DEVELOPMENT OF CuO-TiO_2-$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ MIXED IONIC-ELECTRONIC CONDUCTING CERAMIC MEMBRANE FOR OXYGEN SEPARATION

by

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"Ever tried. Ever failed. No matter. Try again. Fail again. Fail better."
- Samuel Beckett (Worstward Ho)

TABLE OF CONTENTS

Acknowledgements…….....ii

Table of Contents……...iii

List of Tables…….vii

List of Figures…….....ix

List of Plates…….....xii

List of Abbreviations……..……..xiv

List of Symbols…….....xvi

Abstrak……...…xviii

Abstract…….....xx

CHAPTER ONE – INTRODUCTION

1.1 Overview……....1

1.2 Problem Statement…….2

1.3 Research Objectives……...5

1.4 Scope of the Study…….….5

1.5 Organization of the Thesis…….7

CHAPTER TWO - LITERATURE REVIEW

2.1 The Advances of Oxygen Production Technologies……...9

2.2 Perovskite MIEC Materials…….….13

2.3 Preparation of MIEC Membranes…….……16

2.3.1 Powder Synthesis…….……16

2.3.2 Shaping……18

2.3.3 Sintering……..……19

2.3.4 Additives for Low Temperature Sintering……..21

2.4 Oxygen Permeation Performance of MIEC Membranes…….24

2.5 Oxygen Permeation Model of MIEC Membranes……...……29

2.6 Concluding Remarks……...….32

CHAPTER THREE- MATERIALS AND METHODS

3.1 Chemicals and Equipment……...….35

3.2 Membrane Preparation…….....37

3.3 Characterization Methods…….....39

3.3.1 X- ray Diffraction (XRD)……..……39

3.3.2 Sintering Behaviour…….……..40

3.3.3 Dilatometry …….…..41

3.3.4 Scanning Electron Microscopy (SEM)…….….42

3.3.5 Three Point Bending Test…….….42

3.4 Experimental Set-up…….…42

3.4.1 Feed and Sweep Gas Delivery System……..43

3.4.2 Membrane Separator System…….43

3.4.3 On-line Gas Analysis…….47

3.5 Experimental Design……48

3.6 Optimization of Experimental Conditions……...49

3.7 Oxygen Permeation Measurements…….……51

3.8 Oxygen Permeation Model…….……..52

3.8.1 Determination of D_v, k_f and k_r ……55

3.8.2 Determination of Oxygen Permeation Rate-Limiting Step……56

3.9 Concluding Remarks……58

CHAPTER FOUR - RESULTS AND DISCUSSION

4.1 Membrane Characterization……59

4.1.1 X-ray Diffraction (XRD)……...59

4.1.2 Sintering Behaviour……...68

4.1.3 Dilatometric Measurement……73

4.1.4 Scanning Electron Microscopy (SEM)……..75

4.1.5 Three Point Bending Test……..94

4.1.6 Oxygen Permeation Test……99

4.1.7 Summary of Characterization Results……..105

4.2 Oxygen Permeation Performance Studies……..105

4.2.1 Effect of Temperature and Thickness……..106

4.2.2 Effect of Oxygen Partial Pressure in the Feed……109

4.2.3 Effect of Sweep Gas Flow Rate……...111

4.2.4 Optimization of Experimental Conditions……113

4.3 Oxygen Permeation Model……118

4.3.1 Determination of D_v, k_f and k_r ……118

4.3.2 Comparison of Experimental and Predicted Data……119

4.3.3 Oxygen Permeation Rate-Limiting Step……..124

4.4 Closing Remarks……127

CHAPTER FIVE - CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions……128

5.2 Recommendations……..130

REFERENCES……....132

APPENDICES

Appendix A Determining Important Parameter for Sintering of $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-ó}$ (LSCF) Membranes……..152

