STRUCTURAL CHARACTERIZATION OF ASYMMETRIC YTTRIA-STABILIZED ZIRCONIA HOLLOW FIBRE MEMBRANE

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ABSTRACT

Ceramic membrane is proven to overcome a limitation of using polymeric membrane for applications that requires a high temperature and pressure. In this study, Yttria-stabilized zirconia (YSZ) was selected as a ceramic material due to its superior mechanical strength. YSZ hollow fibre membrane was fabricated using combined dry-wet phase inversion and sintering technique. Four parameters involved during fabrication process have been varied systematically to study the effect on YSZ hollow fibre membrane structure and properties. The ceramic loading was varied from 55 wt.% to 67 wt.% and the YSZ/polyethersulfone (PESf) ratio was varied from 7 to 10 during YSZ suspension preparations. Then, the air-gap length was varied from 15 cm to 30 cm during spinning process. Lastly, the sintering temperature was varied from 1250 ^{o}C to 1400 ^{o}C during sintering step. The YSZ hollow fibre membrane produced were characterized in terms of morphology, mechanical strength, apparent porosity, pure water flux and solute rejection. The results successfully showed an asymmetric YSZ hollow fibre membranes consist of finger-like voids and sponge-like voids were produced. The YSZ suspension viscosity was increased with the increase of YSZ loading and decrease of YSZ/PESf ratio. High suspension viscosity favored the growth of finger-like voids and limited the formation of sponge-like region across the membrane. This result was similar to increase of the air-gap length during spinning. Significant densification occurred at the sponge-like region during sintering. The formation of isolated voids at 1400 ^{o}C hindered the pure water permeation. However, the mechanical strength increased with the sintering temperature. From the permeation test, the YSZ hollow fiber membrane prepared with 65 wt.% loading, ceramic/polymer ratio of 10, spinning at 20 cm air-gap length and sintered at 1300 ^{o}C was the most preferable membrane. This membrane had a pure water flux of 118.4 $Lm^{-2}.hr^{-1}$ with a molecular weight cut off of 50 – 60 kDa and mechanical strength of 224 MPa.

ABSTRAK

Membran seramik terbukti boleh mengatasi masalah penggunaan membran polimer untuk aplikasi yang memerlukan suhu dan tekanan yang tinggi. Yttria-stabil zirkonia (YSZ) telah dipilih sebagai bahan seramik dalam kajian ini kerana kekuatan mekanikal yang tinggi. Membran asimetrik gentian gerongga YSZ telah dihasilkan menggunakan gabungan teknik penyongsangan fasa kering dan pensinteran. Empat parameter yang terlibat telah diubah semasa proses penghasilan untuk mengkaji kesan terhadap struktur dan sifat membran gentian gerongga YSZ. Kandungan seramik diubah dari 55 % jisim hingga 67 % jisim dan nisbah YSZ/polietersulfon (PESf) telah diubah dari 7 hingga 10 semasa penghasilan larutan YSZ. Selain itu, panjang sela udara semasa proses pemejaman diubah daripada 15 cm hingga 30 cm. Akhir sekali, suhu ketika proses pembakaran dinaikkan dari 1250 ^{o}C hingga 1400 ^{o}C. Membran gentian gerongga YSZ yang terhasil dicirikan dari segi morfologi, kekuatan mekanikal, keliangan ketara, kebolehtelapan air tulen dan penolakan bahan larut. Keputusan menunjukkan membran asimetrik gentian gerongga YSZ terdiri daripada lompang seperti jari dan lompang seperti span berjaya dihasilkan. Kelikatan larutan YSZ meningkat dengan peningkatan kandungan YSZ dan pengurangan nisbah YSZ/PESf. Kelikatan yang tinggi, kadar pertumbuhan lompang seperti jari adalah tinggi dan menyekat pertumbuhan lompang seperti span dalam membran. Keputusan ini sama dengan kesan peningkatan jarak sela udara semasa proses pemejaman. Peningkatan suhu pembakaran menyebabkan pemadatan pada bahagian struktur-mikro dan mengurangkan keliangan. Pembentukan lompang terpencil pada suhu 1400 ^{o}C telah menghalang penelapan air tulen. Namun, peningkatan suhu pembakaran telah meningkatkan kekuatan mekanikal. Ujian penelapan menunjukkan, membran gentian gerongga YSZ yang dihasilkan dengan kandungan 65 % jisim, nisbah seramik/polimer 10, panjang sela udara 20 cm dan disinter pada suhu 1300 ^{o}C menghasilkan fluks air tulen sebanyak 118.4 $Lm^{-2}.hr^{-1}$ dengan berat molekul terputus sebanyak 50 hingga 60 kDa dan kekuatan mekanikal 224 MPa.

