A Morphological Study of Ceramic Hollow Fibre Membranes: A Perspective on Multifunctional Catalytic Membrane Reactors

By

Benjamin F. K. Kingsbury

A Thesis Submitted for the Degree of Doctor of Philosophy and the Diploma of Imperial College

June 2010
Declaration of Originality

I hereby declare that this thesis and the work reported herein was composed by and originated entirely from me. Information derived from the published and unpublished work of others has been acknowledged in the text and the relevant references are included in this thesis.

Benjamin Kingsbury

Imperial College, June 2010
Abstract

In recent years ceramic membrane technology has advanced considerably and ceramic membranes are now being applied to a number of high temperature applications, in particular in the energy industry as membrane reactors. Due to the thermal stability of ceramic materials, development in this area is extremely promising as these applications cannot be realized using polymeric membrane technology. Although a wide range of ceramic materials have been developed and processing techniques have improved considerably, the high production cost and lack of control over membrane properties when fabrication processes are scaled up are prohibitive in the commercial application of ceramic membrane technology.

However, by using a dry-wet spinning process and the combined phase inversion and sintering technique, novel asymmetric hollow fibre morphologies consisting of a porous sponge-like structure and finger-like macrovoids in which catalyst may be deposited can be prepared in a cost effective way. These asymmetric hollow fibres are prepared from raw materials and are suitable for use in catalytic membrane reactors. Fibre morphology is determined by the rheological properties of the ceramic spinning suspension as well as the parameters used during fibre spinning and the effect of sintering during heat treatment. A generic mechanism has been suggested for the formation of asymmetric structures and the parameters at each of these three stages have been varied systematically in order to predict and control hollow fibre structure. Hollow fibres prepared in this way have been characterized in terms of morphology, pore size distribution, porosity and mechanical strength in terms of their applicability to membrane reactor applications.
The versatility of this preparation technique is demonstrated by the inclusion of a chapter describing a catalytic membrane reactor for hydrogen production by water-gas-shift as well as a reactor for the dehydrogenation of propane. It should also be noted that this reactor design could be applied to a number of other catalytic gas phase reactions.
Acknowledgements

First of all I would like to thank Prof. Kang Li for his excellent guidance and support throughout my PhD study and for the many opportunities I have been given to collaborate with other groups and present my work. Scientific discussion with Prof. Li was always constructive and I felt comfortable expressing my opinion at all times, which helped a great deal to build confidence and develop research skills. I am grateful to have benefited from his extensive experience and knowledge not only in membrane science but also in many other aspects of life as a researcher in general.

I would also like to thank Dr. Zhentao Wu for the excellent advice that he offered throughout my PhD and for the many helpful discussions that we had relating to all aspects of my work. He always made time to help with research and offer advice, which was greatly appreciated.

I also appreciate the help I have received from present and past members of Prof Li’s group including Dr. Chiao-chien Wei and Dr. Sirichai Koonaphaapdeelert who often spent time discussing the various aspects of my PhD research with me as well as Ejirooghene Gbenedio, Krzystof Kanawka, Ifran Mohd Mohamed, Barbara Zydorczak, Mohd Hafiz Dzarfan Othman, Nur Hashim, Hashrina Hashbullah, Dr. Yutie Liu, Mohammad Reza Moghareh Abed, Mukhlis A Rahman and Dr Santosh Kumbharkar for the help they have given me and for providing such a pleasant working environment. I would also like to thank Prof. Ahmad Fauzi Ismail, Be cheer Ng and everyone in the AMTEC team for their exceptional hospitality during my time at Universiti Teknologi Malaysia.
I would also like to offer my thanks Dr. Ardakani and Prof. Luckham for the provision and help with SEM and rheological characterization, respectively, and to Mrs. Patricia Carry for laboratory analysis. I also appreciate the work done by the technical and administrative staff to keep things running smoothly, especially Susi Underwood for processing my documentation over the course of my PhD and Keith Walker for supplying equipment and materials.

The funding given by EPSRC for the duration of my PhD research is also greatly appreciated and finally, I would like to thank my family and friends who have been a constant source of encouragement throughout my PhD study.
Table of Contents

Abstract

Acknowledgements

Table of Contents

List of Figures

List of Tables

Chapter 1: Introduction

1.1 Background

1.2 Thesis objectives

1.2.1 Suspension preparation

1.2.2 Morphological study

1.2.3 Characterization

1.2.4 Applications

1.3 Thesis structure and presentation

1.4 References

Chapter 2: Literature review

2.1 Ceramic membranes

2.2 Module designs and membrane configurations

2.3 Ceramic membrane preparation methods

2.3.1 Slip casting

2.3.2 Extrusion

2.3.3 Dip-coating

2.3.4 Chemical vapour deposition

5
Chapter 3: A Study on the Rheology and Extrusion of Ceramic/Polymer/Solvent Suspensions for the Fabrication of Ceramic Hollow Fibre Membranes and Membrane Supports

Abstract

3.1 Introduction

3.2 Experimental

3.2.1 Materials

3.2.2 Suspension preparation

3.2.3 Viscosity measurements

3.2.4 Microscopy

3.2.5 The design of the spinneret

3.3 Results and discussion

3.3.1 Fibre formation

3.3.2 Fibre elongation

3.3.3 Suspension rheology

3.4 Conclusions

3.5 References

Chapter 4: A Morphological Study of Ceramic Hollow Fibre Membranes and Membrane Supports
Table of Contents

5.2.5 Gas permeation_________________________________________128
5.2.6 Mechanical strength____________________________________128
5.2.7 Nitrogen adsorption____________________________________129
5.3 Results and discussion____________________________________130
  5.3.1 Calcination temperature________________________________130
  5.3.2 Suspension viscosity____________________________________143
  5.3.3 Internal precipitant flow rate____________________________148
  5.3.4 Air-gap_______________________________________________151
5.4 Conclusions_____________________________________________155
5.5 References______________________________________________156

Chapter 6: Ceramic Hollow Fibre Applications____________________158

Abstract____________________________________________________158

6.1 Introduction________________________________________________159
  6.1.1 Membrane reactors______________________________________159
  6.1.2 Ceramic hollow fibre membrane microreactors_______________160
  6.1.3 Catalyst impregnation____________________________________165
6.2 A novel catalytic membrane microreactor for CO₂ free H₂ production_____168
6.3 The dehydrogenation of propane to propene____________________172
6.4 Conclusions________________________________________________177
6.5 References________________________________________________178

Chapter 7: Conclusions and Future Work_________________________181

7.1 General conclusions________________________________________181
  7.1.1 Suspension preparation__________________________________181
Table of Contents

7.1.2 Morphology 182
7.1.3 Characterization 183
7.1.4 Applications 184

7.2 Future work 184
7.2.1 Suspension rheology 184
7.2.2 Shear rate within the spinneret 185
7.2.3 Viscous fingering 185
7.2.4 Morphology and applications 186

7.3 References 186

Publications, Presentations and Collaborative Work 188
List of Figures

Figure 1.1: The progression of polymeric and ceramic membrane technology from its inception in 1750 to the present day.

Figure 2.1: Inocep alumina capillary membrane modules produced by Hyflux Membranes (Singapore).

Figure 2.2: Flow chart depicting the various stages of hollow fibre preparation using the combined phase inversion and sintering technique.

Figure 2.3: Fibre spinning apparatus.

Figure 2.4: Schematic representation of a triple orifice (tube-in-orifice-in-orifice) spinneret.

Figure 2.5: A typical calcination profile for hollow fibres prepared in this work.

Figure 2.6: The effect of sintering temperature on grain size and membrane shrinkage.

Figure 2.7: A qualitative model of grain growth. (a): Two particles of differing size in contact with each other, (b): “neck” growth by surface diffusion between particles and (c): grain growth.

Figure 2.8: Pore stability and evolution in two dimensions.

Figure 2.9: A schematic representation of the effect on mechanical strength of a simultaneous reduction in porosity and increase in grain size.

Figure 3.1: Photographic images of (a): the entire spinneret assembly, (b): view of suspension injection channels and the inner annulus, (c): internal cavity and (d): outer surface of spinneret showing inner and outer annuli.

Figure 3.2: A schematic diagram of optimal suspension flow through a tube-in-orifice spinneret.

Figure 3.3: A schematic diagram of insufficient suspension flow through a tube-in-orifice spinneret.

Figure 3.4: A schematic representation of a non-uniform fibre wall resulting from an insufficient suspension viscosity and/or extrusion rate.

Figure 3.5: An example of an alumina hollow fibre with a uniform wall thickness.

Figure 3.6: Hollow fibre precursor deposited at the bottom of a precipitation tank containing 120 L of water.
Figure 3.7: Schematic representation of the angle at which the nascent fibre exits the spinneret.

Figure 3.8: An SEM image of a ceramic hollow fibre with an asymmetric lumen.

Figure 3.9: The rheological behaviour of a polymer solution, a ceramic suspension and a polymer/ceramic suspension at varying shear rates.

Figure 3.10: Rheological profiles of alumina/PESf/NMP suspensions prepared with a range of particle sizes from 0.01-180 µm.

Figure 3.11: The effect of additional mixing after the addition of polymer binder for suspensions milled for 5 and 10 hours.

Figure 3.12: The effect of milling time on the rheology of Suspension F.

Figure 3.13: Hysteresis in the rheological profile of Suspension F when subjected to a shear rate cycle of 6 – 1000 – 6 s⁻¹.

Figure 4.1: Flat sheet membranes prepared from ceramic suspensions with viscosities at 30 s⁻¹ of (a): 7 Pa.s, (b): 12.1 Pa.s and (c): 21.2 Pa.s.

Figure 4.2: A still image from a dynamic video microscopy study of the formation of finger-like structures as a result of viscous fingering.

Figure 4.3: Finger-like void propagation as a function of time as observed using dynamic video microscopy.

Figure 4.4: Cross-sectional images of Fibres 1-7 with air-gaps between 0 - 13 cm: (a) Fibre 1, 0 cm, (b): Fibre 2, 3 cm, (c): Fibre 3, 5 cm, (d): Fibre 4, 7 cm, (e): Fibre 5, 9 cm, (f): Fibre 6, 11 cm and (g): Fibre 7, 13 cm.

Figure 4.5: Cross-sectional images of Fibres 8-13 with air-gaps between 1 - 13 cm and with an internal precipitant flow rate of 12 ml/min. (a): 1 cm, (b): 3 cm, (c): 7 cm, (d): 9 cm, (e): 11 cm and (f): 13 cm.

Figure 4.6: Cross-sectional SEM images of fibres prepared with varying internal precipitant flow rates and an air-gap of 15 cm (a): 3 ml/min, (b): 6 ml/min, (c): 7 ml/min, (d): 8 ml/min, (e): 9 ml/min, (f): 12 ml/min, (g): 15 ml/min.

Figure 4.7: Viscosity of spinning suspensions prepared with 0-10 wt% water (as a percentage of the total solvent content).

Figure 4.8: Cross-sectional SEM images of Fibres 21-26 made from spinning suspensions containing varying amounts of water. (a): Fibre 21, 0 wt% water, (b):
enlargement of Fibre 23 outer edge, 4 wt% water, (c): Fibre 22, 2 wt% water, (d): isolated void in Fibre 23, 4 wt% water, (e): enlargement of isolated void in Fibre 5, 4 wt% water, (f): Fibre 23, 4 wt% water, (g): Fibre 6, 6 wt% water, (h): enlargement of Fibre 6 outer edge, 6 wt% water, (i): Fibre 25, 8 wt% water, (j): Fibre 26, 10 wt% water.

Figure 4.9: Cross-sectional images of Fibres 27-31 made from spinning suspensions containing varying amounts of water and spun with different internal precipitant flow rates (a): Fibre 27, 2 wt% water, 13.8 ml/min, (b): Fibre 28, 4 wt% water, 15.6 ml/min, (c): Fibre 29, 6 wt% water, 18 ml/min, (d): Fibre 30, 8 wt% water, 27.6 ml/min, (e): Fibre 31, 10 wt% water, 37.2 ml/min, (f): Fibre 28, 4 wt% water, 15.6 ml/min (outer edge) and (g): Fibre 29, 6 wt% water, 18 ml/min (outer edge).

Figure 4.10: Viscosity of spinning suspensions prepared with 0-10 wt% ethanol (as a percentage of the total solvent content).

Figure 4.11: Cross-sectional SEM images of ceramic hollow fibres prepared with varying quantities of ethanol in the spinning suspension and at an internal precipitant flow rate of 10 ml/min. (a): Fibre 21, 0%, (b): Fibre 33, 2%, (c): Fibre 34, 4%, (d): Fibre 35, 6%, (e): Fibre 36, 8% and (f): Fibre 37, 10%.

Figure 5.1: Schematic representation of the 3 point bending strength testing apparatus.

Figure 5.2: 3 point bending strength data for fibres prepared from suspensions with varying particle size distributions.

Figure 5.3: SEM images of fibres prepared from suspensions containing (a): 1 and 0.3 µm particles and (b): 1 µm, 0.05 µm and 0.01 µm particles.

Figure 5.4: A hollow fibre calcined at 1450 °C used in a catalytic membrane reactor for the dehydrogenation of propane.

Figure 5.5: Mercury intrusion data of pore size vs. calcination temperature for an asymmetric hollow fibre prepared with an air-gap of 15 cm and an internal precipitant flow rate of 10 ml/min.

Figure 5.6: Gas-liquid displacement data on pore size vs. calcination temperature for the asymmetric fibre shown in Figure 5.4, calcined at 1400 °C and 1450 °C.
List of Figures

Figure 5.7: Porosity calculated from mercury intrusion data and a gas permeation technique as a function of calcination temperature.

Figure 5.8: Nitrogen adsorption data showing BET surface area as well as BJH adsorption and desorption pore area and the single point pore volume.

Figure 5.9: Surface SEM images of hollow fibres calcined at temperatures between 1200 and 1600 °C.

Figure 5.10: Mercury intrusion data for fibres prepared with a 15 cm air gap and 0-10 wt% water (as a percentage of the total solvent content) in the spinning suspension, calcined at 1200 °C.

Figure 5.11: Mercury intrusion data for fibres prepared with a 15 cm air-gap and 0-10 wt% ethanol (as a percentage of the total solvent content) in the spinning suspension, calcined at 1450 °C.

Figure 5.12: Mercury intrusion data for fibres prepared with internal precipitant flow rates between 3 and 15 ml/min and an air-gap of 15 cm, calcined at 1450 °C.

Figure 5.13: Mercury intrusion data for fibres prepared with air-gaps of 1-13 cm and with an internal precipitant flow rate of 7 ml/min, calcined at 1450 °C.

Figure 5.14: Mercury intrusion data for fibres prepared with air-gaps of 1-13 cm and with an internal precipitant flow rate of 12 ml/min, calcined at 1450 °C.

Figure 6.1: A schematic representation of an asymmetric hollow fibre catalytic membrane reactor consisting of a sponge-like structure and a region of micro-channels.

Figure 6.2: A schematic representation of the effective thickness of a separation layer deposited on a porous support.

Figure 6.3: A schematic representation of a bi-functional hollow fibre catalytic membrane reactor.

Figure 6.4: Cross-sectional SEM image of an asymmetric ceramic hollow fibre consisting of finger-like voids and a sponge-like structure.

Figure 6.5: SEM images of a hollow fibre microreactor for H₂ production. (a): Hollow fibre cross section, (b): hollow fibre cross section at increased magnification and (c): surface of palladium separation layer.
Figure 6.6: SEM images of catalyst deposition in a hollow fibre substrate. (a): Catalyst particles deposited within the finger-like voids and (b): the surface of the finger-like voids at increased magnification.

Figure 6.7: SEM images of a functionalized alumina hollow fibre substrate. (a): Whole view, (b): cross section, (c): inner surface and (d): top view of outer surface.

Figure 6.8: Comparison of weight gain and surface area increase for different catalyst impregnation methods.
List of Tables

Table 2.1: Common gas phase reactions and reaction mechanisms used in chemical vapour deposition of membrane and membrane support layers.

Table 2.2: Mass transport mechanisms operating during sintering and their effect on membrane densification.

Table 3.1 Particle size distributions and suspension compositions for suspensions A-G.

Table 4.1: Compositions of suspensions used in the preparation of flat sheet membranes.

Table 4.2: Suspension compositions, viscosities and fibre preparation parameters for Fibres 1-37 discussed in Chapter 4.
Chapter 1

Introduction

1.1 Background

A membrane is a selective barrier between phases, the properties of which are characterized in terms of flux and selectivity. The ultimate aim when preparing a membrane is to create a structure that has both high flux and selectivity, however, almost invariably an increase in one variable is at the expense of the other. In addition to flux and selectivity, the long and short term durability of a membrane is extremely important as this often determines whether or not the application of membrane technology to a particular process is economically viable, or indeed possible at all. Transport processes across a membrane result from a driving force, which is typically associated with a gradient of concentration, pressure, temperature or electrical potential [1]. Great advances were made in the 18th and 19th centuries and a more scientific basis for the processes involved in the permeation of liquids and gasses through membranes was developed by prominent scientists of the time. Jean-Antoine Nollet, a French clergyman and physicist, is credited with the discovery of the phenomenon of osmosis in 1748, serendipitously, after observing the permeation of water through a pig bladder being used to store alcohol. Following this, 19th century scientists such as the Graham, Knudsen, Fick and van’t Hoff developed theories for the transport of gasses and the analogous diffusion of solutes in liquid media which allowed for the rapid advancement of membrane technology in the following decades. It was not until 1855, however, that the concept of an artificial membrane was introduced by Fick. Since then, a wide range of membrane types and
membrane materials have been developed for an extensive range of applications. Although examples such as the development and implementation of ceramic membranes for uranium enrichment during the Manhattan project in 1942 and later by the French Atomic Agency in the 1950’s, it was not until the 1980’s that ceramic membrane research started to develop in earnest and ceramic membranes were applied to more conventional applications such as filtration and gas separation. Due to the great advances in polymer science which have occurred since 1940, polymeric membranes have dominated the market and have been used for many years in a variety of applications spanning a number of industries. These applications range from filtration, including ultrafiltration [2,3], nanofiltration [4-6] and reverse osmosis [7-9] to gas separation [10-12] in addition to a number of medical applications such as hemodialysis and blood purification [13-17] and artificial lungs [18,19]. In addition, the combination of membranes with a biological component has resulted in the development of membrane bioreactors for applications such as waste water treatment [20-23]. However, high temperature applications such as membrane reactors [24-26], solid oxide fuel cells and high temperature membrane contactors [27-31] are outside the scope of polymeric membrane technology due to the high operating temperatures that are required. Due to advances in ceramic processing technology, ceramic membranes are being developed for a number of applications and may even replace polymeric membranes for some of the more traditional applications such as filtration [32-34] and gas separation [35]. The increased use of membranes in recent years is driven by advantages that membranes have over traditional technologies. These include the elimination of phase changes during a process operation which may reduce the complexity of the process and remove the need for chemical additives, the
ease with which a modular membrane design can be scaled up, the possibility to reduce temperatures and increase conversions for equilibrium limited reactions and the elimination of by-products by manipulation of chemical equilibria. These advantages lead to a more simple mode of operation and substantial savings in both energy and production costs in terms of raw materials and infrastructure. A comparison of a membrane reactor system and a conventional industrial reformer was undertaken by Bernardo et al. [36] and demonstrates well the benefits of membrane reactors in terms of energy and material costs as well as a reduction in the footprint of the hydrogen production plant. Figure 1.1 shows the timeline for the development of membrane technology over the last 260 years.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Van’t Hoff uses membranes for research on osmotic pressure</td>
<td>Hassler: Concept of membrane desalination</td>
<td>First hollow fibre membranes</td>
<td>Advances in gas separation</td>
<td>1937: Polymer science takes off</td>
<td>MF/UF/RO commercialized</td>
<td>Ceramic hollow fibre membranes</td>
<td>Ceramic membrane reactors and contactors</td>
<td>Ceramic nanofiltration</td>
</tr>
<tr>
<td>1907: Bechhold UF membrane (paper &amp; acetic acid colloid)</td>
<td>Loeb and Sourirajan: Reproducible phase inversion membranes</td>
<td>USA: Inorganic membranes for uranium enrichment</td>
<td>Ceramic MF/UF growth</td>
<td>Glass MF membranes</td>
<td>Ceramic membrane reactors and contactors</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 1.1: The progression of polymeric and ceramic membrane technology from its inception in 1750 to the present day.
1.2 Thesis objectives

The objective of this thesis is the development of ceramic hollow fibre membranes and membrane support structures, using the combined phase inversion and sintering technique, for use in a variety of applications. This process involves the preparation of a ceramic suspension, fibre spinning and heat treatment and by studying the effect that certain parameters at each of these stages have on fibre morphology and by determining a generic mechanism for the formation of asymmetric structures, fibre structure can be tailored to specific applications. Therefore in this thesis a rheological study of the ceramic suspension has been undertaken in order to establish the effect that suspension rheology has on fibre morphology. The effect of fibre spinning parameters on fibre morphology have been studied so that fibre structure can be controlled and predicted. Hollow fibres have been characterized in terms of their applicability to certain applications and the effect of suspension properties and spinning parameters on fibre structure has been studied. The versatility of the combined phase inversion and sintering technique for hollow fibre preparation has been demonstrated by the inclusion of applications for which hollow fibres have been developed.

1.2.1 Suspension preparation

1) To prepare ceramic/polymer/solvent suspensions for the fabrication of asymmetric ceramic hollow fibre membranes and membrane supports.

2) To study the effect of the particle size distribution and milling time on the properties of the suspension.
3) To understand how the rheological properties of the suspension affect the fibre spinning process and to optimize the suspension rheology for the preparation of different fibre structures.

1.2.2 Morphological study

1) To establish a generic mechanism that can be used to predict the formation of different fibre morphologies from suspensions with different properties.

2) To vary preparation parameters and suspension composition to achieve a wide range of fibre structures and obtain control over the morphology with respect to the formation of finger-like and sponge-like structures.

1.2.3 Characterization

1) To characterize the fibres with respect to the pore size distribution, porosity and mechanical strength.

2) To establish the effect that variations in the preparation parameters and calcination temperature have on the fibre properties, in terms of the pore size distribution, mechanical strength and porosity.