Appendix B Oxygen Permeation Test Rig and Module…….169

Appendix C Gas Chromatograph Analysis of Oxygen……..170

Appendix D Non-linear Regression Using MATLAB……...…172

Appendix E Oxygen Permeation Experimental Results……174

Appendix F Lattice Parameter Calculation……...178

Appendix G Determination of Oxygen Permeation Parameters……180

LIST OF PUBLICATIONS…….....183

LIST OF TABLES

		Page
Table 2.1	The comparisons of process alternatives for oxygen production (da Costa et al., 2012)	12
Table 2.2	Oxygen permeation trough different disc-shaped MIEC membranes	25
Table 3.1	List of chemicals used in the present study	35
Table 3.2	List of equipment used in the research including those in the permeation test rig	36
Table 3.3	Materials used for the fabrication of oxygen permeation module	36
Table 3.4	Compositions of $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-ó}$ composite powders in weight fraction (wt. %)	37
Table 3.5	Experimental variables for oxygen permeation measurements	48
Table 3.6	Factors and factor level selected in the experiment	50
Table 3.7	Experimental layout and factor distribution of L9 orthogonal array	51
Table 4.1	Relative density (%) of LSCF as a function of sintering temperature and CuO-TiO_2 mixture content	71
Table 4.2	Level average response analysis for oxygen permeation flux	114
Table 4.3	Pre-exponential coefficient and activation energy of D_v, k_f and k_r	118
Table A.1	Factors and factor level selected in the experiment	153
Table A.2	Experimental layout and factor distribution of L9 orthogonal array	154
Table A.3	Experimental results	156
Table A.4	Level average response analysis for shrinkage rate	158
Table A.5	Level average response analysis for sintered density	159

Table A.6	Level average response analysis for porosity	160
Table A.7	Level average response analysis for shrinkage rate using S/N_{LTB} ratio	161
Table A.8	Level average response analysis for sintered density rate using S/N_{LTB} ratio	162
Table A.9	Level average response analysis for porosity using S/N_{STB} ratio	163
Table E.1	Oxygen permeation flux results at 600°C of LSCF as a function of sintering temperature and CuO-TiO_2 mixture content	174
Table E.2	Oxygen permeation flux results at different temperatures and membrane thicknesses. (P'_{O_2} = 0.21 atm; sweep gas flow rate = 100 ml/min)	175
Table E.3	Oxygen permeation flux results at different temperatures and oxygen partial pressures in the feed. (Thickness = 1.10 mm; sweep flow rate = 100 ml/min)	176
Table E.4	Oxygen permeation flux results at different temperatures and sweep gas flow rate. (Membrane thickness = 1.10 mm; P'_{O_2} = 0.21 atm)	177
Table F.1	XRD peak list for LSCF-CT-1-1100 membrane	179

LIST OF FIGURES

		Page
Figure 2.1	Schematic diagram of oxygen transport through mixed ionic-electronic conducting membrane (Li, 2007)	11
Figure 2.2	Ideal structure of perovskite structure ABO_3 (Richter *et al*., 2009)	13
Figure 3.1	Research methodologies flow chart	34
Figure 3.2	Preparation of LSCF-CT membranes	38
Figure 3.3	Schematic of the oxygen permeation studies experimental test rig GR: gas regulator; MC: mixing chamber; MFC: mass flow controller; TC: temperature controller; GC: gas chromatography; TCD: thermal conductivity detector	43
Figure 3.4	Schematic of the oxygen permeation module	45
Figure 3.5	Schematic view of the membrane testing system	46
Figure 3.6	Schematic illustration of oxygen permeation in a membrane continuous stirred tank reactor (CSTR) model	54
Figure 4.1	XRD patterns of (a) LSCF; (b) CuO and (c) TiO_2 powders	60
Figure 4.2	XRD patterns of for different membrane compositions sintered at 1000°C	61
Figure 4.3	XRD patterns of for different membrane compositions sintered at 1100°C	61
Figure 4.4	XRD patterns of for different membrane compositions sintered at 1200°C	62
Figure 4.5	XRD patterns of for different membrane compositions sintered at 1300°C	62
Figure 4.6	XRD patterns of LSCF6428 + 50 wt.% doping amount sintered at (a) 1300°C; (b) 1200°C; (c) 1100°C and (d) 1000°C	64
Figure 4.7	Lattice parameters of LSCF as a function of sintering temperature and CuO-TiO_2 mixture content	66