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LIST OF ABBREVIATIONS

YSZ	-	Yttria-stabilized zirconia
SEM	-	Scanning electron microscopy
AFM	-	Atomic force microscopy
XRD	-	X-ray diffraction
Al_2O_3	-	Aluminum oxide
ZrO_2	-	Zirconia
TiO_2	-	Titanium dioxide
UF	-	Ultrafiltration
Pd	-	Palladium
HFMR	-	Hollow fibre micro reactor
CHFMR	-	Ceramic hollow fibre micro reactor
CHFMMR	-	Ceramic hollow fibre membrane micro reactor
WGS	-	Water gas shift
DRM	-	Dry reforming of methanol
MSR	-	Methanol steam reforming
LSCF	-	Lanthanum-strontium-cobalt-ferric
SOFC	-	Solid oxide fuel cell
NiO_2	-	Nickel oxide
TIPS	-	Thermally induced phase separation
DIPS	-	Diffusion induced phase separation

NMP	-	N-Methylpyrrolidone
NaOH	-	Sodium hydroxide
Na_2ZrO_3	-	Sodium zirconate
Na_2SiO_3	-	Sodium silicate
$Zr(OH)_4$	-	Zirconium hydroxide
$ZrSiO_4$	-	Zirconium silicate
Y_2O_3	-	Yttria
MgO	-	Magnesium oxide
CaO	-	Calcium oxide
CuO	-	Copper oxide
MF	-	Microfiltration
NF	-	Nanofiltration
RO	-	Reverse osmosis
H_2	-	Hydrogen
ESR	-	Ethanol steam reforming
CeO_2	-	Cerium oxide
PESf	-	Polyethersulfone

LIST OF SYMBOLS

A	-	Area of hollow fibre
B_F	-	Bending strength
cm	-	Centimeter
D	-	Dry weight
d	-	Thickness
D_i	-	Inner diameter
D_O	-	Outer diameter
g	-	Gram
L	-	Length
L	-	Length of hollow fibre
m	-	Meter
min	-	Minute
N	-	Load
M	-	Saturated weight
S	-	Suspended weight
T	-	Temperature
t	-	Time
W	-	Watt
wt	-	Weight
°C	-	Degree Celsius

%	-	Percent
μm	-	Micrometer

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Membrane can be defined as a semipermeable barrier between two phases that selectively separate some components from others. In detail, membrane will only allow a selective component to permeate through it and reject the permeation of other components. Figure 1.1 illustrates the membrane process. The basic principles of membrane which is simple in concept and operation, low energy consumption, environmental friendly and more flexible as it is easy to scale-up made it well suited for large-scale operations in various applications. The key pillar in membrane technology is producing a membrane with a structure that have a high selectivity and permeability. The desired membrane structure may be different based on the applications. In addition to the selectivity and permeability, the membrane life time and the durability are another important character which should be taken into consideration to ensure the feasibility of the membrane in particular application and economically viable.

