PREPARATION AND CHARACTERIZATION OF DUAL LAYER LANTHANUM STRONTIUM COBALT FERRITE/ ALUMINA HOLLOW FIBRE MEMBRANE

NORFAZLIANA BINTI ABDULLAH

UNIVERSITI TEKNOLOGI MALAYSIA

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NORFAZLIANA BINTI ABDULLAH

A thesis submitted in fulfillment of the

requirements for the award of the degree of

Master of Engineering (Gas)

Faculty of Chemical and Energy Engineering

Universiti Teknologi Malaysia

FEBUARY 2016

Special dedicated to my lovely parents, supportive siblings, friends, lecturers and AMTEC members for their endless support and encouragement.

ACKNOWLEDGEMENT

Bismillahirrahmanirrahim,
Praise to Allah The Almighty, who gives all the opportunities and strengths to allow for the completions of this thesis.

I would like to convey an honor to my dedicated supervisor, Dr. Mukhlis A. Rahman for his guidance throughout my master study. His assistance helped developed my soft skills and research skills. A special thank you to Dr. Mohd Hafiz Dzarfan as co-supervisor on who gives advices. Both of you provided a great assistance, which contribute to the idea of my research study.

Endless thank you to my research team fellows including Noor Shuhaida, Nor Azureen, Syafikah Huda, Siti Halimah, Siti Munira, Hazlini Dzinun, Mohd Muhazri, Hazlina, Khalisah, Mohamad Azuwa, Nik Nurdhiah, Mohd Taufiq, Mohamad Hilmi Norfadhilatuladha, Faten Ermala and Siti Nur Fatin Nadhirah. I appreciate the time we work together, especially for your supportive encouragement.

I am also appreciating the help received from research officers, Mr. Ng Bee Cher, Mr. Sohaimi, Mr. Razis, Mr. Hanis, Miss Norafiqah and Miss Hafizah. Their expertise contributed the most on the completion my Master study. Thank you to AMTEC members that created conducive research environment, provided infrastructures and research facilities. I am also indebted to Univesiti Teknologi Malaysia and Ministry of Higher Education for their research fund and financial allocation.

ABSTRACT

Ceramic membrane with unique morphology can be prepared using phase inversion and sintering technique. Dual layer lanthanum strontium cobalt ferrite (LSCF)/alumina hollow fibre membrane in this study was prepared using this technique. The contributing parameters in the preparation of asymmetric alumina hollow fibre during fabrication process were investigated. The parameters involved in the process were the alumina/polyethersulfone (PESf) ratio, the internal coagulant temperature and the air-gap distance. Next, the suitable LSCF coating formulations were studied to obtain thin layer of LSCF. This was followed by the impregnations of catalyst prepared using sol-gel Pechini method. The characterizations were carried out for scanning electron microscopy (SEM), energy dispersive X-Ray spectrometry (EDX), apparent porosity, gas permeability test, gas-tightness test, Brunauer–Emmett–Teller technique, dilatometer analysis and mechanical test. The results showed that a reduction of alumina/PESf ratio from 10 to 6 resulted in the formation of asymmetric structure. The 53 weight % of alumina (AL-53) was selected as membrane support with 1.68 mm, 1.08 mm and 168 μm of outside, inside diameter and finger-like length, respectively. The AL-53 had acceptable mechanical strength of 24 MPa and high gas permeability of 13.87 x 10^{-4} mol m^{-2} Pa^{-1} s^{-1}. The 25 weight % of LSCF membrane sintered at 1150 ^{o}C had the lowest nitrogen gas permeability of 2.401 x 10^{-6} mol m^{-2} Pa^{-1} s^{-1} that was considered as gas-tight LSCF layer. The dual layer LSCF/alumina hollow fibre membrane was impregnated with 10 weight % of cerium oxide doped copper oxide catalyst. This catalyst was characterized using the SEM/EDX to ensure the catalyst was placed inside the finger-like structure of alumina membrane support. The dual layer of LSCF/alumina hollow fibre membrane was successfully produced using phase inversion and sintering technique which will be beneficial for multifunctional applications.