Figure 4.8	Linear shrinkages of LSCF as a function of sintering temperature and CuO-TiO_2 mixture content	69
Figure 4.9	Apparent densities of LSCF as a function of sintering temperature and CuO-TiO_2 mixture content	70
Figure 4.10	Dilatometric curves of LSCF as a function of sintering temperature and CuO-TiO_2 mixture content	74
Figure 4.11	Young's Modulus of LSCF as a function of sintering temperature and CuO-TiO_2 mixture content	95
Figure 4.12	Flexural strength of LSCF as a function of sintering temperature and CuO-TiO_2 mixture content	97
Figure 4.13	Oxygen permeation flux at 600°C of LSCF as a function of sintering temperature and CuO-TiO_2 mixture content (Temperature = 600°C membrane thickness = 1.70 mm; oxygen partial pressure in the feed = 0.21 atm; sweep gas flow rate = 100 ml/min)	100
Figure 4.14	Brick model for (a) oxygen ion transport path along grain boundaries and (b) oxygen ion transport path through crystal lattice (Baumann *et al.*, 2010)	104
Figure 4.15	Dependence of oxygen permeation flux on the temperature at different membrane thicknesses. ($P_{O_2}^{'}$ = 0.21 atm; sweep gas flow rate = 100 ml/min)	106
Figure 4.16	Plot of ln (oxygen permeation flux) versus inverse temperature. The solid lines are the best straight lines to fit all the data. ($P_{O_2}^{'}$ = 0.21 atm; sweep gas flow rate = 100 ml/min)	108
Figure 4.17	Dependence of oxygen permeation flux on the oxygen partial pressures in the feed at different temperatures. (Thickness= 1.10 mm; sweep flow rate = 100 ml/min)	110
Figure 4.18	Dependence of oxygen permeation flux on the sweep gas flow rate at different temperatures. (Membrane thickness = 1.10 mm; $P_{O_2}^{'}$ = 0.21 atm)	111
Figure 4.19	Level average responses for parameters A, B, and C of the oxygen permeation flux of LSCF-CT-1-1100 membrane	109

Figure 4.20	Results of confirmation experiments. Optimum combination of control factors for confirmation experiment: temperature = 600°C; oxygen partial pressure in the feed = 1 atm and sweep gas flow rate = 100 ml/min	110
Figure 4.21	Dependence of oxygen flux permeation flux on the temperature. (P'_{O_2} = 0.21 atm; sweep gas flow rate = 100 ml/min)	120
Figure 4.22	Dependence of oxygen permeation flux on the oxygen partial pressure in the feed at different temperatures. (Membrane thickness = 1.10 mm; sweep flow rate = 100 ml/min)	122
Figure 4.23	Dependence of oxygen permeation flux on the sweep gas flow rate at different temperatures. (Membrane thickness = 1.10 mm; P'_{O_2} = 0.21 atm)	123
Figure 4.24	Comparison of experimental oxygen permeation flux with model predictions from Eq. (3.15) corresponding to bulk-diffusion limited	124
Figure 4.25	Comparison of experimental oxygen permeation flux with model predictions from Eq. (3.16) corresponding to surface exchange limited	125
Figure A.1	Percentage contributions for parameters A, B, and C determined by ANOVA	168
Figure C.1	Linear calibration curve for oxygen	170
Figure G.1	Plot of ln (bulk diffusion coefficient) versus inverse temperature. The solid lines are the best straight lines to fit all the data	180
Figure G.2	Plot of ln (forward surface exchange rate constant) versus inverse temperature. The solid lines are the best straight lines to fit all the data	181
Figure G.3	Plot of ln (reverse surface exchange rate constant) versus inverse temperature. The solid lines are the best straight lines to fit all the data	182

LIST OF PLATES

		Page
Plate 4.1	SEM cross-section image of LSCF-CT-0 membrane sintered at 1100°C	76
Plate 4.2	SEM cross-section image of LSCF-CT-0.5 membrane sintered at 1100°C	77
Plate 4.3	SEM cross-section image of LSCF-CT-1 membrane sintered at 1100°C	78
Plate 4.4	SEM cross-section image of LSCF-CT-2 membrane sintered at 1100°C	79
Plate 4.5	SEM cross-section image of LSCF-CT-3 membrane sintered at 1100°C	80
Plate 4.6	SEM cross-section image of LSCF-CT-0 membrane sintered at 1200°C	81
Plate 4.7	SEM cross-section image of LSCF-CT-0.5 membrane sintered at 1200°C	82
Plate 4.8	SEM cross-section image of LSCF-CT-1 membrane sintered at 1200°C	83
Plate 4.9	SEM cross-section image of LSCF-CT-2 membrane sintered at 1200°C	84
Plate 4.10	SEM cross-section image of LSCF-CT-3 membrane sintered at 1200°C	85
Plate 4.11	SEM cross-section image of LSCF-CT-0 membrane sintered at 1300°C	86
Plate 4.12	SEM cross-section image of LSCF-CT-0.5 membrane sintered at 1300°C	87
Plate 4.13	SEM cross-section image of LSCF-CT-1 membrane sintered at 1300°C	88
Plate 4.14	SEM cross-section image of LSCF-CT-2 membrane sintered at 1300°C	89
Plate 4.15	SEM cross-section image of LSCF-CT-3 membrane sintered at 1300°C	90
Plate B.1	Oxygen permeation test rig	169