Back in the 18^{th} century, the emergence development of membrane technology has been started from the phenomenon of water permeation through a pig bladder used to store alcohol which has been noticed by Jean-Antoine Nollet, a physicist. He was probably the first to recognize the relation between a semipermeable membrane and the osmotic pressure. Later, more studies on semipermeable membrane and osmotic pressure were conducted by Thomas Graham on the diffusion of gasses through different media [1]. Then, a rapid advancement of membrane technology in following decades is also aided by Fick and van t'Hoff who explained the diffusion of solutes in liquid media. It can be seen, the early stage of membrane technology is focusing more on theoretical explanation of membrane process. Besides, most of the early studies on membrane permeation were carried out with natural material such as animal bladder.

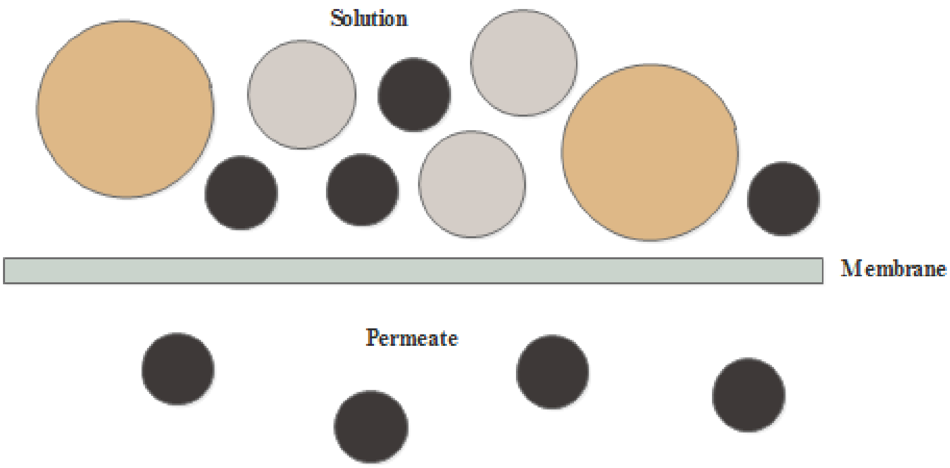

Figure 1.1 The simple mechanism of membrane process

Early twentieth century, membrane science and technology entered a new phase of producing an artificial membrane. A fabrication method that is popularly known as phase inversion and invented by Loeb and Sourirajan [2] gives a new phenomenon in producing artificial membrane. The flat sheet membrane produced is in asymmetric structure with a dense skin at the surface which determined the membrane selectivity and permeation flux while the porous structure provided the mechanical strength. Then, progress in polymer science contributed to the fabrication of polymeric membrane using this method. It is seen in dominating the membrane markets as being used in spanning number of applications includes; filtration [3,4] and gas separation [5]. Subjected to the medical applications, polymeric membrane also found to be used for hemodialysis.

The nature of ceramic materials which were mechanically, thermally and chemically resistance had gather an interest to use it for ceramic membrane fabrication. The ceramic membrane was successfully widening the membranes applications range to membrane reactor [6–8] and fuel cell application [9,10]. Besides, ceramic membrane may even replace the polymeric membrane application in microfiltration [11–13], ultrafiltration [14], nanofiltration [15], reverse osmosis [16] and gas separation [17,18]. Here, the development of membrane technology keep expanding as it moves from the natural material to polymer membrane and then towards ceramic membrane. Figure 1.2 shows the timeline of the development in membrane technology.