3) To determine the optimum preparation parameters for fibres used for different applications.

1.2.4 Applications

1) To demonstrate the versatility of the combined phase inversion and sintering technique for the preparation of ceramic hollow fibres with varying
morphologies by highlighting applications for which hollow fibres have been developed:

a) A catalytic membrane microreactor for CO$_x$ free H$_2$ production.

b) catalytic hollow fibre membrane reactor for the dehydrogenation of propane.

1.3 Thesis structure and presentation

This thesis is comprised of 7 chapters addressing the different aspects of hollow fibre preparation starting from raw materials and culminating in the application of ceramic hollow fibres for reactions and separations. Chapter 1 contains a brief outline of the thesis and its objectives and introduces the concept and history of membrane separation and the development of ceramic membrane technology. Chapter 2 introduces a variety of ceramic membrane preparation techniques and membrane configurations including the combined phase inversion and sintering technique used for fibre preparation in this study. The advantages of this technique as well as the advantages of hollow fibre geometry are highlighted in this chapter. Chapter 3 discusses the importance of the properties and rheology of the ceramic suspension used in the preparation of hollow fibres and how these suspensions must be optimized in order to obtain a wide range of fibre morphologies for a variety of applications. Chapter 4 describes the effect that variations in the many parameters that are relevant during the fibre spinning process have on the fibre morphology and how combinations of these parameters can be used to obtain the desired fibre structure. Chapter 5 contains characterization data with respect to the pore size distributions of fibres as well as important properties such as mechanical strength.
and porosity and describes how these properties change with calcination temperature and fibre preparation parameters. Chapter 6 introduces applications for which asymmetric hollow fibres have been specifically developed using the knowledge gained in the previous chapters. Finally, Chapter 7 contains some general conclusions regarding ceramic hollow fibre preparation and application and some suggestions for future work on this subject.

1.4 References


2.1 Ceramic membranes

In recent years a wide range of ceramic materials have been developed for applications that employ both porous and non-porous membranes. Broadly speaking, membranes can be divided into two categories, those in which the chemical structure of the membrane material plays a part in their function (non-porous) and those that operate exclusively by size exclusion (porous) and in which pore size is often the most important factor. Non-porous membranes function by allowing preferential diffusion of one species through the lattice structure of the membrane material and may achieve theoretical selectivities of 100%. Examples of inorganic non-porous membranes include ionic and/or electronic conducting materials such as lanthanum-strontium-cobalt-ferric oxide (LSCF) \[37,38\] and lanthanum strontium manganite (LSM) for oxygen separation/production \[39\], yttria-stabilized zirconia (YSZ) \[40\] and gadolinium doped ceria (CGO) in solid oxide fuel cells (SOFC) \[41,42\] as well as palladium or palladium alloy membranes for the selective permeation of hydrogen \[43-46\]. The difference between ionic and mixed conducting materials lies in the ability of mixed conducting materials to conduct both electrons and ions whereas purely ionic conductors permit the passage of ions only. Mixed conductors such as LSCF may be used for oxygen separation as oxygen will diffuse through the membrane in its ionic form while a counterbalancing flow of electrons is also present \[47\]. In contrast, ionic conductors require an external circuit to balance the charge which provides the basis for a fuel cell.
Photocatalytic and photolytic membranes may also be prepared using oxides such as SnO$_2$ and TiO$_2$ [48,49] which are usually applied as a coating to a membrane support. When irradiated with UV light these membranes are capable of deactivating microbes such as *E.Coli* and breaking down organic material and consequently have an inherent antifouling capability.

For separation processes based on size exclusion the chemical/lattice structure of the membrane material is less important and factors such as the mechanical strength, durability, pore size and material cost become the dominant factors. As aluminium oxide scores well in these areas it has been used extensively for the fabrication of membranes and membrane supports for many years. Porous ceramic membranes may also function as a membrane contactor in which the ceramic component functions as a phase separation device and separation is based on the principals of phase equilibria. Examples of the application of membrane contactors include high temperature distillation [50] and CO$_2$ absorption [51], a topic that has received a great deal of interest in recent years.

### 2.2 Module designs and membrane configurations

A variety of considerations must be taken into account when selecting a particular membrane/support structure such as production cost, mechanical strength, flux and surface area/volume ratio. Commercially, most available ceramic membranes take the form of discs, plates, tubes or monolith structures and although discs and plates can be stacked to form modules, surface area/volume ratios are rather low. In addition, for SOFC applications, although planar SOFCs in a highly compact configuration show great power density, a design of this type is challenged by the necessity for high temperature sealing
near the edges of the cell as few sealants can endure the thermal cycles experienced during operation [27]. Tubular membranes with surface area/volume ratios between 30-250 m²/m³ are generally prepared by either slip casting or extrusion methods and multichannel tubular configurations have also been developed to increase surface area/volume ratios. Following this, in an effort to increase ratios further, capillary membranes have been developed and are available commercially, Figure 2.1.

Figure 2.1: Inocep alumina capillary membrane modules produced by Hyflux Membranes (Singapore).

More recently, ceramic hollow fibre membranes have been prepared using a combined phase inversion and sintering technique and surface area/volume ratios of 4500 m²/m³ can be achieved using this method. As will be discussed in the following chapters, not only are extremely small fibre diameters possible, but exceptional control over the fibre morphology may be achieved using this technique.
2.3 Ceramic membrane preparation methods

2.3.1 Slip casting

Slip casting is a method commonly used in membrane preparation due to its simplicity and reproducibility. Casting does however take a long time compared with other preparation methods and produces only symmetric membrane structures. The process starts with the preparation of a ceramic suspension or slurry. The slurry is either allowed to settle in a container on top of a porous support through which solvent passes and is collected below (sedimentation), or the slurry is poured into a porous mould and over time the solvent is drawn out of the slurry into the mould by capillary action, resulting in a solidified layer in contact with the mould. The remaining unsolidified slurry is then poured away and the mould is removed. In both cases the solidified layer is then calcined and coated as required. A modification of this process involves the use of a centrifuge, termed centrifugal casting, in this case the mould is spun to aid the absorption of solvent. The duration and speed of centrifugation is important and in both cases the pore size of the mould is an important factor and must be optimized to prevent ceramic material from being drawn into the pores. A benefit of this casting method is that the tube that results is nearly perfectly circular which facilitates sealing during module preparation. In order to achieve a small membrane pore size, particles in the slurry must also be small, which may be achieved using a sol-gel process for the production of nanometre (nm) sized particles and pore sizes of 3-6 nm can be achieved using this method. However, long casting times and difficulty in controlling membrane thickness are major problems.
2.3.2 Extrusion

Extrusion is a common method for the production of ceramic tubes and monolith structures. A ceramic paste is forced through a die of a particular shape to produce the membrane or membrane support structure. The rheological properties of the paste are of the utmost importance if extrusion is to be successful. The paste must be homogenous and exhibit plastic properties in that it behaves as a rigid solid when unperturbed but above a certain yield stress deformation may take place. Typically, an extremely viscous mixture of ceramic material and binder is prepared and extruded under pressure through a die. The pressure, shear and temperature experienced by the ceramic polymer mixture within the extrusion apparatus cause the material to flow and as the pressure, shear and temperature are reduced the nascent capillary tube becomes rigid as it exits the die/extrusion apparatus. The binder is then removed by heat treatment and the ceramic material is sintered to yield the final product.

Although the above mentioned methods are well established it is only possible to prepare a limited range of structures and typically successive layers must be applied to either the inner or outer surfaces of the support using techniques such as sol-gel processing or chemical vapour deposition in order to generate the asymmetric structures that are required to achieve acceptable levels of flux and selectivity.

2.3.3 Dip-coating

It has so far not been possible to prepare ceramic membranes with surface pore sizes in the nanofiltration range without the application of a coating and sol-gel processing and dip-coating are the most widely used techniques to reduce pore size. The dip coating
process involves submerging the membrane support in a ceramic dispersion which may or may not also contain a polymeric binder. The support is then removed and the solvent is evaporated from the surface leaving a layer of ceramic material. Two approaches are possible depending on the membrane pore size that is desired. For larger pore sizes (~20 nm) a dispersion of stabilized nanoparticles is prepared which in some cases form chemically in situ as in the hydrolysis of TiF$_4$ to TiO$_2$ [49]. The coating layer can be chemically altered during calcination as in the formation of $\gamma$-alumina coatings [52]. If pore sizes in the range 2-10 nm are to be achieved then it is necessary to prepare a polymeric sol. In this case a stabilized dispersion of organometallic precursors such as titanium ethoxide is prepared and a layer of polymeric sol is deposited on the support surface. After the formation of a gel by drying followed by heat treatment, the organic component is eliminated and ceramic particles form a coating on the support surface. In both cases, the formation of a gel is induced by variation of conditions such as temperature, pH and solvent concentration. The gel coated membrane support is then calcined to remove the binder and for sintering of the coating layer to occur. However, multiple layers are often required to achieve a high level of selectivity and to eliminate defects. Microporous membranes coated for gas separation may require as many as five coatings, each of which requires sintering. The time and cost of this process is often prohibitive and the coating layer may also delaminate under extreme conditions. Moreover, the stability and properties of the sol or polymeric sol that is used during this process is extremely difficult to control and are affected strongly by small variations in a number of parameters. Although with a high level of expertise control can be achieved on
a small scale, it poses a major problem when producing coated supports on a larger scale and consequently commercial development in this field has been severely hampered.

### 2.3.4 Chemical vapour deposition

A competing technology for the deposition of selective layers onto a ceramic support is chemical vapour deposition (CVD). This involves the deposition of reactive compounds from the gas phase. A carrier gas is used to introduce these compounds to the support surface, often at sub-atmospheric pressures. Compounds in the gas phase react together and are deposited on the substrate surface or may react with the substrate surface directly by mechanisms such as thermal decomposition, oxidation, hydrolysis or reduction, some examples of which are shown in Table 2.1.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Chemical equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal decomposition</td>
<td>$2\text{Al(OC}_3\text{H}_7\text{)}_2 \rightarrow \text{Al}_2\text{O}_3 + 6\text{C}_3\text{H}_6 + 3\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>Oxidation</td>
<td>$\text{SiH}_4 + \text{O}_2 \rightarrow \text{SiO}_2 + 2\text{H}_2$</td>
</tr>
<tr>
<td>Hydrolysis</td>
<td>$2\text{AlCl}_3 + 3\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + 6\text{HCl}$</td>
</tr>
<tr>
<td>Co-reduction</td>
<td>$\text{TiCl}_4 + 2\text{BCl}_3 + 5\text{H}_2 \rightarrow \text{TiB}_2 + 10\text{HCl}$</td>
</tr>
</tbody>
</table>

Table 2.1: Common gas phase reactions and reaction mechanisms used in chemical vapour deposition of membrane and membrane support layers.

As with the sol-gel deposition technique, achieving control and reproducibility of the layer properties can be challenging due to the complexity of the process. In addition, high temperatures are often used and the reactive compounds are often highly toxic and
corrosive. Consequently, an additional step is required to treat the exhaust stream and the equipment must be protected from the corrosive and reactive nature of the feed gases.

2.3.5 Surface modification

Commonly, ceramic membrane materials such as alumina are hydrophilic due to hydroxyl groups present on the surface and it is essential that the hydrophobicity of these membranes is increased if they are to be used for membrane contactor applications, which often involve aqueous and/or hydrophilic systems. In polymer membrane technology this can be achieved more easily as a wide range of polymeric materials are available with vastly different properties, however, this is not the case for ceramic oxides which almost invariably have hydrophilic surface characteristics. Successful preparation of ceramic hydrophobic hollow fibre membranes has been achieved by Koonaphapdeelert and Li [53] who modified membranes with pore sizes between 50-100 nm via a silane coupling reaction used to attach perfluorooctylethoxysilane (FAS) molecules to the surface of an $\alpha$-alumina hollow fibre support. A similar process has also been undertaken by Sah et al. [54] who grafted a variety of organochlorosilanes to the surface of flat sheet alumina membranes. Grafting of polydimethylsiloxane oil onto a porous alumina membrane by Leger et al. [55] yielded a membrane that was highly hydrophobic and was capable of separating water/organic solvent mixtures.

The concentration of hydroxyl groups on the surface of the membrane determines the number of hydrophobic molecules that will bond covalently to the surface. Koonaphapdeelert and Li found that modified membranes calcined at higher temperatures showed lower contact angles than those calcined at lower temperatures. As this is the
reverse trend to that of unmodified membranes it is suggested that the membrane undergoes a change from \( \gamma \)-alumina to \( \alpha \)-alumina during heat treatment. The \( \alpha \)-alumina structure has less surface hydroxyl groups, only \( \sim 5 \text{ nm}^2 \), and is therefore more hydrophobic than its \( \gamma \)-alumina counterpart. The situation is reversed however after the grafting process as there are less hydroxyl groups available for bonding. It has also been demonstrated that the surface modification remains intact after being subjected to a hexane flux for 96 hours and is stable at temperatures up to 230 °C.

### 2.3.6 Phase inversion and sintering

Production of ceramic hollow fibre membranes can be achieved using an immersion induced phase inversion method first described by Loeb and Sourirajan [56] for asymmetric polymeric membrane formation. After the combination of a desired amount of ceramic powder and a polymer solution, if well mixed, the ceramic/polymer/solvent system can be seen as a suspension of polymer coated ceramic particles. Once immersed in a non-solvent for the polymer which is miscible with the solvent, solvent/non-solvent exchange takes place leading to precipitation of the polymer phase. Ceramic particles are immobilized once precipitation has taken place and the membrane macrostructure can be largely determined at this point by manipulating and adjusting the various parameters of the phase inversion process. Critically, using the combined phase inversion and sintering method for the production of hollow fibres, asymmetry can be achieved in a single step and fibres with diameters as small as 0.8 mm can be prepared easily. Figure 2.2 shows a flow chart depicting the preparation of ceramic hollow fibres from raw materials to the
final sintered product and consists of three principal stages, as indicated on the flow chart.

Figure 2.2: Flow chart depicting the various stages of hollow fibre preparation using the combined phase inversion and sintering technique.

**Suspension preparation (Stage 1):** A suitable inorganic dispersant is chosen and is dissolved in a quantity of solvent or solvent mixture. The inorganic material is added and milling is continued until the particles are sufficiently dispersed. Following this a polymer binder is added and mixing is performed until dissolution of the polymer has been achieved. There are certain requirements that the resultant suspension must fulfil for the phase inversion and sintering process to be successful. The solvent must be miscible with water as water is almost invariably the chosen non-solvent to induce phase inversion. The polymer must dissolve in the solvent but be completely insoluble in the
non-solvent (water) and the inorganic content must be sufficiently high so as to prevent the destruction of the fibre structure during calcination.

**The ceramic material/polymer binder ratio:** The importance of the ceramic material/polymer binder ratio in determining hollow fibre properties has been demonstrated by both Liu et al. [57] and Tan et al [58]. If ceramic hollow fibre membranes are to be incorporated into a membrane module it is necessary that they poses a degree of mechanical strength which can be achieved by increasing the ceramic/polymer ratio in the spinning suspension. However, an increase in the this ratio beyond a certain threshold results in the formation of a paste rather than a ceramic suspension, making fibre spinning impractical as a result of the discontinuity of the paste and of particle aggregates which may become lodged in the spinneret. Moreover, the viscosity of a paste is often high and tends to result in a symmetric fibre structure, as will be discussed in Chapter 4. It was found by Tan et al. [58] that alumina hollow fibre precursors could not be spun if the ceramic/polymer ratio is greater than 9, however, by blending particle sizes this ratio may be increased further. It was shown that as the ratio of ceramic material to polymer binder was increased both the maximum (defect) and mean pore size were seen to decrease, with the largest decrease seen for the defect pores and that this effect was accompanied by a reduction in surface porosity. This is expected as the pores are the voids that remain after the polymer has been burned away. The largest surface pores are assumed to be the defect pores and are undesirable as not only do they affect the selectivity of the membrane but may also interfere with processes such as vacuum-assisted dip coating [59] which may be used to create a defect free skin layer. Defects in the membrane surface may give rise to defects in the coating, necessitating the
application of further coatings which is both expensive and time consuming. Liu et al. [57] have shown that for suspensions of 1 \( \mu m \) \( \text{Al}_2\text{O}_3 \) particles a large increase in the 3 point bending strength from 197 to 304 MPa is observed when the \( \text{Al}_2\text{O}_3/\text{polyethersulfone (PESf)} \) ratio is increased from 8 to 10 indicating that for this system the \( \text{Al}_2\text{O}_3/\text{PESf} \) ratio is the dominating factor determining the strength of the fibres. However, an increase in the ceramic content leads to a denser membrane structure and results in a decrease in permeability and flux which is not beneficial for many applications and the fact that gas permeability is seen to tail off at ratios above 7 indicates that a dense membrane structure has been formed [49,57]. The optimum ceramic material/polymer binder ratio, resulting in a membrane that is both sufficiently strong and sufficiently porous will depend on the application, although a minimum 3P value of 100 MPa or above is generally required for module production.

**Particle size:** Tan et al. have also demonstrated the importance of particle size on fibre properties in terms of the pore size distribution and porosity. In order to both increase the \( \text{Al}_2\text{O}_3 \) content in the spinning suspension and to control factors such as maximum and mean surface pore sizes and surface porosity, \( \text{Al}_2\text{O}_3 \) particles of varying sizes may be introduced into the spinning suspension. Experiments by with blends of 1/0.01 \( \mu m \) [58] \( \text{Al}_2\text{O}_3 \) particles have shown that membrane properties have been augmented by the addition of these smaller particles. Using a gas permeation technique developed by Kong and Li [60] it was shown that a reduction in maximum (defect) pore size results from the addition of 0.01 \( \mu m \) particles which is accompanied by a slight increase in mean pore size. It was also shown that both the surface and volumetric porosity increased with the addition of 0.01 \( \mu m \) particles to the spinning suspension. This result is anomalous and
contradicts theoretical calculations on particle packing undertaken by Lu et al. [61]. However, due to the complexities and dynamic nature of the phase inversion process used for the preparation of these fibres the nature of particle packing during this process is unclear. Liu et al. [57] studied the 3 point bending strength of fibres prepared with blends of 1/0.3/0.01 µm particles and determined that substantial increases in mechanical strength over a wide range of calcination temperatures were achieved by the addition of 0.01 µm particles to the spinning suspension.

The effect of the suspension composition on important fibre properties such as pore size, porosity, permeability and mechanical strength has been demonstrated in previous studies. How the properties of the spinning suspension are affected by these compositional variations and how this affects hollow fibre morphology will be discussed in Chapter 3.

**Fibre spinning (Stage 2):** Spinning of hollow fibre membranes using the combined phase inversion and sintering process is an extremely useful technique for the production of asymmetric membranes and membrane supports with varying morphologies. A great deal of control over fibre morphology can be achieved due to the many spinning parameters that are involved and the interdependence of these parameters. Ceramic hollow fibre membranes are essentially prepared in the same manner as their polymeric counterparts as the phase inversion process is utilized as a means of controlling the characteristics and morphology of the fibre. A quantity of inorganic powder forms part of, in its most basic form, a three component system consisting of inorganic powder, binder and solvent but in reality additives are required to produce a usable suspension. Additives may take the form of dispersants, used to prevent the undesired aggregation of
inorganic particles and polymers to influence the viscosity. It is also essential to degas the spinning suspension prior to spinning to prevent gas bubbles from being incorporated into the membrane structure thus reducing its integrity and uniformity. A typical spinning suspension may contain approximately 50-60 wt% inorganic material, 30-40 wt% solvent and 6-7 wt% binder. Inorganic material is by far the main constituent of the suspension and it is important that the precursor suspension is mixed sufficiently so that particles are completely surrounded by the binder. Prior to fibre preparation the spinning parameters must be chosen carefully and tailored to each suspension composition in order to achieve the desired membrane structure. Some parameters are listed below:

- Spinning suspension composition.
- Spinning suspension viscosity.
- Fibre extrusion rate.
- Internal coagulant composition.
- Internal coagulant flow rate.
- External coagulant composition.
- Air-gap between spinneret and precipitation bath.

Although the existence of many parameters that affect the fibre properties can make fibre preparation difficult to predict, if a good level of understanding of the fibre formation process is achieved then the presence of many parameters allows for a high level of
control over the fibre structure. Figure 2.3 shows apparatus used for the preparation of asymmetric hollow fibres.

Figure 2.3: Hollow fibre spinning apparatus.

The spinning suspension is extruded through the outer annulus of the tube-in-orifice spinneret into a bath containing a precipitant, usually water, for the polymer phase present in the suspension. At the same time an internal precipitant, or bore fluid, is injected through the inner annulus of the spinneret to form the fibre lumen.

**Co-extrusion:** The versatility of the combined phase inversion and sintering technique is further demonstrated by the preparation of dual-layer hollow fibres in a single step by using a triple orifice spinneret, shown schematically in Figure 2.4.
The principals regarding the formation of finger-like and sponge-like structures as a result of viscous fingering during the phase inversion process are very similar for both single layer and dual-layer fibre fabrication. A fibre is prepared in the same way except that a second suspension is extruded through the outer annulus of the triple orifice spinneret to form a dual layer hollow fibre. The relative thickness of the two layers is determined by their extrusion rates and in particular the viscosity of the respective suspensions. In addition, the properties of the two suspensions must be similar in order that good adhesion between the two layers is achieved. However, the sintering behaviour of the inner and outer layers is likely to be different if they are composed of different materials and consequently, knowledge of the sintering behaviour of these materials is essential in order to produce a good quality final product.

**Heat treatment (Stage 3):** Calcination of hollow fibre precursors involves three principal stages, pre-sintering, thermolysis and final sintering. Pre-sintering occurs at
temperatures up to 200 °C and is a means of removing residual liquid that may remain after formation of the fibre precursor, any moisture that has been absorbed from the atmosphere and water of crystallization that may be present in the ceramic material [62]. It is important to increase the temperature slowly as expanding vapour within the lattice may cause cracks and fractures. A typical calcination profile is shown in Figure 2.5.

