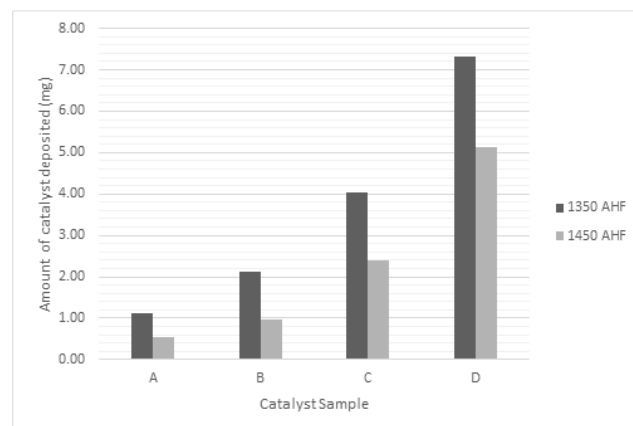


Figure 8 Amount of catalyst deposited after calcination

4.0 CONCLUSION

LSCF perovskite catalytic sol with different viscosities were prepared by using simple Pechini sol-gel method. The viscous catalytic sol was synthesised at different evaporation temperature and time. Two types of alumina hollow fibre membrane which sintered at 1350°C and 1450°C were used in this study and the deposition LSCF catalyst was carried out using vacuum-assisted technique. The pure LSCF perovskite structure was formed at 850°C. It was found that as the viscosity of the catalytic sol increases, the amount of catalyst deposited also increases. Interestingly, the amount of LSCF catalyst deposited was decreases using 1450 AHF because of less porosity compared to 1350 AHF.

The surface-modified alumina hollow fibre membrane using LSCF catalyst in this study will be used for oxygen permeation test in the future. Other perovskite catalysts also will be tested and further studied for oxygen separation.

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