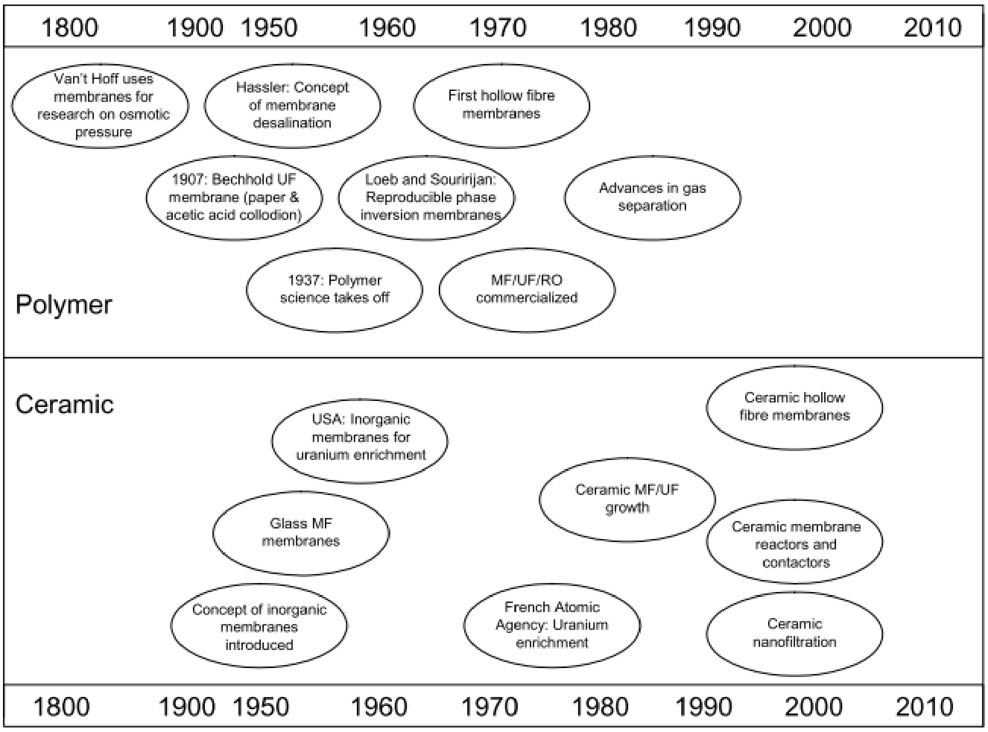

Figure 1.2 Polymer and ceramic membrane timeline [19]

Concerning on the issue of water related problem, treating and/or purifying the contaminated water before channeled for usage is vitality important. Even though water is the most abundance natural resources, only less than 1 % of it is available for human consumption. As man uses water as one of the main resources for daily activities together with the rapid developments of industrial, agricultural and domestic activities, it brings about to the broadening of water related problems. The conventional treating method for water and wastewater includes one or more of the processes; chemical addition, coagulation, flocculation, sedimentation, filtration, adsorption and disinfection. However, the rising technology in membrane area has gathered an interest to replace the conventional process with membrane process. The ability to remove a wide range of components, ranging from suspended solids to small organic compounds and ions have made membrane such a promising technique for water and wastewater treatment. Yet, the renowned ceramic membrane over polymeric membrane encourages of using ceramic membrane for filtration applications.

1.2 Problem Statement

Phase inversion method introduced by Loeb and Sourirajan in fabricating cellulose acetate membrane (polymeric membrane) have become the most common method used in membrane fabrication. However, due to the differences between polymeric and ceramic systems, particularly in dope solution preparation limits the use of the phase inversion information in polymeric systems for ceramic membrane fabrication. In polymeric system, the phase inversion process involved the interaction between polymer, solvent and non-solvent. The solvent was diffused out from the polymer solution while non-solvent was diffused into the dope solution. The solvent and non-solvent exchanged results in solidification of polymer solution and formation of polymeric membrane. Different in ceramic system; the solidification of ceramic suspension solution involves in the movement of ceramic particles during the solvent and non-solvent exchanged. Moreover, low polymer content and high ceramic content in ceramic suspension solution influenced the phase inversion process for ceramic membrane.

Ceramic membranes have been reported to have a number of advantages in various applications. However, ceramic membranes have their own respective desired morphology depending on the ceramic membranes' applications. From the aforementioned literature, it can be deduced that different ceramic materials used for membrane fabrication produced a hollow fibre membrane with different structures and properties. In this study, yttria-stabalized zirconia (YSZ) was selected as a ceramic membrane material. However, limited research have been focused on the structural study of YSZ hollow fibre membrane through phase inversion method drives an interest to study the process conditions effects towards the structure and properties.