![Calcination Profile](image)

**Figure 2.5**: A typical calcination profile for hollow fibres prepared in this work.

Thermolysis of the polymer binder occurs as the temperature is increased to approximately 600 °C. During this stage it is of the utmost importance that the binder is completely removed as any remaining binder may introduce defects [62]. It is also important that sufficient oxygen is available for complete thermolysis to occur so as to avoid the formation of carbon deposits. It has been shown by Liu et al. [57] that greater shrinkage occurs for membranes prepared from smaller particles and this has been put down to the fact that, all other factors being equal, a smaller particle size will result in a greater overall volume of voids between the particles. The voids in the fibre precursor are filled with binder which is removed during thermolysis, leading to greater shrinkage for membranes prepared from smaller particles. The porosity of the fibre after thermolysis
and prior to sintering is also determined by the ceramic material/polymer binder ratio with a high ratio giving rise to a less porous structure and less shrinkage during sintering. Final sintering does not begin in earnest until the temperature reaches approximately two thirds of the melting point of the membrane material, however, as the driving force for sintering is a reduction in surface free energy, smaller particles will sinter more readily than larger ones due to their larger surface areas. This may pose a problem as the degree of sintering that is required to fuse larger particles together may result in an excessive level of sintering for smaller particles. In order to prepare a robust membrane or membrane support sintering must continue for long enough to fuse together larger particles present in the fibre structure. The consequence of this is a lack of control over the degree of sintering of smaller particles. However, it may be possible to combine different inorganic powders with different particle sizes and melting points to better control crystal growth during sintering. Sintering proceeds so as to give an overall reduction in surface free energy and will result in the reduction or elimination of free surfaces. This is due to the presence of partially coordinated atoms at grain boundaries and surfaces which have a higher free energy than fully coordinated atoms in the bulk of the material. Sintering can be divided into three stages, initially densification occurs followed by grain coarsening and finally pore closing [62]. At low temperatures the membrane is seen to undergo rapid densification with negligible grain growth whereas the opposite is true at elevated temperature, Figure 2.6. Table 2.2 lists different mass transport mechanisms present during sintering and their effect on the density of the membrane.
Figure 2.6. The effect of sintering temperature on grain size and membrane shrinkage (figure adapted from Ceramic Membranes for Separation and Reaction, Kang Li, Wiley 2007).

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Densification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface Diffusion</td>
<td>No</td>
</tr>
<tr>
<td>Evaporation-condensation</td>
<td>No</td>
</tr>
<tr>
<td>Grain boundary diffusion</td>
<td>Yes</td>
</tr>
<tr>
<td>Lattice diffusion</td>
<td>Yes</td>
</tr>
<tr>
<td>Viscous flow</td>
<td>Yes</td>
</tr>
<tr>
<td>Plastic flow</td>
<td>Yes</td>
</tr>
</tbody>
</table>

Table 2.2: Mass transport mechanisms operating during sintering and their effect on membrane densification (table adapted from Ceramic Membranes for Separation and Reaction, Kang Li, Wiley 2007).

Neck growth, as shown in Figure 2.7, occurs as a result of variation in vapour pressure as a function of surface curvature. A positive radius of curvature exists at the particle surface while the opposite is true where two particles touch or join. As a result of this,
vapour pressure at the particle surface is greater than at the joint between particles causing a transfer of material from the particle surface to the joint.

![Figure 2.7](image)

Figure 2.7: A qualitative model of grain growth. (a): Two particles of differing size in contact with each other, (b): “neck” growth by surface diffusion between particles and (c): grain growth.

The final sintering stage and its effect on pore structure is one of the most important factors when fabricating separation membranes. The defining feature of a pore that will determine whether it will open or close during sintering is the critical pore coordination number, N [62] which is the number of grains surrounding a pore. When N = 6 the pore has straight sides and is said to be metastable and will neither expand nor contract. For values of N > 6 the pore will have concave sides and pore expansion will occur and for values of N < 6 the pore has convex sides and pore contraction will occur. This can be rationalized when thinking about the geometry of the pore walls, for N > 6 the pore wall will consist of a number of inward facing curved segments and as these segments contract towards their centre of curvature the pore is thus expanded. The opposite is true of pores with N < 6. In this case wall segments are outward facing curved units and contraction
towards their centre of curvature will result in a decrease in pore size. These processes are shown schematically below, Figure 2.8.

Figure 2.8: Pore stability and evolution in two dimensions.

Using this model it may be possible to design pore geometry prior to sintering to create pores that either remain stable or shrink.

**Calcination temperature:** The effect of varying the calcination temperature has been investigated by Tan et al. [58] and in order to negate the influence of the ceramic/polymer ratio on the results, a ratio of 5 was used throughout the experiments. As would be expected, membrane shrinkage occurred during the sintering process as organic binder was removed and particles fused together. The use of a shrinkage ratio, defined as the ratio of the sintered fibre outer diameter to the fibre precursor outer diameter allows easy comparison between calcination temperatures. As the temperature was increased from 1180 to 1600 °C the ratio was seen to decrease from 0.93 to 0.74 illustrating the greater shrinkage that occurs at higher temperatures. An interesting and welcome effect was the reduction of the maximum pore size (defect pores) without the reduction of average pore size.
However, although the average surface pore size was not seen to change greatly after an increase in calcination temperature, the volumetric porosity, calculated using Equation 2.1, were seen to decrease, effects that are unwanted and which pose a problem at elevated calcination temperatures.

Equation 2.1

$$\varepsilon_v = \frac{\left(\omega_{\text{wet}} - \omega_{\text{dry}}\right) / \rho_{\text{H}_2\text{O}}}{\left(1/4\right)\pi L (D_o^2 - D_i^2)}$$

where $\varepsilon_v$ is the volumetric porosity of the membrane, $(\omega_{\text{wet}} - \omega_{\text{dry}})$ is the weight of water absorbed, $L$ is the fibre length and $D_o$ and $D_i$ are the inner and outer diameters of the fibre respectively and $\rho_{\text{H}_2\text{O}}$ is the density of deionised water.

An important point to note is the relationship between calcination temperature and mechanical strength which is increased at elevated temperatures and is expected to reach a global maximum before decreasing. It has been observer by Liu et al. [57] that when the calcination temperature is below 1500 °C the 3 point bending strength value is proportional to the temperature, however, as the temperature is increased above 1500 °C a sharp increase in this value is observed. It is demonstrated in Chapter 5 that a maximum exists in a plot of mechanical strength vs. calcination temperature which will vary depending on the type of ceramic material and the composition of the spinning suspension. This maximum exists as the mechanical strength of the ceramic material is a function of both the porosity and the grain size. As porosity decreases, the strength of the fibre is seen to increase, however, an increase in calcination temperature also leads to an increase in grain size which has a negative effect on mechanical strength. Therefore,
when these two effects are overlapped, shown schematically in Figure 2.9, a maximum value is obtained.

![Figure 2.9: A schematic representation of the effect on mechanical strength of a simultaneous reduction in porosity and increase in grain size.](image)

2.4 Conclusions

Due to developments in polymer science that have taken place over the last 70 years polymeric membranes have advanced considerably during this time. Filtration and gas separation using polymeric membranes has been commercialised for many years, however, high temperature applications are beyond the scope of polymer membrane science and technology. Although ceramic membranes have been used for filtration purposes since the 1970’s it is only relatively recently that they have begun to be used for high temperature applications for which they are best suited. A number of ceramic
materials have been developed in recent years to prepare both porous and non-porous membranes and membrane supports for use in a wide range of high temperature applications, such as membrane reactors and solid oxide fuel cells. Efforts have been made to increase surface area to volume ratios of membrane modules with the introduction of tubular, multi-tubular and capillary ceramic designs. However, traditional preparation techniques used to fabricate these structures are often costly and time consuming in addition to only yielding a limited variety of membrane morphologies. By using the combined phase inversion and sintering technique a wide range of morphologies can be prepared in a cost effective way for use in a great variety of applications. This process involves the preparation of a ceramic/polymer/solvent suspension, fibre spinning and heat treatment and control over hollow fibre properties such as pore size, porosity and mechanical strength is achieved by manipulating parameters at each of these preparation stages.

2.5 References


[39] B. Zydorczak, Z. Wu and K. Li, Fabrication of ultrathin La0.6Sr0.4Co0.2Fe0.8O3-[delta] hollow fibre membranes for oxygen permeation, Chemical Engineering Science 64 (21) (2009) 4383-4388.


Chapter 3

A Study on the Rheology and Extrusion of Ceramic/Polymer/Solvent Suspensions for the Fabrication of Ceramic Hollow Fibre Membranes and Membrane Supports

Abstract

The focus of this chapter is the preparation and rheological properties of ceramic/polymer suspensions used for the preparation of ceramic hollow fibres by the combined phase inversion and sintering method. The properties of the spinning suspension are paramount in determining the quality of the final product, the reproducibility of the production process and in particular, the degree of control over the fibre structure that can be achieved during fibre spinning. It has been shown that factors such as the content of ceramic material, the particle size distribution and the milling time have a great effect on the rheology of the spinning suspension and due to the three component nature of the suspension and the wide variation in particle size, the rheology may be complex and unpredictable.
3.1 Introduction

It has been shown that a number of factors affect the suspension rheology, including the composition of the suspension with respect to the ceramic content and the particle size distribution as well as the time taken to mill the ceramic/solvent mixture. As there are two components present in the suspension excluding the solvent (ceramic material and polymer binder) the system is far more complex than a polymeric solution or a ceramic dispersion alone. Such suspensions are highly non-Newtonian and may exhibit a wide range of behaviours when subjected to different shear rates. The principal factors affecting the properties of the suspension are the ceramic content, the particle size distribution and the milling time.

Although the preparation of ceramic suspensions and ceramic-polymer suspensions from particles with sizes in the range 0.1-5 µm is routinely achieved for the purposes of tape casting [63], slip casting [64,65] and fibre extrusion [66], the dispersion of smaller particles has proved problematic. The solids content of a suspension not only depends on particle size but also on particle size distribution, particle shape and the effective volume of the particle. It is usual to combine the volume occupied by both the particle and the steric layer, formed by the adhesion of dispersant molecules to the particle surface, together to give a value for the effective packing fraction, given by Equation 3.1.

\[
\phi_{\text{eff}} = \phi \left(1 + \frac{\delta}{r}\right)^3
\]

where \(\delta\) = the thickness of the dispersant interaction length and \(r\) is the radius of the particle.
Although steric stabilization is effective for ceramic dispersions containing particles above 100 nm, as particle size is reduced below this threshold the volume occupied by the steric layer is no longer negligible compared with the particle volume [67]. This poses a problem when preparing ceramic suspensions for fibre spinning as an increase in the concentration of smaller particles is often, but not always, desired as an increase in mechanical strength and a decrease in pore size is observed after calcination [68]. Although aqueous ceramic dispersions and suspensions have been prepared from alumina powders with particle sizes in the nanometre range [69,70], the solids loadings of these systems are not sufficient to form fibres using the combined phase inversion and sintering technique and the aqueous nature of the system is not compatible with the phase inversion process. In addition, these systems do not contain a polymer binder which is likely to reduce the total possible solids loading. In order to increase the solid content of suspensions in the sub 100 nm range a suitable combination of electrostatic and steric stabilization must be present and parameters such as pH, ionic strength and dispersant concentration must be optimized. For ceramic/polymer suspensions prepared for fibre spinning a polymer binder component is present and the interaction of the polymer binder with the dispersant is unknown. Moreover, the use of N-methyl-2-pyrrolidone (NMP), an aprotic solvent, is not beneficial when preparing suspensions of particles with hydroxylated oxide surfaces such as alumina. However, the particle size distribution has been shown to have a considerable effect on the maximum packing fraction of ceramic suspensions [71,72]. Therefore, in this study a commercially available dispersant (Arlacel P135) has been used at an optimum concentration determined in a previous study and the
focus has been on the variation of the particle size distribution and the milling time of the ceramic/solvent mixture.

A study on the effect of the suspension rheology during the spinning process has been conducted with particular regard to the suspension viscosity which is strongly dependant on the properties mentioned above. The fibre preparation process begins with the dissolution of a suitable dispersant in a chosen phase inversion solvent such as NMP, which is miscible with water. The use of a suitable dispersant leads to the formation of a homogenous suspension, allowing for the preparation of a final product with a more homogenous structure and a lower concentration of defects. Following the addition of ceramic material to the solvent/dispersant mixture, the resultant ceramic/solvent dispersant mixture is ball milled to produce a homogenous suspension and it will be shown that this milling stage is absolutely critical in determining the final properties of the suspension and hence the properties of the final product. As mentioned previously, the particle size distribution has a large effect on the rheology of the suspension and hence the behaviour of the suspension during spinning. During the milling process, aggregates of particles are broken down and are coated with dispersant molecules, therefore, the milling process strongly affects the effective particle size in the suspension and consequently a variation in milling time can lead to suspensions with identical compositions having vastly different final characteristics. If fibres are to be successfully prepared then there are two principal concerns with respect to the viscosity of the spinning suspension, namely, the design of the spinneret and the precipitation and elongation of the nascent fibre. As the suspension viscosity is critical in determining the quality and structure of the prepared fibres, it is logical to first discuss the effect that a
variation in viscosity has on the formation of the fibre and then to investigate the factors that determine the viscosity during the suspension preparation stage.

3.2 Experimental

3.2.1 Materials

Aluminium oxide powders, mean particle size = 180 µm (alpha phase, purity = 99.7 % metals basis), mean particle size = 1 µm (alpha phase, purity = 99.9 % metals basis, surface area 6-8 m²/g), mean particle size = 0.3 µm (gamma/alpha phase, purity = 99.9 % metals basis, surface area 15 m²/g), mean particle size = 0.05 µm (gamma/alpha phase, purity = 99.5 % metals basis, surface area 32-40 m²/g) and mean particle size = 0.01 µm (gamma/alpha phase, purity = 99.98 % metals basis, surface area 100 m²/g) were purchased from Alfa Aesar (a Johnson Matthey company) and were used as supplied. Polyethersulfone (Radel A300, MW = 42500 g/mol, Ameco Performance, USA), N-methyl-2-pyrrolidone (MW = 99.13 g/mol, HPLC grade, Rathbone) and Arlacel P135 (Polyethyleneglycol 30-dipolyhydroxystearate, Uniqema) were used as binder, solvent and dispersant respectively.

3.2.2 Suspension preparation

Arlacel P135 at a concentration of 0.1 wt%/total surface area of the ceramic material was dissolved in NMP prior to the addition of aluminum oxide powders. The suspension was rolled/milled with 20 mm agate milling balls with an approximate Al₂O₃/agate weight ratio of 2 for between 2 days and 2 weeks. Mixing was performed for a further 1.73 x 10⁵-2.27 x 10⁵ s (48-63 hours) after the addition of PESf (6.1 wt%). The suspension was
then transferred to a gas tight reservoir and degassed under vacuum while stirring until no bubbles could be seen at the surface. PESf/NMP solutions were prepared by adding PESf pellets (20 wt%) to NMP and stirring overnight. Solutions were then left to stand at ambient temperature and pressure until no bubbles were visible in the solution prior to rheological characterization.

3.2.3 Viscosity measurements

Viscosity data was collected (Physica UDS-200 rheometer) using concentric cylinder geometry at shear rates between 6-1000 s\(^{-1}\) at 20 °C with a gap height of 37.5 mm, a gap width of 1.06 mm and a sample volume of 17 ml. Samples were taken for analysis immediately after the degassing procedure.

3.2.4 Microscopy

SEM characterization was conducted for sintered fibres which were flexed at ambient temperature until a fracture occurred prior to being mounted on an SEM slide. Samples were gold coated under vacuum for 180 s at 20 mA (EMITECH Model K550) and SEM images were collected (JEOL JSM – 5610 LV).

3.2.5 Spinneret design

Figure 3.1 shows photographic images of a spinneret assembly with inner and outer annuli diameters of 1.2 and 3 mm respectively.
Figure 3.1: Photographic images of (a): the entire spinneret assembly, (b): view of suspension injection channels and the inner annulus, (c): internal cavity and (d): outer surface of spinneret showing inner and outer annuli.

The ceramic suspension is fed into the internal cavity within the spinneret structure shown in Figure 3.1(c) through four injection channels indicated in Figure 3.1(b) and from there the suspension exits the spinneret assembly through the region between the inner and outer annuli, Figure 3.1(d). Internal precipitant is simultaneously injected through the inner annulus to form the fibre lumen.
3.3 Results and discussion

3.3.1 Fibre formation

The process of fibre spinning involves the extrusion of the ceramic suspension through a tube-in-orifice spinneret followed by precipitation of the polymer phase to yield a ceramic hollow fibre precursor. The processes involved in the formation of the fibre morphology are discussed in the following chapters, and it is shown that the viscosity of the suspension and the precipitation rate of the polymer phase are key factors in this process. However, it is also necessary to match the viscosity of the suspension with the design of the spinneret.

For the fibre wall to be a continuous structure, suspension must exit the outer annulus uniformly around its entire diameter, shown schematically in Figure 3.2.

![Schematic Diagram](image_url)

Figure 3.2: A schematic diagram of optimal suspension flow through a tube-in-orifice spinneret.
The grey area represents the ceramic suspension that has been injected into the internal cavity through the injection channels and the arrows represent the flow of the suspension out of the spinneret. For successful fibre formation to occur the internal cavity must be filled with suspension (grey area in Figure 3.2) and if this criteria is not fulfilled then the fibre wall will not be continuous and will consist of four individual sections, one for each of the four injection channels, as shown schematically in Figure 3.3.

![Image](image-url)

**Figure 3.3:** A schematic diagram of insufficient suspension flow through a tube-in-orifice spinneret.

In this situation, the internal cavity is not filled and the suspension flows directly from the injection channels down the wall of the internal cavity and exits the spinneret in four separate streams, leading to a non-uniform fibre precursor wall and in extreme cases, four individual strands.
Whether or not the internal cavity is filled with suspension depends on the dimensions of the spinneret, the diameter of the outer annulus and most importantly the suspension viscosity and extrusion rate. A schematic representation of a non-uniform fibre wall resulting from an insufficient suspension viscosity and/or extrusion rate can be seen in Figure 3.4.

![Figure 3.4: A schematic representation of a non-uniform fibre wall resulting from an insufficient suspension viscosity and/or extrusion rate.](image)

By matching the extrusion rate and the suspension viscosity (a high extrusion rate for a low viscosity) fibres can be prepared with a uniform wall thickness, as shown in the SEM image in Figure 3.5.
Figure 3.5: An example of an alumina hollow fibre with a uniform wall thickness.

In this case the fibre possesses a wall of uniform thickness as an increase in extrusion rate and/or suspension viscosity results in the complete filling of the chamber within the spinneret structure. Therefore, for a given viscosity and outer annulus diameter there is a minimum extrusion rate that is necessary for successful fibre formation. This severely limits the level of control that can be achieved over the fibre morphology for reasons discussed in the following chapters as it is not possible to vary the extrusion rate, one of the most critical parameters, over a wide range.

### 3.3.2 Fibre elongation

The use of an air-gap between the spinneret and the precipitation bath allows for the preparation of asymmetric structures that are extremely useful for a number of applications. Due to the desired high ceramic content in suspensions used for ceramic hollow fibre preparation, the suspension tends to be relatively heavy. This allows the fibre to be spun directly into a precipitation bath where it coils at the bottom of the
container due to its considerable weight. This process has the advantage that fibre precursors that are extremely brittle/delicate due to high solids loadings can be formed without the use of collecting drums which may break such fibres during the fabrication process. However, due to the weight of the nascent fibre, the fibre precursor is stretched due to gravity as it is being formed, which has two effects. (A) The fibre is stretched and this stretching may result in the fibre breaking during spinning and (B) the stretching of the fibre may result in the nascent fibre not filling the region between the inner and outer annuli completely and consequently the outside of the nascent fibre does not make contact with the outer annulus. These issues will be addressed in turn.

(A): As the suspension exits the outer annulus of the spinneret and makes contact with the internal precipitant supplied through the inner annulus, polymer precipitation is initiated, the suspension viscosity is increased and the nascent fibre is imparted with some degree of mechanical strength, which gives resistance to elongation of the fibre and breakage. If the viscosity of the suspension is initially low then the time taken for the nascent fibre to gain sufficient strength to resist breakage is too long and the fibre will be stretched to breaking point before gaining sufficient strength. The degree of fibre elongation and the tendency of a fibre to break are dependent on the weight/length of nascent fibre that is supported by the region close to the spinneret, which is determined by the depth of the precipitation bath. If the initial viscosity of the suspension is sufficiently high then as the nascent fibre is brought into contact with the internal precipitant the fibre is imparted with mechanical strength quite rapidly and will resist elongation and breakage. Likewise, if the depth of the precipitation bath is reduced, the weight of the fibre that is supported by the region close to the exit of the spinneret is also reduced and fibre elongation and
breakage is prevented. Therefore, by reducing the depth of the precipitation bath, fibres may be formed from suspensions with lower viscosities. However, as discussed in the following section, for suspensions with low viscosities, additional problems are associated with reducing the depth of the precipitation bath which may result in a non-central fibre lumen. The process of fibre elongation and/or breakage is closely tied with the viscosity of the suspension which is in turn connected to the precipitation rate of the polymer phase. By increasing the internal precipitant flow rate the precipitation rate of the polymer phase can be increased as the ratio of non-solvent to suspension is greater and the fibre can be imparted with sufficient strength. However, this severely limits the level of control over fibre morphology that can be achieved as the range over which the internal precipitant flow rate can be varied is severely reduced.

(B): Elongation of fibres prepared from suspensions with lower viscosities may increase to such a degree that the suspension no longer occupies the outer annulus completely. If the depth of the precipitation bath is sufficient, this fact results in a fibre with a reduced diameter and wall thickness which is not necessarily disadvantageous. However, as discussed above, to avoid fibre breakage the depth of the precipitation bath must be reduced, which results in a fibre lumen that is not in the centre of the fibre cross section for the following reason.

The nascent fibre is deposited in a circular fashion at the bottom of the precipitation bath, Figure 3.6, and consequently, the point at which the fibre exits the spinneret and the point at which it makes contact with the bottom of the precipitation bath are offset and the fibre is forced to exit the spinneret at an angle.
Figure 3.6: Hollow fibre precursor deposited at the bottom of a precipitation tank containing 120 L of water.