Plate B.2 Oxygen permeation module 169

Plate C.1 Example of gas chromatograph result 171

LIST OF ABBREVIATIONS

Abbreviation	Description
Al_2O_3	Alumina
Ar	Argon
BN	Boron nitrate
BSCF	$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$
BSFZ	$Ba_{0.5}Sr_{0.5}Fe_{0.8}Zn_{0.2}O_{3-\delta}$
CSTR	Continuous stirred tank reactor
CO_2	Carbon dioxide
CuO	Copper oxide
GC	Gas chromatography
IGCC	Integrated gasification combined cycle
ITM	Ion transport membrane
LS	Linear shrinkage
LSCF	$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$
MFC	Mass flow controller
MgO	Magnesia
MIEC	Mixed ionic-electronic conducting
N_2	Nitrogen
NiO	Nickel oxide
OTM	Oxygen transport membrane
O_2	Oxygen
PSA	Pressure swing adsorption
SCN	$SrCo_{0.9}Nb_{0.1}O_{3-\delta}$

SEM	Scanning electron microscopy
TCD	Thermal conductivity detector
TiO_2	Titania
XRD	X-ray diffraction
ZnO	Zinc oxide

LIST OF SYMBOLS

Symbol	Description	Unit
C_v	Oxygen vacancy concentration	mol/cm³
C'_{eq}	Oxygen vacancy concentrations in the material under thermal equilibrium of high oxygen pressure sides of the membrane	mol/cm³
C''_{eq}	Oxygen vacancy concentrations in the material under thermal equilibrium of low oxygen pressure sides of the membrane	mol/cm³
C_{O_2}	Oxygen concentration of exit gas	%
D_v	Oxygen vacancy diffusion coefficient	cm^2/s
$E_{A,i}$	Activation energy	J/mol.K
J_{O_2}	Oxygen permeation flux	ml/cm^2.min or mol/cm².s
k_f	Forward surface exchange rate constant	$cm/atm^{0.5}/s$
k_r	Reverse surface exchange rate constant	$mol/cm^2/s$
K'_{ex}	Membrane surface exchange at the feed side	cm/s
K''_{ex}	Membrane surface exchange at the permeate side	cm/s
K_s	Surface exchange coefficient	cm/s
$l_\circ$	Length of green sample	mm
l	Length of sintered sample	mm
L	Membrane thickness	mm or cm
L_c	Membrane characteristic thickness	cm
$O_O^\times$	Oxygen lattice	-
P'_{O_2}	Oxygen partial pressure in the feed	atm
P''_{O_2}	Oxygen partial pressure in the permeate	atm

P_t	Total pressure	atm
Q	Flow rate of the elute from the downstream	ml/min
Q_{O_2}	Oxygen permeation flow rate	ml/min
Q_{sweep}	Sweep gas flow rate	ml/min
R	Gas constant	J/mol.K
S	Membrane surface area	cm^2
T	Temperature	K or °C
$V_{\ddot{O}}$	Oxygen vacancy	-
$w_{\circ}$	Weight of dried sample	g
w_1	Suspended weight	g
w_2	Saturated weight	g

Greek Letters

$\rho_{sintered}$	Bulk density	g/cm^3
$\rho_{theoretical}$	Bulk theoretical density	g/cm^3

PEMBANGUNAN MEMBRAN SERAMIK CAMPURAN KONDUKTOR IONIK DAN ELEKTRONIK CuO-TiO_2-$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ UNTUK PEMISAHAN OKSIGEN