The fabrication of ceramic membrane through this phase inversion method composed of three main steps and in every step, the process conditions were contributed to the structure formation. Aforementioned study reported that the ceramic loading and the ceramic/polymer ratio influenced the structure formation for alumina oxide (Al_2O_3) membrane. However, no study was reported on these parameters for YSZ hollow fibre membrane structure formation. Besides, the air-gap lengths during spinning process were reported to give a significant effect for Al_2O_3 hollow fibre membrane structure formation. This gathers an attention to study the effect air-gap length on the YSZ hollow fibre membrane prior to the selection of membrane for certain applications. Lastly, the sintering process gave impact particularly in term of the surface morphology, microstructure, grain growth and pore evaluation or elimination. Thus, this stage played an important role to determine the final properties of ceramic membrane. The sintering temperature must be controlled subjected to the feasibility of YSZ membrane for water purification application as using YSZ membrane for this application is still new.

1.3 Objective

Referring to the problems stated in 1.2, the aim of this research study is to fabricate a ceramic hollow fibre membrane made from Yttria-stabilized zirconia by using combined phase inversion method and sintering process. This study involves the preparation of ceramic suspension solution, spinning and sintering process. In each process, there having parameters that gives influenced on the structure of ceramic hollow fibre membrane. Thus, a morphological study of YSZ hollow fibre membrane is important as it may be a guideline for the fabrication of YSZ hollow fibre membrane for a specific application. In order to achieve this aim, the following objectives were carried out:

1) To study the effect of ceramic loading and ceramic/polymer ratio during suspension preparation on the morphology structure and the properties of YSZ hollow fibre membrane

2) To study the effect of air-gap length during spinning process on the morphology structure and the properties of YSZ hollow fibre membrane

3) To study the effect of sintering temperature on the microstructure and the properties of YSZ hollow fibre membrane for water purification application

1.4 Scope of Study

The following scope of work is carried out to achieve objectives stated in 1.3:

1) Preparing the ceramic suspensions for spinning process using planetary ball mill at different ceramic loadings and ceramic/polymer ratios

2) Measuring the viscosities of ceramic suspensions using viscometer

3) Fabricating the ceramic hollow fibre precursor by dry-wet phase inversion at different air-gap length

4) Sintering the ceramic hollow fibre precursors at different sintering temperature using high temperature furnace

5) Characterizing the effect of ceramic loading, ceramic/polymer ratio, air-gap length and sintering temperature on the morphology structure and properties of ceramic hollow fibre membrane by using scanning electron microscopy (SEM), atomic force microscopy (AFM), three point bending test, X-ray diffraction (XRD), apparent porosity, pure water permeation tests and solute rejection tests

1.5 Significant of Study

A structural study related to YSZ hollow fibre membrane was not well studied yet. This research will give an overview on the effect of the process conditions during membrane fabrication on the morphology of YSZ hollow fibre membrane produced. Besides, it gives a guideline for the future study to prepare YSZ membrane with a desired structure base on the application. Moreover, the development of ceramic hollow fibre membrane through combined phase inversion and sintering process are promising in reducing the production cost together with the simple technology concept that can reduce the time consumed. Other than that, this study discovers the feasibility of YSZ hollow fibre membrane to be used in water separation applications.

1.6 Thesis Structure

This report consists of five chapters. In the first chapter, a brief description on the research backgrounds, research problems, research objectives and scopes were presented. In Chapter 2, the literature review discussed on the development of ceramic membrane, the advantages of ceramic membrane over polymeric membrane, the fabrication method of ceramic membrane and the application of ceramic membrane were presented. In Chapter 3, the research methodology included the materials, the analytical procedures and the characterization involves during study is presented. Chapter 4 presents the results and discussions to answer the objectives stated above. It discusses the changes occur over varying the parameters during YSZ hollow fibre membrane fabrication onto the structure and the properties. Lastly, the conclusion of whole study was presented in Chapter 5. Besides, few recommendations are also listed for future study and enhancement.

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