This angle is determined by the diameter of the fibre coil, which is in turn determined by the rigidity of the nascent fibre as it is deposited at the bottom of the precipitation tank, and the distance between the spinneret and the coiled fibre. If the viscosity and/or the precipitation rate of the suspension is insufficient then the bottom of the precipitation tank must be raised to avoid excessive fibre elongation and breakage. If the suspension occupies the outer annulus completely then this fact is of no consequence as the fibre wall will be uniform and the thickness will be determined by the dimensions of the spinneret and the combination of spinning parameters. However, for suspensions with low viscosities this may not be the case and a gap may exist between the outside of the nascent fibre and the circumference of the outer annulus, due to fibre elongation. If this is the case and if the depth of the precipitation bath is sufficient then this angle is reduced to the point of being negligible. However, by reducing the depth of the precipitation bath this angle is increased from $\theta$ to $\theta'$ as shown in Figure 3.7.
Figure 3.7: Schematic representation of the angle at which the nascent fibre exits the spinneret.

Eventually, as the angle is increased, a point will be reached where the nascent fibre makes contact with the outer annulus. This point of contact will move around the circumference of the outer annulus as the fibre is deposited at the bottom of the precipitation tank in a circular fashion. This results in the formation of a fibre with a lumen that is not central within the fibre cross section, Figure 3.8.
Figure 3.8: An SEM image of a ceramic hollow fibre with an asymmetric lumen.

The effect that suspension viscosity has on the practical aspects of fibre spinning not only limits the level of control over the fibre morphology that can be achieved, by reducing the ranges over which spinning parameters and suspension compositions can be varied, but may also be a major consideration when attempting to scale-up the process. However, with prior knowledge of these phenomena it is possible to design a spinning system and formulate a suspension composition to take these considerations into account and to synchronise the many parameters involved in the spinning process so as to avoid or minimise these problems.

3.3.3 Suspension rheology

Rheology is the study of the deformation and flow of matter. Many liquids are considered to be Newtonian in nature in that their viscosity does not change as they are subjected to varying levels of shear. For non-Newtonian fluids this is not the case and the viscosity may either increase with increasing shear (shear thickening) or decrease with increasing
shear (shear thinning). Many more systems, both polymeric and ceramic, are found to be shear thinning. Suspensions containing solvent, polymer and ceramic materials, with a broad range of particle sizes exhibit complex rheology over a range of shear rates. Figure 3.9 shows the viscosity at shear rates between 6-1000 s$^{-1}$ of a solution of 20 wt% polyethersulfone (PESf) in N-methyl-2-pyrrolidone (NMP), a suspension of alumina particles of varying sizes in NMP before the addition of PESf, as well as the same suspension after the addition of PESf. The rheological profile for the PESf/NMP solution and for the alumina/NMP suspension both obey traditional power law models for shear thinning behaviour. However, the rheological profile for the alumina/PESf/NMP system is far more complex and exhibits several different behaviours at different shear rates.

![Rheological behaviour of polymer and ceramic suspensions](image)

Figure 3.9: The rheological behaviour of a polymer solution, a ceramic suspension and a polymer/ceramic suspension at varying shear rates.
At low shear the alumina/polymer/solvent system exhibits shear thinning behaviour similar to that of the alumina/NMP suspension. However, as the shear rate approaches 50 s\textsuperscript{-1} shear thickening behaviour is seen to emerge. Shear thinning behaviour is re-established at 100 s\textsuperscript{-1} and continues until approximately 900 s\textsuperscript{-1} where a Newtonian plateau is observed. Due to the wide range of behaviours exhibited for such spinning suspensions it is extremely difficult to predict the rheological profile from the composition of the suspension alone. Therefore, in order to predict the final fibre morphology it is essential to have prior knowledge of the suspension rheology and to vary the spinning parameters accordingly to generate the desired structure.

Due to the complex nature of ceramic/polymer/solvent systems with high solids loadings and blended particle sizes, preparing suspensions with reproducible properties can be challenging. It has been established in this work and is discussed in the following sections that the particle size distribution and milling time are critical in determining the rheological properties. Therefore, slight variations in aspects of the suspension preparation process can lead to slightly different rheological profiles for suspensions supposedly prepared under the same conditions, these include:

1. The nature of the ceramic powders and the particle size distribution which may vary slightly between batches. This includes how the powders are stored which may affect the level of particle aggregation prior to milling.

2. The speed of rotation of the milling device as well as the weight, number and size of the milling balls used. All of these factors determine the extent to which the ceramic material is milled and the interaction between the suspension and the
milling balls. Consequently, the effect of the size and shape of the container as well as the quantity of material inside and the level to which the container is filled all contribute to the resulting rheological profile of the suspension after milling.

As it is difficult to prepare suspensions with perfect reproducibility, the need to determine the rheological profile prior to fibre spinning is paramount so that any necessary adjustments can be made to the spinning parameters to achieve the desired fibre structure.

**Particle size distribution:** The introduction of smaller particles into the spinning suspension may be beneficial under certain circumstances as a reduction in membrane pore size and an increase in mechanical strength may result. It is shown in Chapter 5, Section 5.3.1 that fibres containing a higher percentage of smaller particles have greater mechanical strength when calcined at the same temperature and work conducted by Tan et al. [68] has shown that a reduction in pore size can be achieved by the addition of nanometre size particles to the suspension. However, the addition of smaller particles leads to a dramatic increase in the particle surface area which leads to particle aggregation due to van der Waals interactions between the particle surfaces. Therefore there is a maximum solids loading that can be achieved for a given particle size without the occurrence of particle aggregation and the formation of a paste.

Aggregation of particles can be loosely defined as either agglomeration or flocculation, although many different conformations exist within these definitions. Agglomeration refers to the formation of particle clusters, resulting from direct interparticle contact, which are difficult to break up while flocculation on the other hand refers to the formation of weakly bound extended structures which can be destroyed with moderate
shear stresses. Not only does the formation of a paste lead to inhomogeneity in the membrane structure but may also lead to blockage of spinnerets with narrow diameters. Furthermore, for reasons discussed in Chapter 4, Section 4.3.1 it is difficult to form asymmetric membrane structures when the suspension viscosity is above a certain level. Therefore, a balance must be achieved in which the suspension viscosity is above the level at which spinning is facilitated but below the level at which particle aggregation takes place and the formation of asymmetric structures becomes difficult. All suspensions studied were prepared according to the compositions shown in Table 3.1 with the only variation being that of particle size distribution. The optimum dispersant concentration was determined in a previous study and corresponds to the global minimum in a plot of viscosity vs. dispersant concentration, divided by the surface area of the ceramic material to give an optimum concentration in g/m². Therefore, the weight of dispersant divided by the total surface area of the ceramic material was maintained at 0.001 so as to achieve equal particle surface coverage as the surface area of the particles in the suspension is increased. Consequently, differences in the quantity of dispersant used in each suspension results in slight variations in the weight percentages of the other components. However, these small variations are negligible and the weight ratio of ceramic material to polymer binder remains the same throughout. Table 3.1 shows the concentration of components in suspensions A-G.
Table 3.1: Alumina powder ratios and suspension compositions for suspensions A-G.

Figure 3.10 shows viscosity data over a shear rate range of 6-100 s\(^{-1}\). The dramatic effect of a decrease in particle size can be clearly seen from the viscosity data, the key for which is shown in Table 3.1.

<table>
<thead>
<tr>
<th>Suspension</th>
<th>NMP (wt%)</th>
<th>Alumina (wt%)</th>
<th>Alumina particle size (wt% of total alumina content)</th>
<th>PESf (wt%)</th>
<th>Arlacel P135 (wt%)</th>
<th>Alumina/PESf ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>34.3</td>
<td>59.4</td>
<td>1 micron = 50 180 micron = 50</td>
<td>6.1</td>
<td>0.2</td>
<td>9.7</td>
</tr>
<tr>
<td>B</td>
<td>34.2</td>
<td>59.3</td>
<td>1 micron = 75 180 micron = 25</td>
<td>6.1</td>
<td>0.3</td>
<td>9.7</td>
</tr>
<tr>
<td>C</td>
<td>34.2</td>
<td>59.3</td>
<td>1 micron = 100</td>
<td>6.1</td>
<td>0.4</td>
<td>9.7</td>
</tr>
<tr>
<td>D</td>
<td>34.1</td>
<td>59.1</td>
<td>1 micron = 50 0.3 micron = 50</td>
<td>6.1</td>
<td>0.6</td>
<td>9.7</td>
</tr>
<tr>
<td>E</td>
<td>34</td>
<td>58.9</td>
<td>1 micron = 78 50 nm = 15 10 nm = 7</td>
<td>6.1</td>
<td>1.1</td>
<td>9.7</td>
</tr>
<tr>
<td>F</td>
<td>33.9</td>
<td>58.7</td>
<td>1 micron = 70 50 nm = 20 10 nm = 10</td>
<td>6.1</td>
<td>1.3</td>
<td>9.7</td>
</tr>
<tr>
<td>G</td>
<td>33.8</td>
<td>58.6</td>
<td>1 micron = 70 50 nm = 15 10 nm = 15</td>
<td>6.1</td>
<td>1.5</td>
<td>9.7</td>
</tr>
</tbody>
</table>
Figure 3.10: Rheological profiles of alumina/PESf/NMP suspensions A-G, prepared with a particle size range of 0.01-180 µm.

All viscosity values are quoted at a shear rate of 50 s\(^{-1}\) and particle concentrations are calculated as the wt% of the total ceramic content. Suspensions A and B are not suitable for fibre preparation due to the large size of the 180 µm particles but have been included to show the large increase in viscosity associated with the introduction of smaller particles. Although the ratio of 1/180 µm particles increases from 50/50 (Suspension A) to 75/25 (Suspension B) to 100/0 (Suspension C) the suspension viscosity is seen to increase by approximately only 1.3 Pa.s while the addition of 0.3 µm particles at a 1/0.3 µm ratio of 50/50 (Suspension D) leads to an approximate doubling of the viscosity. The large increase in viscosity after the addition of 50 and 10 nm particles at a combined
value of 22 wt% is clear from the data (Suspension E). Again, the viscosity is almost doubled compared to the suspension containing only 1 and 0.3 µm particles despite the addition of only 22 wt%, compared to the addition of 50 wt% of 0.3 µm particles (Suspension D). For Suspension F the percentage of 50 nm particles is increased from 15 to 20 wt% and the concentration of 10 nm particles is increased from 7 to 10 wt% resulting in a increase in viscosity to approximately 12.3 Pa.s, demonstrating the large increases in viscosity that result from the introduction of nanometre sized particles. In addition, the onset of shear thickening behaviour is seen as the particle size is reduced. By increasing the percentage of both 50 and 10 nm particles to 15 wt% the viscosity is increased further to approximately 14.1 Pa.s. At this viscosity the formation of asymmetric membrane structures is hindered and consequently Suspension F has been chosen for further study and membrane preparation.

By preparing a spinning suspension from a blend of particle sizes, the benefits of small particles in the suspension can be utilised while at the same time maintaining an appreciable total solids loading and a viscosity which is high enough to facilitate fibre preparation and low enough to allow for the formation of asymmetric membrane structures.

**Milling time:** The preparation of spinning suspensions consists of three stages. A suitable dispersant is dissolved in a solvent, after which the ceramic component is added and milling is performed for the desired amount of time in order to break down particle aggregates and coat the particle surfaces with dispersant molecules. After completion of the milling stage, the polymer binder is added and the mixture is mixed until the polymer is completely dissolved. It is important to note the difference between the milling and
mixing stages. During milling, the particle aggregates are broken down and the rheological behaviour of the suspension is fundamentally changed, however, the mixing stage is present only to dissolve the polymer binder and has no effect on the rheological nature of the suspension. This is demonstrated in Figure 3.11 which shows plots of viscosity vs. shear rate for suspensions milled for $1.8 \times 10^4$ and $3.6 \times 10^4$ s (5 and 10 hours) after which polymer binder (PESf) was added and mixing was performed until the polymer had completely dissolved (approximately $8.64 \times 10^4$ s, 24 hours). Samples were taken for rheological analysis and subjected to shear rates of between 5-1000 s$^{-1}$ after which mixing was continued for a further $5.4 \times 10^4$ s (15 hours) and the test was repeated. It can be seen from the data that although there is a substantial difference in the viscosity of the suspensions milled for $1.8 \times 10^4$ and $3.6 \times 10^4$ s (5 and 10 hours), their viscosities and rheological behaviour are virtually unchanged after an additional 15 hours of mixing.
Figure 3.11: The effect of additional mixing after the addition of the polymer binder for suspensions milled for 5 and 10 hours.

The data demonstrates that milling, prior to the addition of the polymer binder, is the critical phase in suspension preparation and determines the suspension properties. Figure 3.12 shows rheological data for Suspension F milled for varying amounts of time, ranging from 5 hours to 2 weeks.

![The effect of milling time on suspension rheology](image)

Figure 3.12: The effect of milling time on the rheology of Suspension F.

Despite the identical composition of all the suspensions studied, the large differences in rheology are clear from the plots of viscosity vs. shear rate. Initially, as the milling time is increased from 5-10-15 hours a reduction in viscosity is observed. However, as the
milling time is increased further, the viscosity is seen to increase dramatically, a shear thickening region develops at approximately 100 s\(^{-1}\) and the suspension becomes more shear thinning in nature, giving rise to a very different rheological profile. It is reasonable to assume that two effects are taking place in this case. Initially, milling serves to disperse the particles and allows for the absorption of dispersant on the particle surface, giving rise to a gradual reduction in suspension viscosity. As milling proceeds, the particle aggregates that are present are broken down and effectively the particle size is reduced and the surface area is increased, leading to an increase in suspension viscosity.

**Hysteresis of viscosity vs. shear rate:** Figure 3.13 shows the rheological profiles of suspensions milled for between 5 hours and 2 weeks and subjected to a shear rate cycle of 6-1000-6 s\(^{-1}\). The existence of hysteresis can be clearly seen in all suspensions regardless of their initial viscosity. Due to the increase in shear thinning behaviour for suspensions subjected to increased milling times, the viscosity of all suspensions tend to the same value as the shear rate approaches 1000 s\(^{-1}\). It can also be seen that regardless of the path that the rheological profile takes up to 1000 s\(^{-1}\), all suspensions return along the same path.
Figure 3.13: Hysterisis in the rheological profile of Suspension F when subjected to a shear rate cycle of 6-1000-6 s\(^{-1}\).

Point A indicated in Figure 3.13 shows the viscosity of Suspension F at a shear rate of 100 s\(^{-1}\) 2 hours after completion of the hysteresis loop. This demonstrates that the relaxation time for the Al\(_2\)O\(_3\)/NMP/PESf system is longer than two hours and that the viscosity of the suspension lies on the returning hysteresis curve for at least this duration. This has important consequences during the preparation of spinning suspensions and hollow fibres. For example, the suspension is stirred during the degassing process which will subject the suspension to a certain level of shear so the stirring rate should be minimized in order minimize the reduction in viscosity that may be associated with this process. In addition, the suspension may be subjected to high shear rates by pumping
equipment during fibre spinning which may also cause an unwanted reduction in viscosity and uncontrolled variation in the suspension properties.

3.4 Conclusions

The preparation of a ceramic/polymer/solvent suspension is the first stage in the preparation of ceramic hollow fibre membranes from raw materials. The properties of the suspension with respect to the composition and rheology are absolutely critical in determining the microstructure and macrostructure of the final product. In particular, the viscosity of the suspension plays a key role when preparing ceramic hollow fibre precursors as the viscosity affects mechanisms involved in the development of fibre morphology and greatly affects the final fibre structure. However, equally important is the practical considerations that must be considered when forming the hollow fibre precursor. It has been shown in this chapter that not all suspensions can successfully produce fibres with the desired structure depending on the design of the spinneret. In some cases, due to the properties of the suspension, certain parameters such as the extrusion rate, internal precipitant flow rate and precipitation bath depth are restricted to within certain ranges if fibres are to be successfully prepared. This severely limits the structural control that can be achieved using the combined phase inversion and sintering technique. Therefore, in order to maximize the potential of this preparation technique it is essential to match the properties of the suspension to the design of the spinneret and the possible spinning parameters that might be required to generate the desired structure. The rheology of the suspension is greatly affected by the particle size distribution and the duration of milling and by blending particle sizes, the quantity of ceramic material can be increased and the properties of the final product can be improved for some applications.
However, a high ceramic content and a small particle size is not always the desired, for example, to produce a membrane with increased porosity and a larger pore size the ceramic content (ceramic/polymer ratio) must be decreased and the particle size must be increased, which will severely reduce the viscosity of the suspension. In this situation, the same spinning parameters can not be used to generate the desired structures and a redesign of the spinneret and/or a change in the spinning parameters is necessary. Therefore, it is essential to have knowledge of the suspension rheology prior to spinning so that a trial and error approach can be avoided. Broadly speaking, an increase in ceramic content and a reduction in particle size leads to an increase in suspension viscosity due to the increased surface area of small particles and an increase in van der Walls interactions between them. The effect of milling time is slightly less well defined. Initially, an increase in milling time leads to a reduction in suspension viscosity up to a point, after which the viscosity is seen to increase dramatically due to the breakdown of particle aggregates which results in an effective reduction in particle size. In short, although the composition of the suspension, in terms of ceramic content and particle size distribution, is critical in determining the microstructure of the hollow fibre, the rheological profile is the dominant factor in determining the range of parameters that must be used and the resulting fibre macrostructure.

3.5 References


[65] Y. Hotta, Effect of slurry flocculation on the microstructure of alumina green bodies prepared by slip casting, Ceramic Transactions (2002), 133 (Improved Ceramics through New Measurements, Processing, and Standards), 159-164.


Chapter 4

A Morphological Study of Ceramic Hollow Fibre Membranes and Membrane Supports

Abstract

Both symmetric and asymmetric ceramic hollow fibres with a wide range of morphologies have been prepared using the combined phase inversion and sintering technique. The morphologies of ceramic hollow fibre membranes and membrane supports prepared from suspensions of Al$_2$O$_3$, N-methyl-2-pyrrolidone (NMP) and polyethersulfone (PESf) using a dry-wet spinning/sintering process have been studied experimentally. The results indicate that two types of membrane morphologies, i.e. finger-like and sponge-like structures can be expected. It is believed that finger-like void formation in asymmetric ceramic membranes is initiated by hydrodynamically unstable viscous fingering developed when a less viscous fluid (non-solvent) is in contact with a higher viscosity fluid (ceramic suspension containing invertible polymer binder). Finger-like void growth occurs only below a critical suspension viscosity, above which a sponge-like structure is observed over the entire hollow fibre cross section. The effects of the air-gap, viscosity and non-solvent concentration on fibre morphology have been studied and it has been determined that viscosity is the dominating factor for ceramic systems.
4.1 Introduction

Production of ceramic hollow fibre membranes can be achieved using an immersion induced phase inversion method first described by Loeb and Sourirajan [73] for asymmetric polymeric membrane formation. After the combination of a desired amount of ceramic powder and a polymer solution, if well mixed, the ceramic/polymer/solvent system can be seen as a suspension of polymer coated ceramic particles. Once immersed in a non-solvent for the polymer which is miscible with the solvent, solvent/non-solvent exchange takes place leading to precipitation of the polymer phase. Ceramic particles are immobilized once precipitation has taken place and the membrane macrostructure can be largely determined at this point by manipulating and adjusting the various parameters of the phase inversion process.

Great effort has been made to both control and understand the formation mechanisms for the wide range of structures observed in polymeric membrane formation [74-80]. However, due to the large differences between polymeric and ceramic systems, in particular the low polymer concentration, this information is of limited use during ceramic membrane preparation. In fact, only two morphologies have so far been observed in ceramic/polymer systems, i.e. (1) finger-like voids and (2) a sponge-like structure. The macrostructure of the fibre precursor designed during the phase inversion process is retained during sintering (calcination/heat treatment). Finger-like voids above a certain size are not usually eliminated, although at elevated sintering temperature sponge-like regions will densify and eventually become gas tight for some ceramic materials [81].
Chapter 4                  A Morphological Study of Ceramic Hollow Fibre Membranes and Membrane Supports

The focus of this chapter is, therefore, to examine how the choice of the preparation parameters affects ceramic membrane morphology.

Hydrodynamically unstable viscous fingering is a well known phenomenon that occurs at the interface between fluids with different viscosities in the first moments of mixing and has been applied here to explain the formation of finger-like voids in ceramic membrane precursors. When the suspension is in contact with non-solvent, a steep concentration gradient results in solvent/non-solvent exchange, a rapid increase in local viscosity and finally precipitation of the polymer phase. However, due to instabilities at the interface between the suspension and the precipitant there is a tendency for viscous fingering to occur, initiating the formation of finger-like voids. The relative thickness of finger-like and sponge-like regions greatly affects the properties of the membrane or membrane support such as mechanical strength and permeation flux and, due to the versatility of ceramic hollow fibres, it is essential that fibre morphology can be controlled so that it may be tailored to specific applications.

In this chapter, it has been shown that finger-like voids can be initiated from both the inner and outer surfaces simultaneously or from the inner surface alone. Finger-like void length from the inner surface can be varied between 0% of the fibre thickness, i.e. a symmetric sponge-like membrane structure, to approximately 80-90% of the fibre cross section. A generic mechanism for the prediction of the length of finger-like voids, the thickness of the sponge-like region and the formation and elimination of isolated/encapsulated voids has been suggested and correlated with air-gap, suspension viscosity, non-solvent additive and internal precipitant flow rate.
4.2 Experimental

4.2.1 Materials

Materials data for suspension components can be found in Chapter 3, Section 3.2.1. In addition, tap water was used as the external precipitant and de-ionized water was used as the internal precipitant (bore fluid). Polyvinylpyrrolidone (PVP K90, MW = 1300000), Ethanol (99.9% Sigma-aldrich) and de-ionised water were used as additives in the spinning suspensions in some cases.