ABSTRAK

Membran seramik dengan morfologi yang unik boleh disediakan menggunakan teknik penyongsangan fasa dan pensinteran. Membran gentian gerongga dwi lapisan lantanum strontium kobalt ferit (LSCF)/alumina disediakan menggunakan teknik ini. Parameter penyumbang dalam penyediaan alumina gentian geronggang tidak simetri ketika proses fabrikasi telah dikaji. Parameter yang terlibat dalam proses ialah nisbah alumina/polietersulfon (PESf), suhu bahan pengental dalaman dan jarak sela udara. Seterusnya, formula salutan LSCF yang sesuai dikaji untuk mendapatkan lapisan LSCF yang nipis. Ini diikuti oleh impregnasi pemangkin yang disediakan menggunakan kaedah sol-gel Pechini. Pencirian telah dijalankan bagi mikroskop imbasan elektron (SEM), spektroskopi serakan tenaga sinar X (EDX), keliangan ketara, ujikaji kebolehtelapan gas, ujikaji kedap gas, teknik Brunauer–Emmett–Teller, analisis meter kembang dan ujikaji mekanikal. Keputusan menunjukkan bahawa pengurangan nisbah alumina/PESf dari 10 kepada 6 mengakibatkan pembentukan struktur tidak simetri. Alumina pada jisim 53 % (AL-53) telah dipilih sebagai sokongan membran dengan masing-masing 1.68 mm, 1.08 mm dan 168 µm bagi diameter luar, diameter dalam dan panjang struktur seperti jari. AL-53 mempunyai kekuatan mekanikal yang boleh diterima iaitu 24 MPa dan kebolehtelapan gas yang tinggi iaitu 13.87 x 10^{-4} mol m^{-2} Pa^{-1} s^{-1}. Membran LSCF pada jisim 25 % yang disinter pada 1150 °C memberi keputusan kebolehtelapan gas nitrogen yang terendah iaitu 2.401 x 10^{-6} mol m^{-2} Pa^{-1} s^{-1} yang dianggap sebagai lapisan LSCF kedap gas. Membran gentian geronggang dwi lapisan LSCF/alumina telah diimpregnasikan dengan mangkin serium dioksida dop kuprum oksida pada 10 % jisim. Mangkin ini telah dicirikan menggunakan SEM/EDX untuk memastikan mangkin berada didalam struktur seperti jari sokongan membran alumina. Membran gentian geronggang dwi lapisan LSCF/alumina telah berjaya dihasilkan menggunakan teknik penyongsangan fasa dan pensinteran yang bermanfaat untuk aplikasi pelbagai fungsi.

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LIST OF ABBREVIATIONS

AL	-	Alumina
AFL	-	Anode functional layer
AG	-	Air-gap
AR	-	Analytical reagent
ASTM	-	American Society for Testing and Materials
AWG	-	American wire gauge
BCFZ	-	Barium cobalt ferrite zirconium
BET	-	Brunauer, Emmett and Teller
CFD	-	Computational fluid dynamic
CGO	-	Ceria-gadolinium oxide
CTE	-	Coefficient of thermal expansion
CVD	-	Chemical vapor coation
EDX	-	Elemental dispersive X-ray spectroscopy
EG	-	Ethylene glycol
EP	-	Electroless plating
GTL	-	Gas-to-liquid
LSCF	-	Lanthanum strontium cobalt ferrite
LSM	-	Lanthanum strontium maanganese