ABSTRAK

Kajian ini memfokuskan kepada penyediaan membran $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) untuk pemisahan oksigen pada suhu persinteran yang lebih rendah menggunakan campuran 83.3 mol% CuO-16.7 mol% TiO_2 (0-3% berat) sebagai aditif. Kesan penambahan aditif terhadap sifat persinteran, struktur kristal, mikrostruktur, modulus Young, kekuatan lenturan dan kadar penelapan oksigen bagi membran LSCF telah dikaji. Penambahan campuran CuO-TiO_2 tidak menganggu struktur kristal membran LSCF. Penambahan 1% berat campuran CuO-TiO_2 telah menurunkan suhu persinteran membran LSCF sebanyak 200°C. Membran LSCF dengan 1% berat campuran CuO-TiO_2 yang disinter pada suhu serendah 1100°C menghasilkan kemampatan relatif melebihi 94% serta mempunyai kekuatan lenturan dan modulus Young yang tinggi. Kadar penelapan oksigen pada suhu 600°C bagi membran tersebut adalah yang tertinggi (0.079 ± 0.001 ml/cm².min); iaitu 1.8 kali ganda lebih tinggi berbanding membran LSCF tanpa campuran CuO-TiO_2 yang disinter pada 1300°C (0.04 ± 0.003 ml/cm².min). Justeru, membran LSCF dengan 1% berat campuran CuO-TiO_2 yang disinter pada 1100°C telah dipilih untuk mengkaji kadar penelapan oksigen pada kondisi yang berbeza. Data eksperimen menunjukkan bahawa kadar penelapan oksigen meningkat dengan peningkatan suhu, tekanan separa oksigen dalam komposisi suapan dan kelajuan gas penyapuan; dan menurun dengan peningkatan ketebalan membran. Untuk membran dengan ketebalan 1.10

mm, kondisi eksperimen optimum bagi kadar penelapan oksigen ialah pada suhu 600°C, tekanan separa oksigen dalam komposisi suapan 1 atm dan kelajuan gas penyapuan 100 ml/min. Kadar penelapan oksigen sebanyak 0.180 ± 0.02 ml/cm².min telah diperoleh dengan gabungan kondisi eksperimen tersebut. Model matematik yang bersesuaian telah diusulkan untuk menentukan parameter penelapan oksigen berdasarkan data eksperimen. Data prediksi telah dibandingkan dengan data eksperimen untuk pengesahan model matematik yang diusulkan. Perbandingan antara data eksperimen dengan data prediksi menunjukkan keselarasan yang baik. Model matematik yang diusulkan juga menunjukkan bahawa kadar penelapan oksigen bagi ketebalan membran dalam julat 1.10-2.70 mm yang digunakan dalam kajian ini dipengaruhi oleh mekanisma difusi ruah.

DEVELOPMENT OF CuO-TiO_2-$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ MIXED IONIC-ELECTRONIC CONDUCTING CERAMIC MEMBRANE FOR OXYGEN SEPARATION

ABSTRACT

This study focuses on the preparation of $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) membrane for oxygen separation at low sintering temperature by using 83.3 mol% CuO-16.7 mol% TiO_2 mixture (0-3 wt.%) as additives. The effect of the additives on the sintering behavior, crystal structure, microstructure, Young's modulus, flexural strength and oxygen permeation flux of the LSCF membrane have been investigated. The crystal structure of the LSCF membrane has not been affected by the CuO-TiO_2 mixture addition. The addition of 1 wt.% CuO-TiO_2 mixture has reduced the sintering temperature of the LSCF membrane by 200°C. The LSCF membrane with 1 wt.% CuO-TiO_2 mixture sintered at 1100°C has obtained a relative density of over 94% with high flexural strength and Young's modulus. Its oxygen permeation flux at 600°C is also the highest (0.079 ± 0.001 ml/cm².min); which is about 1.8 times higher than the pure LSCF membrane sintered at 1300°C (0.044 ± 0.003 ml/cm².min). The LSCF membrane with 1 wt.% CuO-TiO_2 mixture sintered at 1100°C has been chosen for further oxygen permeation performance studies at different conditions. The experimental results show that the oxygen permeation flux increases with the increase of temperature, oxygen partial pressure in the feed side and sweep gas flow rate; and decreases with the increase of membrane thickness. For the 1.10 mm thick membrane, the optimum experimental conditions for oxygen permeation flux have been found to be 600°C temperature, 1 atm oxygen partial pressure in the feed side and 100 ml/min sweep gas flow

rate. The oxygen permeation flux of 0.180 ± 0.02 ml/cm².min has been obtained using these co-optimized experimental conditions. The oxygen permeation parameters have been determined from the experimental data by proposing a suitable mathematical model. The predicted data have been compared with the experimental data in order to validate the proposed model. Good agreement has been achieved between predictions and experimental data. The proposed model also indicates that in the 1.10-2.70 mm thickness range used in the present study, the oxygen flux is predominatly controlled by bulk diffusion mechanism across the membrane.