4.2.2 Preparation of alumina hollow fibres

Arlacel P135 at a concentration of 1.3 wt% was dissolved in NMP, NMP/water or NMP/ethanol mixtures prior to the addition of aluminum oxide powders (58.7 wt%) at a ratio of 1:2:7 (0.01:0.05:1 µm). The suspension was rolled/milled with 20 mm agate milling balls with an approximate Al₂O₃/agate weight ratio of 2 for between 2 days and 1 week. Mixing was performed for a further 48 hours after the addition of polyethersulfone (6.1 wt%). The suspension was then transferred to a gas tight reservoir and degassed under vacuum while stirring until no bubbles could be seen at the surface.

For the preparation of flat sheet membranes, immediately after degassing, casting was performed (Brave Instruments, model 4330M001) at an approximate rate of 2 cm/s using approximately 40 ml of casting suspension. The freshly cast membranes were then immersed immediately in de-ionized water.

For the preparation of hollow fibre membranes, immediately after degassing, the spinning suspensions were either pressurized at a gauge pressure of $4.83 \times 10^4$-1.38 $\times 10^5$ Pa (7-20
psig) using nitrogen gas and were extruded through a tube-in-orifice spinneret (outer diameter 3 mm, inner diameter 1.2 mm) into tap water with an air-gap of between 0 cm and 15 cm or were transferred to a 200 ml Harvard stainless steel syringe and the extrusion rate of the spinning suspension and the flow rate of the internal precipitant were accurately controlled and monitored by two individual Harvard PHD 22/2000 Hpsi syringe pumps, ensuring the uniformity of the prepared precursor fibres. The procedure is described in detail elsewhere [82]. De-ionized water was used as the internal precipitant at a flow rate of 10-37.2 ml/min.

For both flat sheet and hollow fibre membranes, the fibre precursors were left in the external precipitation bath overnight to allow for completion of phase inversion. They were then immersed in an excess of tap water which was replaced periodically over a period of 48 hours in order to remove traces of NMP. Finally, the hollow fibre and flat sheet membrane precursors were calcined in air (CARBOLITE furnace) to yield ceramic hollow fibre and flat sheet membranes. The temperature was increased from room temperature to 600 °C at a rate of 2 °C/min and held for 2 hours, then to 1000 °C at a rate of 5 °C/min and held for 2 hours and finally to 1450 °C at a rate of 5 °C/min and held for 4 hours. The temperature was then reduced to room temperature at a rate of 5 °C/min.

4.2.3 Characterization

Viscosity data was collected (Physica UDS-200 rheometer) using concentric cylinder geometry at shear rates between 6-1000 s⁻¹ at 20 °C and spinning suspension samples were taken and tested immediately prior to membrane preparation. SEM samples were
gold coated under vacuum for 3 minutes at 20 mA (EMITECH Model K550) and SEM images at varying magnifications were collected (JEOL JSM – 5610 LV).

The formation of finger-like voids was recorded using an optical microscope, AnalysisPro imaging software was used to record the propagation of finger-like voids in real time. A small quantity of suspension was deposited on a microscope slide and an additional slide was pressed down on top of the suspension so as to produce a thin suspension film. De-ionized water was then introduced at the edge of the slide and was drawn in towards the suspension by capillary forces. A light source was provided underneath the microscope slide and an optical microscope was used to image the process from above.

4.3 Results and discussion

4.3.1 Hydrodynamically unstable viscous fingering

As discussed in Chapter 3, the rheology and viscosity of alumina suspensions used for the preparation of hollow fibres is strongly dependant on the composition of the ceramic suspension. The cornerstone of the versatility of ceramic hollow fibres prepared using the combined phase inversion and sintering technique is the wide range of structures that can be designed which may range from a symmetric fibre to highly asymmetric structures. Asymmetric fibres consist of regions of finger-like voids and a sponge-like structure (packed pore). In polymeric membrane science, finger-like macrovoids are seen as defects which lead to a reduction in mechanical strength and great care is taken to eliminate these structures. However, when preparing ceramic hollow fibres for membrane
reactor applications these structures are utilized as a substrate for catalyst deposition and each finger-like void can be seen as an individual micro-reactor. Reactors formed in this way have several advantages over traditional designs such as high mass and heat transfer fluxes resulting from their larger surface area to volume ratios and shorter transport distances.

In order for finger-like voids to be utilized as a substrate for catalyst deposition in a catalytic membrane reactor, a high level of control over their formation must be achieved so that fibres can be tailored to specific applications. Hydromagnetically unstable viscous fingering is a well known phenomenon that occurs at the interface between fluids with different viscosities in the first moments of mixing and has been applied here to explain the formation of finger-like voids in ceramic membrane precursors. When the suspension is in contact with non-solvent, a steep concentration gradient results in solvent/non-solvent exchange, a rapid increase in local viscosity and finally precipitation of the polymer phase. However, due to instabilities at the interface between the suspension and the precipitant there is a tendency for viscous fingering to occur, initiating the formation of finger-like voids. Under normal circumstances a stable interface would be established between the two phases of differing viscosities, however, due to the presence of invertible polymer binder a rapid viscosity increase followed by polymer precipitation retains the viscous fingering structure.

A great wealth of data exists on the formation of finger-like macrovoid structures in polymeric membranes prepared using the phase inversion technique and several different mechanisms have been proposed for a wide range of polymer/solvent/non-solvent
systems [75,83-86]. However, this data is of limited use when studying the formation of finger-like voids in ceramic hollow fibre membranes using the combined phase inversion and sintering technique due to the very low concentration of the polymer phase. It can be assumed that in the presence of an excess of water, the polymeric phase will precipitate rapidly and irreversibly and the membrane structure will be formed at that point.

A great deal of research has also been undertaken to establish the circumstances under which viscous fingering occurs and the factors that are involved in its propagation in model systems [87-93]. However, the study of viscous fingering phenomenon during the preparation of ceramic hollow fibre precursors is complicated by the dynamic nature of the process. It has been shown that the principal factors affecting the formation of viscous fingers are the relative viscosities of the stationary and invading phases, the interfacial tension between the two phases and the velocity of the invading phase. Typically, experiments on viscous fingering are conducted in a Helle-Shaw cell in which all these parameters can be easily controlled. This level of control is not achievable when preparing ceramic hollow fibres as both the relative viscosities and interfacial tensions change during the phase inversion process due to precipitation of the polymer phase. The driving forces acting on the invading phase are dependent on factors such as concentration gradients and convective flows which are not well understood in this system. However, it has been shown in this work that viscous fingering occurring during the formation of ceramic hollow fibre precursors only occurs below a critical suspension viscosity and this fact can be used to control the fibre morphology.
As fibre formation involving phase inversion is a dynamic process involving the precipitation of the polymer phase, the viscosity is seen to increase during this process, eventually resulting in the formation of a hollow fibre precursor. Therefore, both the initial suspension viscosity and the rate at which the viscosity increases during the fibre formation process are important in determining the final fibre structure. The initial suspension viscosity prior to phase inversion dictates how close the system is to the viscosity at which viscous fingering is eliminated (critical viscosity). If the system is close to this point then the critical value will be exceeded very soon after the phase inversion process is initiated by contact with non-solvent and viscous fingering will be reduced. This is demonstrated by the preparation of three flat sheet membranes from casting suspensions with different viscosities, Figure 4.1. In this case the viscosity has been increased by increasing the ratio of small to large particles in the system or by the addition of a small quantity of polyvinyl pyrrolidone. The casting suspension compositions and viscosities are shown in Table 4.1.
Figure 4.1: Flat sheet membranes prepared from ceramic suspensions with viscosities at 30 s\(^{-1}\) of (a): 7 Pa.s, (b): 12.1 Pa.s and (c): 21.2 Pa.s.

<table>
<thead>
<tr>
<th>Suspension</th>
<th>NMP (wt%)</th>
<th>Alumina (wt%)</th>
<th>Alumina particle size (wt% of total alumina content)</th>
<th>PESf (wt%)</th>
<th>PVP (wt%)</th>
<th>Arlacel P135 (wt%)</th>
<th>Alumina/PESf ratio</th>
<th>Viscosity (Pa.s) @ 30s(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>34</td>
<td>58.9</td>
<td>1 micron = 78, 50 nm = 15, 10 nm = 7</td>
<td>6.1</td>
<td>0</td>
<td>1.1</td>
<td>9.7</td>
<td>7</td>
</tr>
<tr>
<td>B</td>
<td>33.9</td>
<td>58.7</td>
<td>1 micron = 70, 50 nm = 20, 10 nm = 10</td>
<td>6.1</td>
<td>0</td>
<td>1.3</td>
<td>9.7</td>
<td>12.1</td>
</tr>
<tr>
<td>C</td>
<td>34.8</td>
<td>58</td>
<td>1 micron = 78, 50 nm = 15, 10 nm = 7</td>
<td>6.2</td>
<td>0.1</td>
<td>0.95</td>
<td>9.7</td>
<td>21.2</td>
</tr>
</tbody>
</table>

Table 4.1: Compositions of suspensions used in the preparation of flat sheet membranes.

Figure 4.1(a) shows a cross sectional SEM image of a flat sheet membrane prepared from Casting Suspension A as shown in Table 4.1. The image shows that an appreciable level of viscous fingering has occurred and that finger-like voids penetrate approximately 60-70% into the membrane cross section. Figure 4.1(b) shows a membrane cast from Suspension B. In this case the weight percentages of the various components in the casting solution remain the same but the ratio of particle sizes has been varied in favour of 50 and 10 nm particles, giving rise to an increase in suspension viscosity at 30 s\(^{-1}\) from 7 to 12.1 Pa.s. The SEM image clearly shows that a reduction in the extent of viscous fingering has occurred both in terms of the number of finger-like voids and in the
penetration depth into the membrane cross section. Figure 4.1(c) shows an SEM image of a flat sheet membrane prepared from Suspension C. In this case the composition and ratio of particle sizes is consistent with Suspension A but 0.1wt% of polyvinylpyrrolidone (PVP) has been added to the suspension, resulting in a viscosity increase to 21.2 Pa.s at a shear rate of 30 s⁻¹ and it can be seen that viscous fingering has been all but eliminated as a result of this increase in viscosity. As flat sheet membranes A-C were prepared from suspensions with identical compositions and only the particle size and viscosity of the suspension were varied, the variation in morphology can be attributed to the change in the initial suspension viscosity alone and it has been demonstrated that the initial viscosity of Suspension C is above the threshold at which viscous fingering occurs in this system.

The formation of finger-like voids by the viscous fingering mechanism requires a certain amount of time and will be halted when the suspension has exceeded a critical viscosity. Therefore, the development of the membrane morphology can be seen as a competition between viscous fingering and polymer precipitation. It has been shown that this competition exists during the formation of polymeric membranes by phase inversion [77] and the same process is observed for ceramic systems studied in this chapter. Dynamic video microscopy, described in Section 4.2.3, has been used to image the formation of finger-like voids, Figure 4.2.
Figure 4.2: A still image from a dynamic video microscopy study of the formation of finger-like structures as a result of viscous fingering, recorded through an optical microscope.

Similar techniques have been used to study the formation of macrovoids in polymeric systems, however, due to the transparent nature of many polymeric solutions it is possible for light to transmit through the polymer film and imaging is facilitated. Unfortunately, due to the opaque nature of the ceramic suspensions studied in this work it is necessary to produce an extremely thin film. In this situation the intrusion of water creates a region where only a small amount of suspension remains on the glass of the microscope slide and light can transmit more easily. Therefore, Figure 4.2 shows the viscous fingering phenomenon in only 2 dimensions. However, it is reasonable to assume, due to the extreme similarity between the shape and distribution of finger-like voids in the 2
dimensional system shown in Figure 4.2 and in SEM images of ceramic hollow fibres, that the two systems are analogous.

The precipitation front, indicated by the dashed white line labelled in Figure 4.2, is distinguished as the interface between the darker and lighter regions in the image which are clearly visible in the original digital image. The white areas are regions of non-solvent (water) intrusion into the suspension film where the suspension is pushed aside in an analogous mechanism to that observed during fibre spinning. As the virtually opaque ceramic suspension is pushed aside, light is free to pass through, clearly showing the finger-like shape observed in both the flat sheet and hollow fibre membranes prepared using the phase inversion method. Finger-like voids that lie behind the precipitation front (region of increased viscosity) have been terminated as the high viscosity in this region is prohibitive to finger-like void growth. Only finger-like voids with ends present ahead of the precipitation front continue to propagate as the viscosity in this region is below the critical viscosity value.

The driving force for the formation of finger-like voids has been studied extensively and several suggestions have been put forward. While in fundamental studies of viscous fingering in Helle-Shaw cells the driving force for intrusion of the invading phase is supplied mechanically by the operator, in phase inversion systems the driving force is the concentration gradient that exists between the miscible solvent and non-solvent present in the suspension film and the invading phase, respectively. In addition to transport by Fickian diffusion, surface tension gradients lead to convective flows which are also
responsible for intrusion of the less viscous phase (non-solvent/water). Figure 4.3 shows the formation of finger-like voids plotted against time and against time$^{0.5}$.

Figure 4.3: Finger-like void propagation as a function of time as observed using dynamic video microscopy.

It can be seen from the plot of finger-like void length against time that finger-like void growth is faster in the initial stages and then slows down as the process proceeds. It has been shown by Lai et al. [85], using a similar imaging technique and with the addition of rhodamine B as a high molecular weight component in the invading phase, that non-solvent intrusion results from either/or Fickian diffusion and convective flows depending on the circumstances. It can be seen from the plot of finger-like void length vs. time$^{0.5}$.
shown in Figure 4.3 that in this case the relationship is not linear over the entire data range (solid trend-line), a requirement for purely Fickian diffusion. The data suggests that only in the latter stages of finger-like void growth is the process driven by diffusion alone (dashed trend-line). Therefore, due to the presence of multiple growth mechanisms and the dynamic nature of the variables affecting the growth of finger-like voids it is extremely difficult to transfer fundamental knowledge of viscous fingering phenomena to the formation of finger-like voids during the preparation of ceramic membranes involving a phase inversion step. In particular, the many parameters involved in the preparation of hollow fibres using dry-wet spinning only serves to increase the number and complexity of the variables involved. However, by preparing hollow fibres while varying a number of different parameters systematically, it has been shown that the suspension viscosity, the polymer precipitation rate and solvent/non-solvent concentrations are extremely important factors in determining hollow fibre morphology and the growth of finger-like voids. Table 4.2 lists suspension viscosities and spinning parameters for the fibres discussed in the following sections.
<table>
<thead>
<tr>
<th>Fibre</th>
<th>Solvent composition (wt% of total solvent content)</th>
<th>Internal precipitant flow rate (ml/min)</th>
<th>Air-gap (cm)</th>
<th>Viscosity @ 30 s⁻¹ (Pa.s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NMP 100, Water 0, Ethanol 0</td>
<td>10</td>
<td>0</td>
<td>12.1</td>
</tr>
<tr>
<td>2</td>
<td>NMP 100, Water 0, Ethanol 0</td>
<td>7</td>
<td>3</td>
<td>10.6</td>
</tr>
<tr>
<td>3</td>
<td>NMP 100, Water 0, Ethanol 0</td>
<td>7</td>
<td>5</td>
<td>10.6</td>
</tr>
<tr>
<td>4</td>
<td>NMP 100, Water 0, Ethanol 0</td>
<td>7</td>
<td>7</td>
<td>10.6</td>
</tr>
<tr>
<td>5</td>
<td>NMP 100, Water 0, Ethanol 0</td>
<td>7</td>
<td>9</td>
<td>10.6</td>
</tr>
<tr>
<td>6</td>
<td>NMP 100, Water 0, Ethanol 0</td>
<td>7</td>
<td>11</td>
<td>10.6</td>
</tr>
<tr>
<td>7</td>
<td>NMP 100, Water 0, Ethanol 0</td>
<td>7</td>
<td>13</td>
<td>10.6</td>
</tr>
<tr>
<td>8</td>
<td>NMP 100, Water 0, Ethanol 0</td>
<td>12</td>
<td>1</td>
<td>10.6</td>
</tr>
<tr>
<td>9</td>
<td>NMP 100, Water 0, Ethanol 0</td>
<td>12</td>
<td>3</td>
<td>10.6</td>
</tr>
<tr>
<td>10</td>
<td>NMP 100, Water 0, Ethanol 0</td>
<td>12</td>
<td>7</td>
<td>10.6</td>
</tr>
<tr>
<td>11</td>
<td>NMP 100, Water 0, Ethanol 0</td>
<td>12</td>
<td>9</td>
<td>10.6</td>
</tr>
<tr>
<td>12</td>
<td>NMP 100, Water 0, Ethanol 0</td>
<td>12</td>
<td>11</td>
<td>10.6</td>
</tr>
<tr>
<td>13</td>
<td>NMP 100, Water 0, Ethanol 0</td>
<td>12</td>
<td>13</td>
<td>10.6</td>
</tr>
<tr>
<td>14</td>
<td>NMP 100, Water 0, Ethanol 0</td>
<td>3</td>
<td>15</td>
<td>10.6</td>
</tr>
<tr>
<td>15</td>
<td>NMP 100, Water 0, Ethanol 0</td>
<td>6</td>
<td>15</td>
<td>10.6</td>
</tr>
<tr>
<td>16</td>
<td>NMP 100, Water 0, Ethanol 0</td>
<td>7</td>
<td>15</td>
<td>10.6</td>
</tr>
<tr>
<td>17</td>
<td>NMP 100, Water 0, Ethanol 0</td>
<td>8</td>
<td>15</td>
<td>10.6</td>
</tr>
<tr>
<td>18</td>
<td>NMP 100, Water 0, Ethanol 0</td>
<td>9</td>
<td>15</td>
<td>10.6</td>
</tr>
<tr>
<td>19</td>
<td>NMP 100, Water 0, Ethanol 0</td>
<td>12</td>
<td>15</td>
<td>10.6</td>
</tr>
<tr>
<td>20</td>
<td>NMP 100, Water 0, Ethanol 0</td>
<td>15</td>
<td>15</td>
<td>10.6</td>
</tr>
<tr>
<td>21</td>
<td>NMP 100, Water 0, Ethanol 0</td>
<td>10</td>
<td>15</td>
<td>12.1</td>
</tr>
<tr>
<td>22</td>
<td>NMP 98, Water 2, Ethanol 0</td>
<td>10</td>
<td>15</td>
<td>16.7</td>
</tr>
<tr>
<td>23</td>
<td>NMP 96, Water 4, Ethanol 0</td>
<td>10</td>
<td>15</td>
<td>18.5</td>
</tr>
<tr>
<td>24</td>
<td>NMP 94, Water 6, Ethanol 0</td>
<td>10</td>
<td>15</td>
<td>22</td>
</tr>
<tr>
<td>25</td>
<td>NMP 92, Water 8, Ethanol 0</td>
<td>10</td>
<td>15</td>
<td>33.3</td>
</tr>
<tr>
<td>26</td>
<td>NMP 90, Water 10, Ethanol 0</td>
<td>10</td>
<td>15</td>
<td>45</td>
</tr>
<tr>
<td>27</td>
<td>NMP 98, Water 2, Ethanol 0</td>
<td>10</td>
<td>15</td>
<td>16.7</td>
</tr>
<tr>
<td>28</td>
<td>NMP 96, Water 4, Ethanol 0</td>
<td>10</td>
<td>15</td>
<td>16.5</td>
</tr>
<tr>
<td>29</td>
<td>NMP 94, Water 6, Ethanol 0</td>
<td>10</td>
<td>15</td>
<td>22</td>
</tr>
<tr>
<td>30</td>
<td>NMP 92, Water 8, Ethanol 0</td>
<td>10</td>
<td>15</td>
<td>33.3</td>
</tr>
<tr>
<td>31</td>
<td>NMP 90, Water 10, Ethanol 0</td>
<td>10</td>
<td>15</td>
<td>45</td>
</tr>
<tr>
<td>32</td>
<td>NMP 100, Water 0, Ethanol 0</td>
<td>10</td>
<td>15</td>
<td>12.1</td>
</tr>
<tr>
<td>33</td>
<td>NMP 98, Water 2, Ethanol 0</td>
<td>10</td>
<td>15</td>
<td>10.2</td>
</tr>
<tr>
<td>34</td>
<td>NMP 96, Water 4, Ethanol 0</td>
<td>10</td>
<td>15</td>
<td>9.9</td>
</tr>
<tr>
<td>35</td>
<td>NMP 94, Water 6, Ethanol 0</td>
<td>10</td>
<td>15</td>
<td>0.40</td>
</tr>
<tr>
<td>36</td>
<td>NMP 92, Water 8, Ethanol 0</td>
<td>10</td>
<td>15</td>
<td>8.47</td>
</tr>
<tr>
<td>37</td>
<td>NMP 90, Water 10, Ethanol 0</td>
<td>10</td>
<td>15</td>
<td>0.54</td>
</tr>
</tbody>
</table>

Table 4.2: Suspension compositions, viscosities and fibre preparation parameters for Fibres 1-37 discussed in Chapter 4.
4.3.2 Air-gap

Figures 4.4(a-g) show a fibre prepared with air an air-gap of 0 cm at an internal precipitant flow rate of 10 ml/min (Fibre 1), and fibres prepared with air-gaps of 3, 5, 7, 9, 11 and 13 cm at an internal precipitant flow rate of 7 ml/min and an extrusion rate of 7 ml/min (Fibres 2-7).
It can be seen from Figure 4.4(a) that the morphology of a fibre spun directly into a non-solvent precipitation bath (0 cm air-gap) consists of finger-like voids originating from both the inner and outer fibre surfaces which extend almost to the centre of the fibre cross section. A central sponge-like region is present which provides the majority of the mechanical strength and separation characteristics. Maximum void length is approximately the same for voids originating from both the inner and outer surfaces and as in all the prepared fibres a void length distribution exists, some being only a few microns in length while others penetrate far into the fibre cross section. This structure
may not be ideal for some of the traditional applications of ceramic hollow fibre membranes such as solvent filtration which generally require the separation layer (packed pore originating from the sponge-like region after heat treatment) to be at either the inner or outer edge. However, the above structure may be beneficial for the development of catalytic membranes, as finger-like voids may serve as substrates for catalyst particle impregnation. For example, a multifunctional catalytic membrane could be developed with different catalytic functions at the inner and outer surfaces with the central region of the membrane determining the permeation characteristics. This could be achieved by depositing two different types of catalyst targeted at different reactions within the inner and outer finger-like voids respectively.