MIEC	-	Mixed ionic-electronic conducting
MIECM	-	Mixed ionic-electronic conducting membrane
MT-SOFC	-	Micro-tubular solid oxide fuel cell
NMP	-	N-methyl-2-pyrrolidone
PEG	-	Polyethylene glycol
PESf	-	Polyethersulfone
POM	-	Partial oxidation of methane
PTFE	-	Polytetrafluoroethylene
SEM	-	Scanning electron microscopy
SOFC	-	Solid oxide fuel cell
STD	-	Standard deviation
TEOS	-	Tetraethylorthosilicate
TGA	-	Thermogravimetry analysis
TIPS	-	Thermal induced phase separation
TMOS	-	Tetramethylorthosilicate
TPB	-	Triple phase boundary
WGS	-	Water gas shit
XRD	-	X-ray diffraction
YSZ	-	Yttria stabilized zirconia

LIST OF SYMBOLS

A	-	Membrane area (m^2)
bf	-	Bore fluid
D	-	Dry weight (g)
D_i	-	Inside diameter (m)
D_o	-	Outer diameter (m)
F_m	-	Measured load at which fracture occurred (N)
F	-	Faraday constant (9.6487 x 10^4 C mol^{-1})
J	-	Gas permeability of helium (mol m^{-2} s^{-1} Pa^{-1})
l	-	Length of alumina ceramic hollow fibre membrane (m)
L	-	Thickness of perovskite material (mm)
L_P	-	Finger-like length (µm)
P	-	Permeance of the test membrane (mol m^{-2} s^{-1} Pa^{-1})
P_a	-	Atmospheric pressure (Pa)
P_{gauge}	-	Gauge pressure reading (bar)
P_o	-	Initial pressure reading (Pa)
P_t	-	Final pressure reading (Pa)
P'_{O2}	-	High oxygen partial pressure (Pa)
P''_{O2}	-	Low oxygen partial pressure (Pa)

Q	-	Total He permeation rate (mol s^{-1})
R	-	Gas constant (8.314 J mol^{-1} K^{-1})
R_i	-	Inner radius (m)
R_o	-	Outer radius (m)
S	-	Suspended weight (g)
S_{BET}	-	Specific surface area (m^2/g)
T	-	Temperature (K)
T_{bp}	-	Boiling temperature (°C)
T_m	-	Melting temperature (°C)
t_s	-	Time (s)
t	-	Thickness (mm)
V	-	Volume of the test cylinder (m^3)
$Vo^{\bullet\bullet}$	-	Oxygen vacancies (dimensionless)
W	-	Saturated weight (g)

Greek letters

π	-	Pi = 3.142 (dimensionless)
ΔP	-	Pressure difference (Pa)
σ	-	Bending strength (MPa)
σ_{amb}	-	Ambipolar conductivity (dimensionless)
ε	-	Apparent porosity (%)

CHAPTER 1

INTRODUCTION

1.1 Research Background

Membrane technology plays a vital role in broad range of industrial applications. The concept of membrane-based separation was first introduced in early 18th century and was believed to be beneficial over most of the conventional separation processes e.g. distillation, adsorption, and absorption due to energy saving attributes by its characteristics [1]. Membrane is described based on its characteristics as a permselective barrier between two phases which separation of desired species occurs in the present of driving forces i.e. pressure gradient, temperature gradient, concentration gradient, and voltage difference [2]. The properties of the membrane are generally depends on precursor materials. There are polymeric membrane, ceramic membrane, carbon membrane and metallic membrane. The membrane structures can be either in porous or nonporous structures which can be tailored for specific applications [1–3].

Polymeric membrane is the most commercialized membrane commonly available widely in the market. However, the use of ceramic membranes in fluid separation attract interest as it offers a number of advantages such as high resistance under acidic and alkali medium, high thermal stabilities, high chemical stabilities and excellent mechanical strength in comparison to polymeric membrane. The commonly used materials for the ceramic membrane are aluminium oxide or alumina (Al_2O_3), titanium dioxide/titania (TiO_2), zirconium dioxide/zirconia (ZrO_2), silica dioxide/silica (SiO_2), mixed ionic-electronic conducting (MIEC) and combination of ceramic materials [4]. Each of the materials has their own commercial values. Alumina is commonly used as mechanical devices, manufacturing products (thermal insulator, ceramic jar, pottery and etc.) and membrane support [5]. Titania has a great potential in photocatalytic applications such as air purification, water purification and heavy metal degradation [6]. Zirconia is typical studied ceramic materials used in medical devices and fuel cell membrane study [7]. Meanwhile, silica is used primarily as a precursor for glass, silicon productions and microporous membrane [8]. MIEC has a unique characteristic to be used as membrane at higher temperature applications particularly in air separation industry [9].