CHAPTER ONE

INTRODUCTION

1.1 Overview

Interest in mixed ionic-electronic conducting (MIEC) materials for oxygen separation from air arose in the 1980s when a number of new materials such as $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ and $La(Co,Fe)O_3$ were developed and studied for their transport properties, chemical and thermal stabilities and potential applications. Due to species transport in dissociated or ionized form rather than conventional molecular diffusion, MIEC membranes offer a unique separation mechanism and extremely high selectivity. The most important application of high temperature ceramics in this context is high purity oxygen production as a replacement of conventional cryogenic air separation units for IGCC and oxyfuel power plant processes (Kneer *et al*., 2010; Miracca *et al*., 2005; Repasky *et al*., 2012).

Besides research and development (R&D) on high purity oxygen production, considerable attention has been spent on the integration of the permeation process into chemical reactors. Membrane reactors; which combine reaction and separation or distribution and reaction in one unit, are the result of these efforts. Of all the potential applications for MIEC membranes, the partial oxidation of methane (POM) to syngas is claimed to be of particular commercial relevance with capital cost saving potentials up to 30 % over conventional technologies (Smart *et al*., 2010). Lower cost oxygen would broaden the applicability for oxygen-blown integrated gasification combined cycle (IGCC) power plant, oxygen-enhanced coal combustion and coal conversion into clean liquid transportation fuels and hydrogen (Smart *et al*., 2010).

1.2 Problem Statement

$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) is one of the most investigated MIEC membrane materials (Cox-Galhotra and McIntosh, 2010; Ge *et al*., 2009a; Ge *et al*., 2009c; Tan *et al*., 2008; Wang *et al*., 2011; Zou *et al*., 2011). Compared to the alternative $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ (SCF) and $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) perovskites; LSCF has lower oxygen permeability but exhibits excellent stability, and consequently is more suitable for long-term oxygen separation in industrial applications (Han *et al*., 2014; Meng *et al*., 2009; Watanabe *et al*., 2009; Zhang *et al*., 2010).

This membrane material is also well-known for its moderate thermal and chemically-induced expansion, mechanical and chemical stability under a wide range of oxygen chemical potentials, low cost of the raw materials and viable preparation methods (Shao *et al*., 2013; Zou *et al*., 2011). Although extensive research has been conducted in the past years, there are several issues in LSCF membrane that need to be addressed. The issues include: (1) the membranes should be prepared at low sintering temperature to reduce preparation cost; (2) the low temperature sintering technique should be viable and inexpensive; (3) the low-temperature sintered membranes should have sufficient mechanical strength; and (4) the low-temperature sintered membranes should possess considerably high oxygen permeation flux.

The preparation of LSCF membrane has been complicated by the high temperatures needed to obtain the desired ceramic densification (>1300°C) (Huang *et al*., 2010; Shao *et al*., 2013; Zeng *et al*., 2007b; Zou *et al*., 2011). High sintering temperature required for treatment of the densification is challenging because of the scope, extent, complexity and incomplete understanding of the topic. The

disadvantages of high sintering temperature include high production cost, high maintenance fee, difficult quality control and high equipment cost as well as high energy consumption.

High sintering temperature also promotes significant grain growth, causing a reduction of mechanical strength (Rahaman, 2008). Further challenge in the sintering process is to sinter the membranes to very high densities with theoretical limit of zero porosity. The presence of isolatedly enclosed pores in ceramic membranes after sintering could lead to a decrease in the oxygen permeation flux. This is due to the extended oxygen ion diffusion distance or the large resistance induced by many cycles of surface reactions (Ran *et al*., 2011). These pores may also impair the membrane integrity and reduce the mechanical strengh.

Decreasing the particle size to increase the surface activity of the starting powder with advanced sintering techniques is a strategy that has been employed to reduce the sintering temperature of LSCF membranes (Lei *et al.*, 2006; Wu *et al.*, 2007; Zou *et al.*, 2011). In addition to large surface area that increases the driving force for sintering; nano-powders promote low temperature sintering because smaller particle size allows densification to occur primarily via grain boundary diffusion, instead of lattice diffusion (Nicholas and De Jonghe, 2007). These advanced techniques however, could increase the complexity of membrane preparation; and thus, economically unfavourable for industrial application.

Another approach; liquid phase sintering, has also been used to improve the sintering of ceramics. This simple and inexpensive method reduces sintering