Figures 4.4(b-g) show the morphology of fibres prepared with increasing air-gaps, from 3-13 cm and an internal precipitant flow rate of 7 ml/min. It can be seen that the introduction of a 3 cm air-gap between the spinneret and the precipitation bath substantially changes the fibre morphology. In this case a highly asymmetric morphology is generated in which finger-like voids occupy approximately 35% of the fibre cross section and approximately 65% of the fibre cross section is occupied by a sponge-like structure. The presence of isolated voids can also be seen in the sponge-like region of the fibre. As the air-gap is increased, the length of the finger-like voids is seen to increase to approximately 40% of the fibre cross section with an air-gap of 5 cm, to approximately 50% for air-gaps of 7 and 9 cm, to 60% at 11 cm and finally to approximately 75% with an air-gap of 13 cm.
The morphology of the fibre shown in Figure 4.4(a) is believed to result from hydrodynamically unstable viscous fingering occurring simultaneously and to a similar extent at both the inner and outer fibre surfaces. The situation is somewhat different when a 3 cm air-gap is present, Figure 4.4(b). In this case simultaneous solvent evaporation and moisture (non-solvent) condensation causes a local viscosity increase in the outer region of the fibre prior to immersion. During the time the nascent fibre is exposed to the atmosphere (3 cm air-gap), the viscosity of the outer region increases and finger-like voids originating at the inner surface penetrate into the fibre cross section. As the nascent fibre makes contact with the non-solvent bath the increased viscosity of the outer region, as a result of exposure to the atmosphere, inhibits the growth of finger-like voids at the outer edge. However, non-solvent influx from the precipitation bath does still occur, further increasing the suspension viscosity as it penetrates the nascent fibre cross section. This increases the viscosity in front of finger-like voids growing from the inner surface, limiting their length to approximately 35% of the fibre cross section. Therefore finger-like voids forming from the inner surface can be increased in length by increasing the air-gap. The effect of this increase can be clearly seen from the SEM images shown in Figures 4.4(c-g). Under these conditions the viscosity of the outer region is higher when the nascent fibre is immersed and non-solvent influx is reduced, while at the same time voids originating at the inner surface have more time to penetrate further towards the outer edge. Close inspection of outer region of fibres prepared with air-gaps and an internal precipitant flow rate of 7 ml/min reveals the presence of small finger-like voids at the outer surface in addition to isolated voids within the sponge-like structure. The presence of these two types of voids demonstrates clearly the effect that suspension
viscosity has on viscous fingering. Despite exposure to the atmosphere, the viscosity at the outer surface of the nascent fibre is still below the viscous fingering threshold and a limited degree of viscous fingering is still possible in this region. Even if the viscosity near the suspension/air interface has increased considerably before immersion, non-solvent will still diffuse into and through this region when the nascent fibre is immersed. This process causes an increase in viscosity in the region in front of finger-like voids propagating from the inner surface and halts void growth, therefore, a reduction in air-gap leads to a reduction in the length of finger-like voids. In addition to this effect, as non-solvent diffuses through the outer sponge-like region of high viscosity and reaches a region of lower viscosity, viscous fingering takes place and isolated void formation is initiated. Isolated voids will be eliminated if the suspension viscosity in this region is above the viscous fingering threshold before non-solvent influx occurs. Isolated voids are not only detrimental to the mechanical strength but also introduce variation of the fibre performance in terms of permeance, both of which are undesirable. Therefore, it follows that to eliminate isolated voids in the sponge-like structure of the fibre, the viscosity in this region must be above the viscous fingering threshold before non-solvent influx from the precipitation bath takes place, i.e. before the fibre is immersed. As suggested previously, non-solvent influx into the suspension film takes place by both diffusion and convection mechanisms, driven by gradients in concentration and interfacial tension. To increase the driving force for non-solvent penetration into the suspension film the concentration gradient must be increased. This may be achieved by increasing the flow rate of the internal precipitant relative to the flow rate of the suspension, which increases the relative ratio of non-solvent to solvent in the system. The results of an increase in
internal precipitant flow rate are shown in Figure 4.5 for fibres prepared with an internal precipitant flow rate of 12 ml/min and air-gaps ranging from 1-13 cm.

Figure 4.5: Cross-sectional images of Fibres 8-13 with air-gaps between 1-13 cm and with an internal precipitant flow rate of 12 ml/min. (a): 1 cm, (b): 3 cm, (c): 7 cm, (d): 9 cm, (e): 11 cm and (f): 13 cm.
It can be seen from the cross-sectional SEM images that a similar highly asymmetric structure is formed consisting of finger-like voids and a sponge-like structure. However, as expected, due to the increased internal precipitant flow rate finger-like voids penetrate further into the fibre cross section for a given air-gap. Figure 4.5(a) shows a ceramic hollow fibre prepared with an air-gap of 1 cm consisting of finger-like voids penetrating approximately 50% into the fibre cross section. However, despite the reduced length of the finger-like voids, a very limited number of isolated voids are observed in the sponge-like region. An increase in the air-gap to 3 cm, Figure 4.5(b), results in an increase in finger-like void length to approximately 55-60% of the fibre cross section and again isolated voids in the sponge-like structure have been all but eliminated. Further increases of the air-gap lead to finger-like void penetration of approximately 80% at 7 cm, and 85, 87 and 90% for air-gaps of 9, 11 and 13 cm respectively, with isolated voids being eliminated completely in all fibres prepared with air-gaps above 3 cm. It is clear from a comparison of fibre cross sections of fibres prepared with internal precipitant flow rates of 7 ml/min and 12 ml/min that the increase in internal precipitant flow rate with respect to the flow rate of the suspension is not only responsible for an increase in finger-like void length but also for the elimination of isolated voids in the sponge-like structure. The greater concentration gradient created by the increase in internal precipitant flow rate leads to an increase in the driving force for finger-like void formation and non-solvent influx into the suspension film. As discussed above, isolated voids result from viscous fingering and form as a consequence of non-solvent influx from the precipitation bath. It is clear that in fibres prepared with an increased internal precipitant flow rate, the degree of internal precipitant diffusion into the outer regions of the suspension film is greater,
resulting in a greater degree of polymer precipitation and an increase in suspension viscosity in this region. Consequently, this region is above the threshold at which viscous fingering takes place and isolated voids fail to form as precipitant flows in from the external precipitation bath.

4.3.3 Internal precipitant flow rate

As discussed in the previous sections, hollow fibre morphology is determined largely by three main factors, namely, the initial viscosity of the ceramic suspension, the polymer precipitation rate, which determines the dynamic viscosity during the phase inversion process, and the concentration gradient between the solvent and non-solvent. By manipulating these parameters, either before or during the spinning process, the morphology of the resulting fibres can be controlled effectively. While the suspension composition and the air-gap are the chosen methods of manipulating the polymer precipitation rate, the composition and flow rate of the internal precipitant may be used to manipulate the concentration gradient across the suspension film during phase inversion. This is discussed below.

Figure 4.6 shows ceramic hollow fibres prepared with a 15 cm air-gap and with internal precipitant flow rates ranging from 3-15 ml/min.
Figure 4.6: Cross-sectional SEM images of fibres prepared with varying internal precipitant flow rates and an air-gap of 15 cm (a): 3 ml/min, (b): 6 ml/min, (c): 7 ml/min, (d): 8 ml/min, (e): 9 ml/min, (f): 12 ml/min and (g): 15 ml/min.
It is clear that an increase in flow rate gives rise to an increase in the length of the finger-like voids. As the ratio of non-solvent to solvent is increased, the extent of the concentration gradient across the interface between the non-solvent and the suspension film is greater and is sustained for a longer period of time. This leads to an increase in the length of the finger-like voids and also in the degree of non-solvent diffusion into the suspension film. For the fibre prepared with an internal precipitant flow rate of 3 ml/min, Figure 4.6(a), the number of larger finger-like voids is reduced, the penetration is limited to approximately 45% of the fibre cross section and finger-like voids are also seen to propagate from the region close to the outer surface of the fibre. As the flow rate is increased to 6 ml/min finger-like void length is increased to approximately 55% of the fibre cross section and finger-like voids originating from the shell side of the fibre are eliminated. At flow rates between 7-12 ml/min the sponge-like region is seen to occupy 30% of the cross section with finger-like voids occupying approximately 70%. In this situation finger-like void growth will continue as long as the concentration gradient that is present between the suspension film and the internal precipitant provides a sufficient driving force for viscous fingering to proceed. At low internal precipitant flow rates the concentration gradient is eliminated quickly and consequently finger-like void growth is limited. Likewise, if the air-gap is short, the concentration gradient is eliminated quickly by non-solvent influx from the shell side of the fibre (external precipitation bath) and finger-like void growth from the inner fibre surface is again limited. Therefore, at high internal precipitant flow rates and with long air-gaps the concentration gradient is maintained and finger-like void growth is extensive.
The driving force for the formation of finger-like voids by viscous fingering is the concentration gradient that exists between the non-solvent and the suspension film rather than the hydrodynamic pressure of the internal precipitant. This is demonstrated by the formation of finger-like voids across up to approximately 70-80% of the cross section of membranes cast as flat sheets, Figure 4.1(a). In this case penetration of non-solvent into the suspension film results solely from diffusion or convection mechanisms, as discussed in Section 4.3.1. After casting of a flat sheet membrane, the nascent film is submerged in a large excess of non-solvent and the concentration gradient is maintained until effectively all the solvent is replaced by non-solvent. This is not necessarily the case when preparing hollow fibre precursors using a tube-in-orifice spinneret as the quantity of internal precipitant is finite. For example, for a spinneret with an outer diameter of 3 mm and an inner diameter of 1.2 mm, the areas of the inner and outer annuli are 0.013 cm$^2$ and 0.059 cm$^2$ respectively. The volume fraction of NMP in the suspension is 0.85 so at a suspension flow rate of 7 ml/min the flow rate of NMP is 5.95 ml/min. If the flow velocity of the suspension and the internal precipitant are the same then the flow rate of the internal precipitant would be 1.33 ml/min. This value is far below the quantity of NMP present and is insufficient to replace all the solvent in the suspension with non-solvent. For finger-like void growth to occur, the driving force for non-solvent influx into the suspension film must be above a certain level which is dependent on the viscosity of the suspension, however, solvent/non-solvent exchange will still occur if the driving force is below this limit albeit without the formation of finger-like voids. As the nascent fibre leaves the spinneret a steep concentration gradient exists and, if the suspension is below the critical viscosity, non-solvent influx will result in viscous fingering and the formation
of finger-like voids. As the internal precipitant travels down the lumen of the nascent fibre this gradient is diminished as the concentration of NMP in the internal precipitant increases and as the diffusion rate of non-solvent into the suspension film decreases, at some point, finger-like void growth will halt. Immersion of the fibre in the precipitation bath will reduce the concentration gradient further due to non-solvent influx from the shell side of the fibre and the final structure will be determined at this point. Therefore, by increasing the velocity of the internal precipitant, the concentration gradient can be maintained at a higher level for longer, leading to the continued growth of finger-like voids and an increase in their length before the fibre is immersed in the external precipitation bath.

### 4.3.4 Addition of water as a non-solvent additive

To investigate the effect of the rate at which the viscosity changes during phase inversion (dynamic viscosity/precipitation rate) on fibre morphology, either water or ethanol were used as non-solvent additives to alter the suspension viscosity. Manipulating the viscosity by other means, such as by varying the ratio of solvent/polymer/alumina or by the introduction of additives such as polyvinylpyrrolidone (PVP), may affect the membrane properties and for this reason, water and ethanol were chosen as a viscosity enhancer and reducer, respectively. The addition of water to spinning suspensions, measured as a percentage of the total solvent content, caused an increase in viscosity as shown in Figure 4.7.
Figure 4.7: Viscosity of spinning suspensions prepared with 0-10 wt% water (as a percentage of the total solvent content).

The suspension viscosity value of 12.1 Pa.s at 0 wt% water increased to 16.7, 18.5 and 22 Pa.s at 2, 4 and 6 wt % water content respectively. Further addition of water resulted in large viscosity increases to 33.3 and 45 Pa.s at 8 and 10 wt% respectively. The rate of viscosity increase as a function of water content is seen to increase at 6 wt% indicating that if all other parameters remain the same, fibre morphology may change abruptly at this point. The extrusion rate was maintained at a constant value over the range of suspension compositions.

Figure 4.8 illustrates the effect of spinning suspension viscosity on fibre morphology for calcined fibres prepared with a 15 cm air-gap and an internal precipitant flow rate of 10 ml/min.
Figure 4.8: Cross-sectional images of Fibres 21-26 made from spinning suspensions containing varying amounts of water. (a): Fibre 21, 0 wt% water, (b): enlargement of Fibre 23 outer edge, 4 wt% water, (c): Fibre 22, 2 wt% water, (d): isolated void in Fibre 23, 4 wt% water, (e): enlargement of isolated void in Fibre 23, 4 wt% water, (f): Fibre 23, 4 wt% water, (g): Fibre 24, 6 wt% water and (h): enlargement of Fibre 24 outer edge, 6 wt% water, (i): Fibre 25, 8 wt% water, (j): Fibre 26, 10 wt% water.

It can be seen in Figure 4.8(a) that at 0 wt% water content, finger-like voids extent across approximately 80% of the fibre cross section with the remaining 20% consisting of a sponge-like region. At higher magnification, Figure 4.8(b) shows the existence of small finger-like voids at the outer fibre edge which are present in fibres prepared with water concentrations below 6 wt%. Addition of 2 wt% water results in a large reduction in finger-like void length to approximately 40% of the cross section as shown in Figure 4.8(c) and in the appearance of inward facing isolated voids in the centre of the sponge-like region which can be seen in Figures 4.8(d) and 4.8(e). Figure 4.8(f) shows the effect of the addition of 4 wt% water. Again, finger-like voids from the inner surface penetrate approximately 40% of the cross section but isolated void formation is reduced in this case. The total elimination of isolated voids resulting from the addition of 6 wt% water
can be seen in Figure 4.8(g) and at higher magnification Figure 4.8(h) shows the elimination of small finger-like voids at the outer edge. However, it is shown in Figure 4.8(g) that void penetration from the inner surface remained unchanged at 40% while Figure 4.8(i) shows a reduction in void length to about 30% at 8 wt% water content. Total void elimination results from the addition 10 wt% water, i.e. the symmetric membrane structure shown in Figure 4.8(j).

In order to probe the relationship between the formation of finger-like voids by the viscous fingering mechanism and the viscosity/precipitation rate of the suspension film, fibres were prepared with varying concentrations of water as a non-solvent additive in the spinning suspension and with bore fluid flow rates increased so that the ratio of flow rate to viscosity at 30 s\(^{-1}\) = 0.83, i.e. the value for Fibre 21 (0 wt% water, Figure 4.8(a)), thus partially overcoming the resistance to viscous fingering at the inner surface.
Figure 4.9: Cross-sectional images of Fibres 27-31 made from spinning suspensions containing varying amounts of water and spun with different internal precipitant flow rates (a): Fibre 27, 2 wt% water, 13.8 ml/min, (b): Fibre 28, 4 wt% water, 15.6 ml/min,
(c): Fibre 29, 6 wt% water, 18 ml/min, (d): Fibre 30, 8 wt% water, 27.6 ml/min, (e): Fibre 31, 10 wt% water, 37.2 ml/min, (f): Fibre 28, 4 wt% water, 15.6 ml/min (outer edge) and (g): Fibre 29, 6 wt% water, 18 ml/min (outer edge).

In this case isolated voids were not observed in any of the fibres prepared and finger-like void length varied in a more linear fashion, i.e. decreasing from 80% at 0 wt% water to 70, 60, 40, 35 and 25% for water contents of 2, 4, 6, 8 and 10 wt% respectively. It can be seen at higher magnification that the small finger-like voids at the outer fibre edge observed in Figure 4.9(f) at water concentrations below 6 wt% were eliminated with an increased internal precipitant flow rate at 6 wt% water and above as shown in Figure 4.9(g).

The presence of water in the spinning suspension has two effects. Firstly, the initial suspension viscosity is increased as water is a non-solvent for the polymer phase and secondly, the polymer phase precipitates more rapidly when in contact with additional non-solvent, or as a result of solvent evaporation, as the polymer phase is closer to its precipitation point. An increase in suspension viscosity inhibits viscous fingering at both the inner and outer surfaces of the fibre and finger-like void length is reduced. As expected, increasing the internal precipitant flow rate promotes viscous fingering so finger-like void length is reduced less in fibres prepared with increased flow rates. Figures 4.8(c), 4.8(f), 4.9(a) and 4.9(b) show fibres prepared with 2 and 4 wt% water at different internal precipitant flow rates. Close examination of the outer fibre edges reveals small finger-like voids - shown at higher magnification in Figures 4.8(b) and 4.9(f) - resulting from non-solvent influx from the precipitation bath which, although
small, are likely to diminish mechanical strength by reducing the integrity of the sponge-like structure. Despite the presence of a 15 cm air-gap, at water concentrations below 6 wt% the viscosity of the outer region is below the viscous fingering threshold when the fibre is immersed and small finger-like voids are seen in all fibres regardless of the internal precipitant flow rate. These small finger-like voids are eliminated if the viscosity of the outer region is above a critical value before the outer fibre surface is brought into contact with non-solvent. This threshold is exceeded for fibres prepared with at least 6 wt% water and a 15 cm air-gap.

It can also be seen from Figures 4.8(d) and 4.8(e) that the inward facing isolated voids observed in fibres prepared with less than 6wt% water content and an internal precipitant flow rate of 10 ml/min are formed by non-solvent influx from the shell side of the fibre, as described in Section 4.3.2. However, Figures 4.9(a-e) show that isolated voids are not observed in any fibres prepared with increased internal precipitant flow rates. Under these circumstances, internal precipitant influx and finger-like void growth from the inner surface are greater. Consequently, the viscosity of the region in which isolated voids are observed is above the viscous fingering threshold before non-solvent influx from the precipitation bath occurs and a sponge-like structure results. It can be seen from Figure 4.9 that despite the increase in the driving force for finger-like void formation caused by the increased internal precipitant flow rate, the greater initial suspension viscosity and the greater rate at which the viscosity increases during the phase inversion process results in a reduction in the length of finger-like voids and almost to their elimination at a non-solvent concentration of 10 wt%.
4.3.5 Addition of ethanol as a non-solvent additive

It is not only the initial suspension viscosity that is important in determining the morphology but also the rate of the increase in viscosity once the phase inversion process has been initiated, which is determined by the precipitation rate of the polymer phase. This can be demonstrated by the addition of ethanol as a non-solvent additive to the spinning suspension. Although the solubility of polyethersulfone in ethanol is lower than in NMP but higher than in water, the suspension viscosity initially decreases as the concentration of ethanol is increased and is only seen to increase at higher ethanol concentrations, Figure 4.10.

![Suspension viscosity vs. ethanol content](image)

Figure 4.10: Viscosity of spinning suspensions prepared with 0-10 wt% ethanol (as a percentage of the total solvent content).
A viscosity of 12.1 Pa.s is observed in the absence of ethanol in the spinning suspension. A large decrease of almost 2 Pa.s from 12.1 to 10.2 Pa.s is observed with the addition of only 2 wt% ethanol. Smaller decreases to 9.9 and 8.48 Pa.s are observed on the addition of 4 and 6 wt% of ethanol, respectively. There is little change in the viscosity as the concentration of ethanol is increased to 8 wt% and the viscosity is seen to increase as the concentration of ethanol is increased from 8 to 10 wt% as the interaction of ethanol with the polymer phase becomes the dominant factor.

Fibres were prepared using an internal precipitant flow rate of 10 ml/min and an air-gap of 15 cm. Despite the lower initial viscosity of suspensions prepared with ethanol as a non-solvent additive, the resulting fibres, shown in Figure 4.11, experience a similar morphological change to those prepared with water as a non-solvent additive. It can be clearly seen that despite the initial reduction in the suspension viscosity caused by the addition of ethanol, the length of finger-like voids is reduced as the concentration of ethanol is increased. Figure 4.11(a) shows a fibre prepared from a spinning suspension without the addition of a non-solvent additive and finger-like voids penetrate across approximately 80% of the fibre cross section as seen previously. However, as the quantity of ethanol is increased, finger-like void length is progressively reduced and the viscous fingering phenomenon is almost totally eliminated at an ethanol concentration of 10wt%, Figure 4.11(f).
Figure 4.11: Cross-sectional SEM images of ceramic hollow fibres prepared with varying quantities of ethanol in the spinning suspension and at an internal precipitant flow rate of 10 ml/min. (a): Fibre 21, 0%, (b): Fibre 33, 2%, (c): Fibre 34, 4%, (d): Fibre 35, 6%, (e): Fibre 36, 8% and (f): Fibre 37, 10%.
The use of both water and ethanol as a non-solvent additive demonstrates the relationship between the viscous fingering phenomenon responsible for the formation of finger-like void structures and the precipitation rate of the polymer phase which causes the viscosity to increase during the phase inversion process. Although the initial suspension viscosity is of great importance, the time taken for the critical viscosity to be exceeded is also very important in determining hollow fibre morphology and is dependant on the polymer precipitation rate and the composition of the spinning suspension with respect to the ratio of solvent to non-solvent.