Generally, ceramic material is brittle in nature but still can be shaped into membrane module. The phase inversion technique is a common technique to fabricate ceramic membrane into various forms such as planar-disk, tubular, multi-channel monolith and hollow fibre membrane form [4,10]. However, the fabrications of disc, tubular and multi-channel monolith ceramic membrane is time consuming and possesses unfavorable area to volume ratio [5,6]. For example, a multi-channel monolith membrane required to be assembled within a housing [12]. The most promising form of the ceramic membrane using this technique is the hollow fibre configuration. Despite ceramic hollow fibre membranes are not easily formed using this approach, it can provide a higher surface area per volume and have excellent mechanical strength, making them suitable for various applications. Li and his research group has initiated the preparation of the ceramic hollow fibre membrane for various applications such as microreactor [13–15], methane conversion [16–18], oxygen separation [19–22], solid oxide fuel cells (SOFC) [23–26] and waste water treatment [27].

Typically, two distinct structures can be obtained which are symmetrical and asymmetrical structures prepared using aforementioned technique. The symmetrical structure can be either non-porous dense membrane or porous membrane with uniform pore size. The membrane with different structure such as dense and porous can be defined as asymmetrical structure. In ceramic hollow fibre membrane, asymmetric structure comprises of finger-like structures adjacent to the lumen and a dense sponge-like region closer to the outer surface as shown in Figure 1.1 that is advantageous particularly in preparation of multifunctional membranes [28]. This finger-like structure has been reported to act as a thousand microchannels, all of which are perpendicular to a hollow fibre lumen extend to outer layer, that serves as an active site for an in-situ reaction [13–15]. The presence of this active site enhances the catalytic reaction [13,14]. The sponge-like region with small pore size distributions plays a vital role as a selective membrane for separating the product from the finger-like region [29]. Theoretically, the formation of the finger-like structure occurs due to the unstable hydrodynamically viscous fingering phenomenon that is influenced by critical viscosity of ceramic suspension during a ceramic membrane preparation [30,31]. Hence, the asymmetric ceramic hollow fibre membrane prepared by phase inversion and sintering technique can be served as a porous support layer for composite membrane design [11,29].

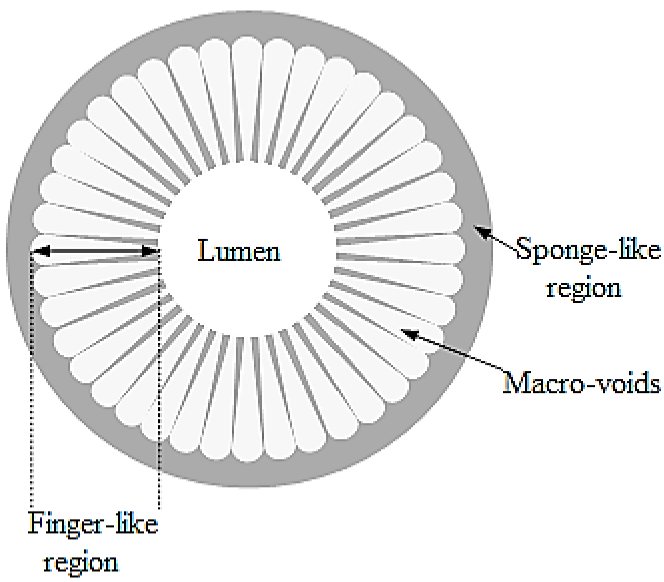

Figure 1.1 Schematic diagram of asymmetric alumina hollow fibre membrane [28]