4.4 Conclusions

Finger-like voids in hollow fibres prepared from alumina/NMP/polyethersulfone spinning suspensions result from hydrodynamically unstable viscous fingering occurring at the interface between the suspension and the non-solvent. By using dynamic video microscopy the growth of finger-like voids can be measured as a function of time and it has been determined from this data that the influx of non-solvent into the suspension film is not driven by Fickian diffusion alone as a linear relationship between finger-like void growth and time$^0.5$ is not observed. The formation of finger-like voids is driven by the concentration gradient between the miscible solvent and non-solvent and finger-like voids will propagate as long as a sufficient gradient exists and the suspension viscosity is below a certain level. Above this critical suspension viscosity the viscous fingering phenomenon is not observed and a sponge-like membrane structure is formed. Therefore, by using the internal precipitant flow rate to control the concentration gradient and the air-gap to manipulate the suspension viscosity, fibre morphology can be controlled.
Furthermore, by varying the viscosity of the spinning suspension and the polymer precipitation rate by using water and/or ethanol as non-solvent additives, fibre morphology can be further controlled. Exposure of the outer fibre surface to the atmosphere causes a local viscosity increase and inhibits the formation of finger-like voids in this region. However, non-solvent may diffuse through this outer layer as the fibre is immersed, halting finger-like void growth from the inner surface and creating isolated voids within the membrane cross section if the internal precipitant flow rate is insufficient. The air-gap and suspension viscosity are critical in determining both the formation of finger-like voids and the integrity of the outer sponge-like region. The addition of water as a non-solvent additive to the spinning suspension causes an increase in viscosity, a reduction in finger-like void length and favours the formation of a sponge-like structure at the outer fibre surface if an air-gap is present. The addition of ethanol, on the other hand, causes a reduction in suspension viscosity and at the same time reduces the extent of viscous fingering due to an increase in the precipitation rate of the polymer phase compared with a suspension containing only solvent (NMP).

4.5 References


Chapter 5

Characterization of Ceramic Hollow Fibre Membranes and Membrane Supports

Abstract

Asymmetric ceramic hollow fibre membranes and membrane supports have been prepared using the combined phase inversion and sintering technique and have been characterized in terms of their applicability to membrane reactor applications. The asymmetric structure is such that the fibre may simultaneously function either as a porous membrane and a matrix for catalyst deposition, or as a porous support for the coating of a gas separation layer and a matrix for catalyst deposition. The effectiveness of catalyst deposition and hence the performance of the catalytic membrane reactor depends strongly on the pore size distribution of the membrane or membrane support, which is bimodal in nature and is affected by the calcination temperature and the fibre preparation parameters. The effect of the calcination temperature and preparation parameters on the pore size distribution, porosity and mechanical strength have been studied systematically and a route to optimizing the fibre structure for catalyst deposition has been suggested.
5.1 Introduction

In the previous chapters the importance of the characteristics of ceramic suspensions used for the preparation of hollow fibres by dry-wet spinning has been discussed and it has been demonstrated that by manipulating the composition of the suspension and the parameters during spinning, a wide range of useful fibre morphologies can be generated. However, to determine how well certain morphologies will perform for their intended applications, further characterisation in terms of the microstructure of the fibres is necessary. In particular, the pore size distribution is critical in determining the performance of a particular morphology when functioning as a catalytic membrane reactor.

If ceramic hollow fibres are to be developed for a certain application, the minimum requirement is that the fibre has sufficient mechanical strength, the degree of which may vary between applications. The effect of increasing the mechanical strength of the support by either increasing the calcination temperature or by increasing the thickness of the sponge-like region has been considered with respect to the ease with which catalyst can be deposited within the support. In addition, factors effecting the formation of pores at both the inner and outer fibre surfaces and the evolution of the pore size distribution as the calcination temperature is increased have been studied in order to optimize the deposition of catalyst within the asymmetric support structure.

It has been shown in this study that asymmetric hollow fibres comprised of finger-like voids and a sponge-like structure exhibit a bimodal pore size distribution and may undergo both coarsening and densification in these regions respectively. It has also been
shown that although the pore size distribution of the sponge-like region changes little with variation of parameters during the spinning process, the same cannot be said of the distribution associated with the finger-like voids, which may vary greatly depending on the suspension composition and the spinning parameters. Conversely, while the properties of the sponge-like region change greatly during sintering, the properties of the pores formed by the entrances to the finger-like voids and the finger-like voids themselves resist change.

5.2 Experimental

5.2.1 Fibre preparation

Fibres were prepared according to the method described in Chapter 4, Section 4.2.2.

5.2.2 Microscopy

SEM characterization was conducted for sintered fibres. Which were flexed at ambient temperature until a fracture occurred prior to being mounted on an SEM slide. Samples were gold coated under vacuum for 180 s at 20 mA (EMITECH Model K550) and SEM images at varying magnifications were collected (JEOL JSM – 5610 LV).

5.2.3 Mercury intrusion porosimetry

Mercury intrusion data was collected at absolute pressures of between 1.38 x10³ and 2.28 x10⁸ Pa (0.2 – 33500 psia) (Micromeritics Autopore IV) with an equilibration time of 10 seconds and assuming a mercury contact angle of 130⁰. The fibres were broken into sections of approximately 4 mm in length prior to mercury intrusion analysis.
5.2.4 Gas-liquid displacement technique

Pore size determination using a gas-liquid displacement technique was undertaken according to an established method [94] using compressed air as the gas and water as the wetting liquid. Fibres of approximately 2 cm in length were fixed into metal holders using epoxy and were sealed at the end of the protruding fibre with a small quantity of epoxy. In order to completely wet the hollow fibre, a vacuum was applied to the lumen side while the fibre was immersed in water. The vacuum was maintained for approximately 1 hour, during which time water was drawn through the fibre wall into the lumen of the fibre. The fibres were subjected to incrementally increased pressures and the gas flow rate was recorded at each pressure.

5.2.5 Gas permeation

Effective porosity was calculated using a technique developed by Kong and Li [95]. Fibres of approximately 2 cm in length were fixed into metal holders using epoxy and were sealed at the protruding end also using epoxy. The samples were subjected to pressures of between 0.5 and 3.5 bar using nitrogen gas and the flow rate was measured at 5 different pressures. Software developed for this purpose was used to calculate the effective porosity.

5.2.6 Mechanical strength

Mechanical strength tests were performed (Instron 5563) after fibres were broken into sections approximately 7 cm long and were placed on two supports as shown in Figure 5.1.
A 1 kN load cell was lowered onto the central region of the fibre and the load required to break the fibre was recorded. Bending strengths were then calculated using Equation 5.1.

\[
\sigma_F = \frac{8F_M L_h D_o}{\pi (D_o^4 - d_i^4)}
\]

where \(\sigma_F\) = bending strength (MPa), \(F_M\) = the force/loading applied at breaking point (N), \(L_h\) = the length of the fibre, \(D_o\) = the fibre outer diameter and \(d_i\) = the fibre inner diameter.

### 5.2.7 Nitrogen adsorption

Nitrogen adsorption analysis was conducted (Tristar 3000, Micromeritics) between 1119.7 – 101161.4 Pa with an equilibration time of 5 seconds. Samples were heated at 200 °C overnight prior to nitrogen adsorption analysis. Surface area was calculated using the BET model while pore area was calculated using the BJH model for both the adsorption and desorption branches of the isotherm. Single point pore volume was determined at \(p/p^0 = 0.97\).
5.3 Results and discussion

Chapters 3 and 4 have focussed on the optimization of spinning suspensions and the control of spinning parameters to achieve desired membrane structures, respectively. However, to determine the usefulness of different fibre morphologies, characterization of properties such as the porosity, mechanical strength and in particular the pore size distribution is essential. In order for the unique, asymmetric membrane morphologies consisting of finger-like voids and a sponge-like structure to be used in catalytic membrane reactors, the deposition of catalyst within the fibre must be optimized. Although the presence of finger-like voids in the support structure of a catalytic membrane reactor may lead to a reduction in the resistance to gas flow, unless the finger-like structures can be used for catalyst deposition the advantages of such asymmetric structures cannot be utilized.

5.3.1 Calcination temperature

Unfortunately, for asymmetric hollow fibres to function effectively as a catalytic hollow fibre membrane reactor, not only must catalyst impregnation be optimized but the fibre must posses sufficient mechanical strength and porosity. As discusses in Chapter 3, it is possible to increase the solids loading of the ceramic suspension used for the preparation of fibres by blending alumina powders with different particle sizes. The addition of nanometre size particles to the spinning suspension results in a substantial increase in the mechanical strength of the fibre. This can be seen from Figure 5.2 showing 3 point bending strength data for the hollow fibres shown in Figure 5.3.
Figure 5.2: 3 point bending strength data for fibres prepared from suspensions with varying particle size distributions.

Figure 5.3: SEM images of fibres prepared from suspensions containing (a): 1 and 0.3 µm particles and (b): 1 µm, 50 nm and 10 nm particles.
Using Equation 5.1 given in Section 5.2.6 the 3 point bending strength is normalized to the dimensions of the tested fibres so that fibres with slightly different wall thicknesses and inner and outer diameters can be compared. It can be seen from the SEM images that the morphology of the fibres are very similar, however the sponge-like region of the fibre prepared from a suspension of 1 and 0.3 µm particles occupies approximately 16% of the wall thickness compared to 22% for the fibre prepared from a suspension containing 1 µm, 50 nm and 10 nm particles. Although this slight increase in the volume of the fibre wall that is occupied by the sponge-like structure would lead to an increase in mechanical strength for the latter fibre, this cannot account for the large difference in the data which shows that the latter fibre is approximately 2.5 times as strong when sintered at 1500 °C. Although this data shows that the introduction of smaller particles into the spinning suspension gives rise to an increase in the mechanical strength, unfortunately there is an upper limit to the quantity of such particles that can be effectively dispersed due to the reasons discussed in Chapter 3.

Therefore, in order to impart the fibre with sufficient mechanical strength for practical applications, a minimum calcination temperature is required, which depends on the fibre morphology. A calcination temperature of 1450 °C is required for the fibre shown in Figure 5.4 which has been used in a catalytic membrane reactor for the dehydrogenation of propane [96,97].
As calcination temperature is a critical factor in determining the mechanical strength of the hollow fibre membrane or membrane support and a minimum calcination temperature is often required, it is important to determine the effect of calcination temperature on the pore size distribution. Therefore, asymmetric hollow fibres were prepared under the same conditions and were calcined at temperatures between 1200-1600 °C at intervals of 100 °C with an additional interval at 1450 °C due to the large amount of morphological change that occurs at temperatures between 1400 and 1500 °C. In order to determine the pore size distribution of both through and dead end pores present in the sponge-like region of the fibre, as well as the pores at the inner fibre surface formed by the entrances to the finger-like voids, both mercury intrusion porosimetry and a gas-liquid displacement technique were employed. Mercury intrusion data for fibres prepared using a 15 cm air-gap and calcined at temperatures between 1200-1600 °C can be seen in Figure 5.5.
It can be seen from the data that a bimodal pore size distribution exists and that as the calcination temperature is increased from 1200-1600 °C the peak pore size of the sponge like region increases from 0.12 µm at 1200 °C to approximately 0.18 µm at 1400 °C and that this increase is accompanied by a progressive reduction in pore volume which
continues up to 1500 °C, after which the sponge-like region is seen to densify [98]. It can be seen from pore size data generated using the gas-liquid displacement technique, Figure 5.6, that the peak pore size for the sponge-like region is present between 0.14-0.16 µm for fibres prepared under the same conditions and calcined at 1400 and 1450 °C.

![Pore size vs. calcination temperature](image)

Figure 5.6: Gas-liquid displacement data on pore size vs. calcination temperature for the asymmetric fibre shown in Figure 5.4, calcined at 1400 °C and 1450 °C.

As only through pores are measured using this technique, compared to both through and dead end pores for mercury intrusion analysis, the pore size distribution of both through and dead end pores present in the sponge-like region of the fibre is shown to compare well, establishing that mercury intrusion porosimetry can be used to infer the pore size of
both through and dead end pores. It is not possible, however, to determine the evolution of the pore size distribution during sintering using the gas-liquid displacement technique due to experimental inaccuracies associated with this method and the low mechanical strength of fibres calcined at temperatures below 1400 °C. It can be seen from mercury intrusion data that a reduction in pore size is not observed for the pores at the inner fibre surface formed by the entrances to the finger-like voids, resulting from the viscous fingering phenomenon, represented by the peak between 6-7 µm. It can also be seen from Figure 5.7, showing a plot of porosity against calcination temperature calculated from mercury intrusion data (left axis) and gas permeation data (right axis), that as the calcination temperature is increased, the sponge-like region of the fibre undergoes a reduction in porosity.

![Porosity of the sponge-like region of the fibre vs. calcination temperature](image)

**Figure 5.7:** Porosity calculated from mercury intrusion data and a gas permeation technique as a function of calcination temperature.
It should be noted that the porosity data in Figure 5.7 calculated from mercury intrusion data has been calculated for the sponge-like region of the fibre alone and the influence of the finger-like void region has been eliminated from the results. However, the mercury intrusion data refers only to the bulk porosity of the sponge-like region and gives no information on through pores due to the nature of mercury intrusion analysis, which is a volume based technique. In order to probe the effect of the calcination temperature on through pores, a gas permeation technique developed by Kong and Li [95] was used. It can be clearly seen that the porosity data calculated using mercury intrusion analysis and the gas permeation technique developed by Kong and Li agree well, again demonstrating the similarity in behaviour between through and dead end pores in this system. A very similar trend is identified using gas adsorption analysis, Figure 5.8.

Figure 5.8: Nitrogen adsorption data showing the BET surface area as well as the BJH adsorption and desorption pore area and the single point pore volume.
The data demonstrates the effect of calcination temperature on the pore/surface area as well as the pore volume. As the calcination temperature is increased from 1200 to 1450 °C both the surface area and pore volume are seen to decrease markedly. As the calcination temperature is increased from 1450-1600 °C the reduction tails off as the sponge-like region of the fibre undergoes densification.

The surface properties of both the lumen and shell side of hollow fibres used for membrane reactor applications are extremely important. The properties of the shell side of the fibre will determine the level of flux that can be achieved as well as the quality of a deposited separation layer while the properties of the inner fibre surface and the changes that occur during sintering will affect the degree to which catalyst can be deposited within the finger-like voids. The effect of calcination on fibre surface morphology can be seen in Figure 5.9.

![Inner surface 1200 °C](image1)

![Outer surface 1200 °C](image2)
Chapter 5  Characterization of Ceramic Hollow Fibre Membranes and Membrane Supports

Inner surface 1250°C

Outer surface 1250 °C

Inner surface 1300 °C

Outer surface 1300 °C

Inner surface 1350 °C

Outer surface 1350 °C
Inner surface 1400 °C

Outer surface 1400 °C

Inner surface 1450 °C

Outer surface 1450 °C

Inner surface 1500 °C

Outer surface 1500 °C
Figure 5.9: Surface SEM images of hollow fibres calcined at temperatures between 1200 and 1600 °C.

The difference between the inner and outer surfaces is immediately obvious. The porosity of the outer surface is reduced as the calcination temperature is increased and the membrane finally becomes dense and smooth at 1600 °C as a result of particle growth during sintering. In contrast, although particle growth is also observed at the inner surface, the structure remains porous. This is an important feature of this membrane morphology as the inner surface must remain porous in order for catalyst to penetrate the inner surface. The increase in pore size and the decrease in porosity that have been shown
from mercury intrusion data are also seen visually from the SEM images in Figure 5.9, i.e. a reduction in the number of pores and an increase in pore size. The stark contrast between the inner and outer surface after calcination, even at high temperature, may be a consequence of their differing properties prior to sintering. Due to the presence of a large air-gap (15 cm) a densely packed layer is formed at the outer surface. The opposite is true of the inner surface which is porous in nature due to the rapid inflow of non-solvent. During sintering, particle growth occurs at both the inner and outer surfaces and it seems that near the outer surface the degree of membrane shrinkage is sufficient to eventually close up any voids that may remain. This is not true of the far more porous inner region. In this case particle growth occurs but the degree of membrane shrinkage is insufficient to eliminate the pore structure. It is also possible however that the difference between the two surfaces is the result of a difference in particle size or other factors affecting sintering.

Therefore, it has been shown that as the calcination temperature is increased, despite the elimination of porosity and the increase in pore size and eventual densification of the sponge-like region and outer surface, the pore size of the pores at the inner surface, formed by the entrances to the finger like voids, is first reduced slightly to approximately 6 µm and then returns to 7 µm at 1600 °C. This fact is essential when preparing fibres for use in a catalytic membrane reactor as the pores at the inner fibre surface formed by the entrances to finger-like voids provide the means by which catalyst can be impregnated within the hollow fibre structure.
5.3.2 Suspension viscosity

It has been shown that for the fibre shown in Figure 5.4 the morphology is such that the calcination temperature can be increased to achieve sufficient mechanical strength with no detrimental effect on the size of the entrances to the finger-like voids and hence the effectiveness of catalyst deposition within the support structure. However, due to the unwanted reduction in porosity associated with an increase in calcination temperature it is desirable for this temperature to be reduced. In order for this to be done without altering the properties of the spinning suspension, such as the solids loading, particle size distribution and ceramic/polymer ratio and while maintaining sufficient mechanical strength, the relative ratio of the sponge-like region to the finger-like region must be increased.

As discussed in Chapter 4, the relative ratios of the finger-like void and sponge-like regions in asymmetric hollow fibres, i.e. the thickness of the sponge-like region of the fibre can be varied by adding a non-solvent additive to the spinning suspension. This greatly affects not only the initial suspension viscosity but also the rate at which the viscosity increases during the phase inversion process. In order to determine the effect of the suspension viscosity on the pore size distribution, fibres were prepared using a 15 cm air-gap with the addition of 0, 2, 4, 6, 8 and 10 wt% water (as a percentage of the total solvent content) to the spinning suspension. It has been shown in Chapter 4, Section 4.3.4, Figure 4.7 that the addition of water as a non-solvent additive causes the viscosity to increase to 22.5 Pa.s as the concentration of water is increased to 6 wt%. Further addition of water leads to a more dramatic increase up to 45 Pa.s at 10 wt% water.
Figure 5.10: Mercury intrusion data for fibres prepared with an air-gap of 15 cm and 0-10 wt% water (as a percentage of the total solvent content) in the spinning suspension, calcined at 1200 °C.

The effect of water addition to the spinning suspension is a reduction in the length of finger-like voids and an increase in the thickness of the sponge-like region of the fibre (Chapter 4, Section 4.3.4, Figure 4.8). Inspection of Figure 5.10 showing mercury
intrusion data for fibres prepared from suspensions containing water as a non-solvent additive clearly shows the dramatic effect that the viscosity increase has on the pore size of the entrances to the finger-like voids.

A peak at approximately 0.1-0.2 µm represents the sponge-like region of the fibre and varies little as the concentration of water is increased. This is not the case however for the pores formed by the entrances to the finger-like voids, which are dramatically reduced in size from 5 µm to approximately 1 µm even after the addition of only 2 and 4 wt% water. Further addition of water results in the elimination of this peak indicating that the entrances to the finger-like voids are no longer present at the inner fibre surface. Therefore, despite the presence of finger-like voids and the asymmetry of the hollow fibre cross section as observed by SEM, the mercury intrusion data shows that addition of water to the spinning suspension first results in a reduction in the size of the pores formed by the entrances to the finger-like voids and then in the formation of a sponge-like region at the inner surface of the fibre. In this situation, a peak representing the finger-like voids is not seen in mercury intrusion data. As the finger-like voids are only accessible through a sponge-like region (pore size of approximately 0.12-0.18 µm), in order for mercury to intrude into the finger-like voids themselves, the intrusion pressure must exceed that of the sponge-like region. Consequently, mercury intrusion into the finger-like voids will be included in the intrusion volume of the sponge-like region in the data. Therefore, the presence or absence of an additional peak in the intrusion data, other than that representing the pores of the sponge-like region, demonstrates whether the finger-like voids are accessible for mercury intrusion and/or catalyst deposition from the fibre surface. If the suspension viscosity is above a critical value, the viscous fingering
phenomenon is not observed and finger-like void growth is prevented. In this case, due to the presence of non-solvent in the spinning suspension and the large availability of non-solvent near the surface of the suspension film, the viscosity in this region is prohibitively high and viscous fingering does not occur. However, as non-solvent diffuses further into the suspension film, where the availability of non-solvent is reduced, the concentration of solvent is higher and the suspension viscosity is lower, viscous fingering then occurs and initiates the formation of finger-like voids in this region. Consequently, the morphology that results is that of a sponge-like region at the inner fibre surface and finger-like voids that originate from within the bulk of the fibre. It is not only the initial suspension viscosity that is important in determining the morphology but also the rate of the increase in viscosity once the phase inversion process has been initiated, which is determined by the precipitation rate of the polymer phase. This can be demonstrated by the addition of ethanol as a non-solvent additive which reduces the suspension viscosity (Chapter 4, Section 4.3.5 Figure 4.10).

The effect of ethanol addition on the pore size of the entrances to the finger-like voids for fibres prepared with a 15 cm air-gap can be seen in Figure 5.11.
Figure 5.11: Mercury intrusion data for fibres prepared with a 15 cm air-gap and 0-10 wt% ethanol (as a percentage of the total solvent content) in the spinning suspension, calcined at 1450 °C.

The data shows that the pore size is relatively unchanged at between 4-6 µm after the addition of 2 and 4 wt% ethanol to the spinning suspension. In this case it is likely that the reduction in initial suspension viscosity is balanced by the increase in precipitation rate brought about by the addition of ethanol, resulting in little or no change in the pore size. However, as the concentration of ethanol is increased to 6 and 10 wt% the pore size drops to approximately 1µm despite the reduction in suspension viscosity to 8.5 Pa.s, demonstrating the importance of the polymer precipitation rate in determining the pore
size of the entrances to the finger-like voids. When controlling the thickness of the sponge-like region by the addition of a non-solvent additive, the pore size of the entrances to the finger-like voids is substantially reduced and finger-like voids may no longer be accessible above a certain non-solvent concentration, depending on the non-solvent in question. Based on this data, it is concluded that increasing the mechanical strength of an asymmetric support by introducing a non-solvent additive into the spinning suspension is an unsuitable method when preparing support structures for catalyst impregnation, due the unfavourable pore size reduction and elimination of the entrances to the finger-like voids present at the inner fibre surface.