Previous studies reported on coating of a well-adhered palladium (Pd) using electroless plating (EP) technique onto alumina supports [9,10,24,27,28]. However, the composite membrane has short life span under alkali or acidic environment. Alternatively, coating thin and dense MIEC offers great advantages in air purifications with high integrity design due to ceramic can withstand in harsh environment. Lanthanum strontium cobalt ferrite (LSCF) is one of the MIEC material that possesses long term stability, excellent oxygen permeability and highly electronic conductivity that can be directly coated onto alumina membrane support [14,16,29,30]. The coated outer layer onto membrane support can be conducted via a conventional coating technique and an advanced technique. There are various methods of the conventional coating techniques including dip coating, spray coating and paint brush coating which applicable to coat LSCF onto alumina membrane support. For advanced technique which is the co-extrusion/co-sintering can be used to fabricate dual layer ceramic hollow fibre comprises of two different ceramic materials.

Nowadays, the co-extrusion/co-sintering technique is well-known for production of dual layer ceramic hollow fibre membrane. The co-extrusion process is initiated when two different dopes are extruded through the spinneret triple orifice simultaneously, allowing the suspension to freely fall in a water bath to complete its phase inversion process and followed by high temperature sintering step to produce a predetermine strength of dual layer ceramic hollow fibre membranes. This single step technique offers great adhesion between two different layers, reducing time and cost [25]. However, the co-extrusion have several limitations particularly during co-sintering due to its incompatibility thermal expansion coefficient (CTE) of different materials [25]. Due to different CTE, the conventional coating technique seems to be practical to coat a thin layer of dense MIEC material onto a membrane support to for gas separation applications.

A thin layer LSCF coated onto an alumina support can enhance oxygen permeation via ion hoping mechanism. However, thin layer is not the only parameters that contribute in increasing gas permeation. Other factors such as porosity, mean pore size and pore size distribution of the support itself need to be considered. Therefore, it was crucial to study the parameters involved in preparation of asymmetric alumina hollow fibre membrane is crucial. One main challenge in the fabrication of asymmetric ceramic hollow fibre membrane with desired characteristics is there are various parameters influencing the formation of microstructure, such as ceramic suspension composition, parameters during membrane spinning process, sintering temperature and heating rate during sintering step [36]. Among them, the composition of the ceramic suspensions has been selected for this study which the factor plays vital role upon fabrication of membrane. Reducing alumina to PESf ratio can obtain desirable morphology and characteristics of alumina support later coated with LSCF membrane.

1.2 Problem Statement

A lanthanum strontium cobalt ferrite (LSCF6428) which is the MIEC material, has been used to fabricate a dual layer LSCF/alumina hollow fibre membrane since it exhibits good oxygen ionic and electronic conductivity and has high stability for long-term operation [9,34,37]. A number of research works have reported the fabrication LSCF in hollow fibre configuration using the phase inversion followed by sintering technique [19,21,38]. However, LSCF6428 is an expensive material to be used both as support and thin layer. Therefore, introducing an inert asymmetric support, such as alumina, can reduce the amount of the LSCF, thus, reducing the overall production cost. In this study, alumina which was prepared using the same aforementioned technique will act as the membrane support. Generally, the dual layer LSCF/alumina ceramic hollow fibre membrane can be fabricated using a novel co-extrusion technique followed by sintering process at high temperature as the combination of both techniques may reduce the production time [25,39].

However, there was a drawback in completing the co-sintering process for the dual layer ceramic hollow fibre membrane that comprised two different materials. It was mainly caused by different coefficient of thermal expansion (CTE) of each material, when co-sintering was considered. LSCF which has low CTE started to shrink in the beginning of the sintering process fracturing the membrane on the surface of alumina support [40]. Therefore, a conventional coating technique with different LSCF formulations can be used as alternative to coat dense and thin LSCF layer onto alumina support layer. In addition, a well match and free delamination between two layers can be obtained by using this technique. Hence, the use of alumina as a support layer for thin and dense of LSCF layer may serve as a good option to minimize the cost since of material used.

1.3 Objectives of Study

To overcome the aforementioned limitations, the main objective of this study is to develop dual layer LSCF/alumina hollow fibre membrane. The specific objectives in study are:

1. To determine the contributing parameters in the preparation of alumina hollow fibre with asymmetrical structures, i.e ceramic to polymer ratio, effect of different bore fluid temperature and the effect of adjusting air-gap.

2. To investigate the different of LSCF coating formulations used in the coating of LSCF layer onto alumina support.

3. To synthesize 10 wt. % CeO_2/CuO catalyst to be impregnated into finger-like structure of alumina membrane support.

4. To characterize the properties of dual layer LSCF/alumina hollow fibre membrane using SEM, EDX, apparent porosity test, gas permeation test, gas tightness test and mechanical strength test.

1.4 Scope of Study

To achieve the research objectives listed above, the scopes of study have been identified as:

1. Performing dilatometer analysis which involves the study on expansion and shrinkage properties of ceramic materials of dual layer ceramic hollow fibre membranes to obtain well match sintering behavior.

2. Adjusting the composition of suspension and viscosity, reducing alumina to PESf ratio and controlling bore fluid temperature that influence the formation of desired morphologies during phase inversion technique.

3. Preparing the ceramic suspension using planetary ball mill for mass production of ceramic hollow fibre membrane.

4. Varying the ratio of LSCF to ethanol and the composition of LSCF suspension for coating technique as well as the optimum concentration to obtain well adhered concentration of LSCF coating onto alumina support layer.

5. Sintering dual layer LSCF/alumina hollow fibre membrane at different sintering temperatures of 1100 °C, 1150 °C and 1200 °C to obtain thin and dense LSCF layer to be coated onto alumina support layer.

6. Synthesizing 10 wt. % CeO_2/CuO catalyst using the sol-gel Pechini method which later placed inside the finger-like voids in alumina hollow fibre support.

7. Characterizing alumina supports using the SEM, viscosity test, bending test, apparent porosity and permeability to determine prominent alumina membrane support.

8. Characterizing thin and dense layer LSCF using the SEM, energy dispersive X-ray spectroscopy (EDX) and gas tightness test and later impregnating with synthesized catalyst which ensured by the SEM/EDX and BET.

1.5 Significance of Study

This type of membrane can be prepared using the phase inversion and sintering technique which have advantages compared to the conventional technique such as pressing method, tape-casting and extrusion. This technique has been applied to develop membrane with asymmetrical structure that the pore structure can be tailored to be suited with different applications such as gas separation and waste water treatment including water purification, heavy metal degradation and inorganic removal. As the ceramic hollow fibre membrane can be regarded as a versatile membrane for various applications, it is crucial to study its development before it can viably applied for large-scale applications and production. So far, the preparation of alumina hollow fibre membranes where the ceramic suspension has been prepared using planetary ball mill has not been extensively discussed. This preparation technique not only enables ceramic suspension to be produced in a higher quantity, but also results in a more uniform ceramic suspension, thus, making it possible for mass production of ceramic hollow fibre membranes.

The alumina hollow fibre membranes are typically functions as a membrane support. In this study, the fabrication of the dual layer ceramic hollow fibre membrane comprises of asymmetric alumina as membrane support and a thin and dense mixed ionic-electronic conducting (MIEC) material which is LSCF is coated at the outer layer as act as separation barrier region. Varying LSCF suspension formulation is a crucial part during coating process to obtain thin and dense active layer that can adhere well with alumina support. This coating technique has been employed to coat self-support material such as carbon membrane, silica and zeolite onto membrane support. From this study, the successful dual layer LSCF/alumina hollow fibre membrane prepared is applicable for simultaneous separation and reaction process such as for high temperature water splitting process incorporating with partial oxidation of methane (POM).

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