**5.3.3 Internal precipitant flow rate**

By varying the internal precipitant flow rate from 3-15 ml/min it has been shown that the thickness of the sponge-like region can be varied greatly (Chapter 4, Section 4.3.3, Figure 4.6). Mercury intrusion data for fibres prepared with internal precipitant flow rates of 3, 6, 7, 8, 9, 12 and 15, ml/min and an air-gap of 15 cm are shown in Figure 5.12.
Figure 5.12: Mercury intrusion data for fibres prepared with internal precipitant flow rates between 3 and 15 ml/min and an air-gap of 15 cm, calcined at 1450 °C.
The characteristic bimodal pore size distribution associated with fibres prepared in this way is evident from the mercury intrusion data. In all cases the peak representing the sponge-like region can be found at approximately 0.1-0.2 µm. However, the peak representing the pores at the inner surface formed by the entrances to the finger-like voids, resulting from the viscous fingering phenomenon, is present at 1.2 µm for a flow rate of 6 ml/min, at approximately 5.5 µm for flow rates of between 7-12 ml/min and at 9 µm for a flow rate of 15 ml/min. Notably absent is a second peak representing the pores formed by the entrances to the finger-like voids for the fibre prepared with an internal precipitant flow rate of only 3 ml/min. In this case, the driving force for the formation of finger-like voids is insufficient to overcome the viscosity of the suspension at the interface between the suspension film and the internal precipitant. Consequently, viscous fingering is not initiated at this interface but is instead initiated within the suspension film itself, where the viscosity is lower. Consequently, a sponge-like region is formed at the inner fibre surface, rendering the fibre unsuitable for catalyst impregnation. Also notable in the fibre prepared with an internal precipitant flow rate of 3 ml/min are finger-like voids originating from the shell side of the fibre. A corresponding peak in the mercury intrusion data is also absent, indicating that the finger-like voids do not originate at the outer fibre surface. In this case, finger-like voids are isolated within the sponge-like structure and serve only to reduce the mechanical strength. Due to the limited concentration gradient that results from a low internal precipitant flow rate, solvent/non-solvent exchange and polymer precipitation is reduced. Therefore, when the nascent fibre is immersed in the external precipitation bath, the viscosity is below the threshold at which viscous fingering is possible. In addition, a concentration gradient still exists due
to the limited availability of non-solvent in the lumen of the fibre and solvent/non-solvent exchange between the suspension and the external precipitation bath results in the formation of finger-like voids originating from the outer region of the fibre. However, due to the presence of an air-gap, the viscosity at the outer fibre surface is above the viscous fingering threshold and consequently finger-like voids do not originate from the fibre surface itself. Based on this data, it is concluded that increasing the mechanical strength of the asymmetric support by reducing the internal precipitant flow rate is an unsuitable method when preparing support structures for catalyst impregnation, due the unfavourable pore size reduction and elimination of the entrances to the finger-like voids present at the inner fibre surface.

5.3.4 Air-gap

It can be seen from the SEM images of fibres prepared with air-gaps of between 3-13 cm and an internal precipitant flow rate of 7 ml/min that a reduction in air-gap gives rise to an increase in the thickness of the sponge-like region and consequently an increase in mechanical strength (Chapter 4, Section 4.3.2, Figure 4.4). However, the appearance of isolated voids in the sponge-like structure, the formation mechanism of which is detailed in Chapter 4, Section 4.3.2, is observed which will lead to a reduction in mechanical strength. In addition, a reduction in the size of the entrances to the finger-like voids is seen from mercury intrusion data, Figure 5.13.
Figure 5.13: Mercury intrusion data for fibres prepared with air-gaps between 3 and 13 cm and with an internal precipitant flow rate of 7 ml/min, calcined at 1450 °C.

Due to the relatively low internal precipitant flow rate, finger-like void entrance size is seen to vary greatly with the highest values of between 4-5 µm for fibres prepared with air-gaps of 3, 7, 9 and 13 cm and 0.4 and 1.3 µm for fibres prepared with air-gaps of 5 and 11 cm respectively. Both isolated voids and a reduction in the size or elimination of
the entrances to the finger-like voids are detrimental to the effectiveness of catalyst impregnation into the asymmetric membrane or membrane support structure.

Therefore, in an attempt to increase the thickness of the sponge-like region while at the same time retaining an acceptable pore size of the entrances to the finger-like voids, as well as preventing the formation of isolated voids in the sponge-like region, fibres were prepared with air-gaps between 1-13 cm and with an internal precipitant flow rate of 12 ml/min. From SEM images (Chapter 4, Section 4.3.2, Figure 4.5), it is shown that despite the progressive increase in the thickness of the sponge-like region as the air-gap is reduced, accounting for over 50 % of the thickness of the fibre cross section in fibres prepared using an air-gap of only 1 cm, the almost total absence of isolated voids is apparent. In addition, despite the reduction of the length of the air-gap, the mercury intrusion data shown in Figure 5.14 demonstrates that the pore size of the entrances to the finger-like voids remains at between 7-9 µm.
Figure 5.14: Mercury intrusion data for fibres prepared with air-gaps of 1-13 cm and with an internal precipitant flow rate of 12 ml/min, calcined at 1450 °C.

Therefore, the thickness of the sponge-like region and hence the mechanical strength of the fibre can be controlled by varying the air-gap only if the internal precipitant flow rate is sufficient to prevent the formation of isolated voids and to generate an acceptable pore size of the entrances to the finger-like voids.
5.4 Conclusions

Using the combined phase inversion and sintering technique, asymmetric ceramic hollow fibre membranes and membrane supports can be prepared in a single step. Fibres prepared in this way may consist of both finger-like voids and a sponge-like structure in varying ratios. The asymmetric fibre may function as either a porous membrane and a matrix for catalyst deposition, or as a porous support for the coating of a gas separation layer and a matrix for catalyst deposition and may function as a highly compact multifunctional catalytic membrane reactor. Both the pore size distribution of the pores formed by the entrances to the finger-like voids and of the sponge-like region are critical in determining the effectiveness of catalyst deposition and the quality of the separation layer, respectively. It has been shown that an increase in calcination temperature leads to an increase in the mechanical strength of the fibre but this is accompanied by an unwanted increase in the mean pore size of the sponge-like region as well as a decrease in porosity. However, it has also been demonstrated that entrances to finger-like voids that are present at the inner fibre surface remain open during the calcination process and resist densification, a crucial property that allows for catalyst deposition within the finger-like voids. The mechanical strength of the fibre can also be augmented by increasing the thickness of the sponge-like region, which provides the bulk of the mechanical strength. In order to control the morphology and mechanical strength of the fibre while at the same time maintaining the desired pore structure, a selection of preparation parameters have been varied systematically. It has been shown in this work that by using a non-solvent additive in the spinning suspension and by varying spinning parameters such as the internal precipitant flow rate and air-gap, the viscosity of the suspension during the
spinning process and the fibre morphology can be manipulated. The addition of a non-
 solvent additive to the spinning suspension leads to both an increase in suspension
 viscosity and an increase in the polymer precipitation rate, resulting in an increase in the
 thickness of the sponge-like region of the fibre cross section. The same morphological
 change results from a reduction in air-gap or internal precipitant flow rate. However, in
 all three cases, the pore size of the entrances to the finger-like voids is dramatically
 reduced or even eliminated altogether and the appearance of isolated voids within the
 sponge-like structure of the fibre is observed, which cause an undesired reduction in
 mechanical strength. It has been shown in this work that, in the absence of a non-solvent
 additive in the spinning suspension and with a sufficiently high internal precipitant flow
 rate, a reduction in air-gap leads to an increase in the thickness of the sponge-like layer
 while at the same time maintaining the pore size of the entrances to the finger-like voids,
 allowing for efficient deposition of catalyst within the hollow fibre support structure.
 Therefore, by varying these parameters in combination, it is possible to optimize the
 hollow fibre support structure with respect to the morphology, mechanical strength and
 pore size distribution.

5.5 References

[94] P. Mikulasek and P. Dolecek, Characterization of Ceramic Tubular Membranes by
 Active Pore-Size Distribution, Separation Science and Technology 29 (9) (1994)
 1183-1192.

[95] J. Kong and K. Li, An improved gas permeation method for characterising and
 predicting the performance of microporous asymmetric hollow fibre membranes


Chapter 6

Ceramic Hollow Fibre Applications

Abstract

Highly asymmetric alumina hollow fibre membrane supports have been prepared using a combined phase inversion and sintering technique for use in a hollow fibre membrane micro-reactor for hydrogen production and a catalytic hollow fibre membrane reactor for the dehydrogenation of propane. The outer surface of the hollow fibre supports have been coated with a hydrogen selective membrane while the finger-like region in the hollow fibre wall functions as a substrate for catalyst particles. Two methods for catalyst deposition have been compared and the feasibility of this novel membrane reactor design has been demonstrated.
6.1 Introduction

In the previous chapters the combined phase inversion and sintering technique for the preparation of inorganic hollow fibre membranes and membrane supports has been shown to be an extremely versatile method in terms of the morphological control that can be achieved in a cost effective way. This results in a wide range of possible applications.

The desire to increase surface area/volume ratios in membrane modules is the principal driving force for the use of hollow fibre geometries and the additional control that can be achieved over the fibre morphology using this method allows for the optimization and control over the performance of such fibres. In this chapter applications are introduced in which the fibre morphology has been designed using the information gained from the work discussed in the previous chapters. The applications for which hollow fibres have been prepared are listed below.


2. A catalytic hollow fibre membrane reactor for the dehydrogenation of propane.

6.1.1 Membrane reactors

Membrane reactors combine separation or distribution and reaction within the same unit. Designing catalytic reactors based on this concept has a number of advantages over traditional reactor technologies. The membrane can separate a product from an equilibrium limited reaction leading to greater conversions and lower operating temperatures [99-101]. In addition, the different phases of the reaction mixture are separated and individual control over the feed and permeate phases can be achieved,
leading to a greater level of control over the operating parameters of the reactor. The presence of a membrane may change the pressure dependence of chemical reactions allowing the reaction to be performed at higher pressures, leading to smaller reactors and better heat transfer characteristics which may be beneficial when combining endothermic and exothermic reactions sequentially. These benefits lead to reactors that are smaller and more efficient when compared with traditional reactor designs.

Ceramic materials are well suited for use in high temperature membrane reactors [102-104] due to their extreme tolerance to heat. In this work ceramic membranes have been developed for use as catalytic membrane reactors for hydrogen production by water-gas-shift and for the dehydrogenation of propane.

6.1.2 Ceramic hollow fibre catalytic membrane microreactors

Due to the small size scales achieved by the implementation of microreactors, heat dissipation is far more efficient than in traditional larger reactor designs. This has several benefits: (1) Reactions involving reactants or products that may be unstable above certain temperatures can be dealt with safely using a microreactor as the temperature of the reactor may be much lower. (2) Due to the reduction in temperature, expensive and exotic materials that are resistant to extreme heat may not be necessary. (3) The unit may reach its operating temperature more quickly leading to much shorter start-up and cooling down times and increased efficiency. (4) Scaling up is facilitated and the performance of larger units may be predicted more easily by simply increasing the number of reactor chambers in a microreactor. (5) Mass transfer rates are increased as a result of the small size of the microreactor leading to increased efficiencies. The principal disadvantage of the micro-
reactor concept is the production cost involved in the fabrication of such reactors and although a number of fabrication techniques have been implemented such as dry and wet etching, micromachining and lithography, these techniques require multiple stages and can be costly and time consuming.

Therefore, by using inorganic hollow fibres with a unique asymmetric pore structure, which have an extremely high surface area to volume ratio and excellent thermal resistance, as either a porous membrane and a matrix for catalyst deposition, or as a porous support for the coating of a gas separation layer and a matrix for catalyst deposition [105], a highly compact multifunctional catalytic membrane reactor can be realized.

Using the combined phase inversion and sintering technique hollow fibres can be prepared consisting of a sponge-like region that can either serve as a separation layer or as the substrate for a separation layer and a region of finger-like voids. This is shown schematically in Figure 6.1.
Figure 6.1: A schematic representation of an asymmetric hollow fibre catalytic reactor consisting of a sponge-like structure and a region of micro-channels.

In such a fibre, each finger-like void functions as a micro-channel and is analogous to the channels that are fabricated using traditional techniques for the preparation of microreactors. The design of the fibre morphology is such that catalyst may be deposited within each finger-like void and a separation layer may be deposited on the outer surface of the fibre. By using this method it is possible to deposit a separation layer such as a palladium hydrogen selective membrane on the outer surface of the fibre directly. When fibres are prepared using other methods it is only possible to generate symmetric structures initially and for a separation layer to be successfully deposited on the fibre surface the pore size and surface roughness must be within certain limits. If the pore size is too large then the effective thickness of the deposited membrane increases, as shown schematically in Figure 6.2.

Figure 6.2: A schematic representation of the effective thickness of a separation layer deposited on a porous support.
On the other hand, if the pore size is too small then adhesion of the membrane to the support may be limited and delamination may take place during operation, a problem that will be exacerbated by a reduction in the porosity of the support. However, a symmetric membrane with a sufficiently small pore size for the successful deposition of a palladium layer would generate an unacceptable resistance to mass transfer across the membrane cross section. Consequently, support structures are prepared with a large pore size and then layers with successively smaller pore sizes are deposited on top of one another to finally yield a surface suitable for the deposition of a palladium or palladium alloy layer. In addition to increasing the chance of reactor failure due to delamination of one of the layers, each successive layer, of which there may be many, requires a separate preparation, drying and sintering step which is both costly and extremely time consuming. By preparing a ceramic hollow fibre microreactor using the combined phase inversion and sintering technique, the support structure and the substrate for the separation layer can be formed in a single step. Moreover, the finger-like region of the fibre serves not only as a support for the substrate for the separation layer but also forms a region of many microchannels which may be packed with catalyst. In this way the lumen of the fibre remains empty, thus reducing the resistance to flow and the pressure drop along the fibre length. It has been shown that the properties of the substrate for the separation layer (outer region of the fibre) are a function of the properties of the ceramic suspension such as the particle size distribution, the total ceramic content and the ratio of ceramic material to polymer binder [106,107]. Therefore, by changing the suspension composition the pore size and porosity of the substrate layer can be varied while still retaining the macrostructure of the fibre.
Furthermore, by preparing a ceramic fibre with a sandwich-like structure as seen in Figure 4.4(a) (Chapter 4) the membrane microreactor concept could be developed further, Figure 6.3.

![Figure 6.3: A schematic representation of a bi-functional hollow fibre catalytic membrane reactor.](image)

Compounds A and B could be reacted in Reaction Zone 1 in the presence of Catalyst 1 to yield product C. The product mixture is then enriched in a particular component as it passes through the separation layer, after which it is reacted with compound D in Reaction Zone 2 in the presence of Catalyst 2 to yield product E. Not only does the separation layer serve to separate reactants from products but it also disperses the permeate phase uniformly in Reaction Zone 2. Such a scheme could be employed to combine reforming and water-gas-shift reactions within the same hollow fibre membrane reactor. For example, a mixture of methanol and water could be converted to hydrogen, carbon dioxide and carbon monoxide in Reaction Zone 1. The permeate mixture, enriched in hydrogen as a consequence of passing through the separation layer, may
undergo a water-gas-shift reaction in Reaction Zone 2 with steam being fed into the lumen side of the fibre, thus increasing the concentration of hydrogen further and reducing the concentration of carbon monoxide. This scheme has been shown to be preferable to the use of a separation layer with a high selectivity for hydrogen due to the low permeance associated with such a selective layer [108]. Greater reactor fluxes and efficiencies can be achieved if the permeance of the separation layer is increased at the expense of hydrogen selectivity and the water-gas-shift reaction is employed to further increase the hydrogen concentration in the permeate stream and to reduce the concentration of CO. As with the combination of reforming and water-gas-shift reactions, an additional increase in reactor efficiency may result from the union of exothermic and endothermic reactions as the heat generated during the exothermic reaction is available to shift the equilibrium of the endothermic reaction towards the product side. In a variation of this scheme, reaction of A with B may yield two or more products which permeate through the sponge-like region and react together in Reaction Zone 2 in the presence of Catalyst 2. In this case, additional reactants are not supplied to the lumen side of the fibre.

6.1.3 Catalyst impregnation

An inorganic hollow fibre with an asymmetric pore structure is shown in Figure 6.4 and consists of an outer sponge-like region (Region 1), finger-like voids (Region 2), and a region close to the inner fibre surface (Region 3) which may either be occupied by a sponge-like structure or by finger-like voids, depending on the fibre preparation parameters.
Figure 6.4: Cross-sectional SEM image of an asymmetric ceramic hollow fibre consisting of finger-like voids and a sponge-like structure.

Unlike previous work [109-111] the combined phase inversion and sintering technique has been employed to generate unique asymmetric structures in a single step. The entrances to the finger-like voids form pores at the inner surface in the absence of an inner sponge-like region, allowing for catalyst to be deposited within the finger-like void structures more easily. In addition, the outer sponge-like region of the fibre may function as either a porous separation layer or as a substrate for the deposition of a separation layer, such as a Pd-based hydrogen permselective membrane [105]. The pore size of the entrances to the finger-like voids present at the inner fibre surface and the finger-like void volume determine the effectiveness of the catalyst deposition process while the pore size distribution of the sponge-like region is critical in determining the efficiency of the separation process or the quality and thickness of the deposited separation layer. By
depositing different catalysts in the finger-like void structures and by depositing an additional separation layer, the developed asymmetric inorganic hollow fibres can thus be used for the construction of a variety of catalytic membrane reactors for a wide range of applications.

In order for the catalytic membrane reactor to function efficiently, the support structure as a whole must produce as little resistance as possible to the permeation of gas. This is achieved by preparing the asymmetric structure mentioned, in which the finger-like voids may be impregnated with catalyst and which minimize resistance to gas permeation, while a palladium membrane may be deposited directly onto the smooth outer surface. The thickness of the sponge-like outer region onto which the palladium membrane is deposited is also minimized and the need to deposit an intermediate layer is eliminated. However, as the sponge-like region provides the bulk of the mechanical strength there is a lower limit to the thickness of this region depending on the application. By varying the spinning suspension composition and the spinning parameters the relative ratios of the finger-like and sponge-like regions, i.e. the thickness of the sponge-like region, can be varied systematically [112]. In most cases, the hollow fibre support material can not function directly as a substrate for catalyst particles so the catalytically active compounds must first be immobilized on a substrate. Deposition of catalyst within the support structure may be achieved in one of three ways. Method 1: Catalyst may be deposited on substrate particles which are then impregnated into the support [105]. Method 2: The catalyst substrate may be deposited in the support, followed by treatment with a homogenous solution containing catalyst precursor compounds [113-116]. Method 3: The support may be treated with a homogenous solution containing both catalyst precursor
and catalyst substrate precursor compounds and the catalyst-substrate complex may for “in-situ” within the support. However, impregnating a support structure which has a sufficiently small pore size to allow the direct deposition of a palladium layer creates a large, additional, undesired resistance to gas permeation. This problem is exacerbated when depositing catalyst using Method 1 as the catalyst-substrate particles will block pores and may aggregate at the point of entry into the support structure. The same applies to catalyst deposited using Method 2, in which a substrate for the catalyst is deposited prior to the introduction of a solution of catalyst precursors, as both the substrate and catalyst may be deposited in the porous structure of the support. Ideally, the porous separation layer or substrate for a separation layer (sponge-like structure) should not come into contact with catalyst particles, its pore structure should remain open and unhindered and the catalyst should be contained in the finger-like void structures only. If Region 3 consists of a sponge-like structure, the entrances to the finger-like voids are not present at the inner fibre surface and a degree of “pore blockage” of the inner sponge-like structure is unavoidable. In this case, Method 1 will result in the greatest amount of blockage due to the larger diameter of the catalyst/substrate particles. If the entrances to the finger-like voids are accessible from the fibre surface then “pore blockage” may be eliminated, with a large finger-like void entrance giving rise to more effective catalyst impregnation and lower resistance to gas permeation.

6.2 A novel catalytic membrane microreactor for COX free H₂ production

In recent years there has been a surge in interest in microreactors for the production of hydrogen for fuel cell applications due to increasing energy consumption and a reduction
in the size of many modern devices that require electrical power. Although there have been great advances in battery technology in recent years, it has now become clear that an alternative technology is needed if the power demands of modern devices are to be satisfied. In particular, the prospect of the use of hydrogen in the transportation sector as a fuel to produce electricity has gained a great deal of interest due to the increasing or unstable cost of fossil fuels and the desire to reduce CO₂ emissions from vehicles. Moreover, the efficiency of electricity production using electrochemical methods may far exceed the efficiencies that can be achieved with an internal combustion engine. The leading technology for onboard, and in some cases stationary, production of hydrogen is the proton exchange membrane fuel cell (PEMFC). In such devices molecular hydrogen is ionized on contact with a platinum catalyst before transversing a polymer electrolyte and combining with oxygen to form water. The electrons liberated by the ionization of molecular hydrogen flow around an electrical circuit to combine with oxygen and protons on the other side of the membrane to form water. Unfortunately, the storage of a sufficient quantity of hydrogen is problematic and advances in this area of research has been limited. Therefore, the onboard production of hydrogen is seen as the most promising technology to allow for the implementation of PEMFC technology in both transportation and portable applications. Two critical factors determining the feasibility of onboard hydrogen production are the size and efficiency of the hydrogen generation device and the elimination of CO from the PEMFC feed stream in order to prevent deactivation of the catalyst.

A convenient and promising method for hydrogen production involves the reforming of ethanol as this feedstock is relatively non-toxic, miscible with water and is easily
transported at ambient temperatures and pressures and in order to produce a CO free hydrogen stream for use in a PEMFC two approaches are possible. (1) CO can be eliminated in the product stream by implementing the water-gas-shift (WGS) reaction or (2) a hydrogen selective membrane can be implemented to produce a pure hydrogen product stream. In the former case, it is not necessary that the membrane has a high selectivity for hydrogen and it has in fact been demonstrated by Lee et al. [117] that the permeability of the membrane rather than the selectivity for hydrogen can be a more important factor in such a system. Therefore, ceramic membranes prepared in this study may be used for this purpose without the need for further modification. However, if a pure hydrogen product stream is the desired outcome, a hydrogen selective layer can be deposited in order to achieve this. Hydrogen selectivity based on size exclusion in ceramic membranes has been demonstrated but the generation of pore sizes in this range can be difficult, expensive and time consuming. By using a dense hydrogen selective layer such as a palladium or palladium alloy membrane, hydrogen selectivities approaching infinity can be achieved and the deposited selective layer can be prepared reproducibly and with greater ease using a method such as electroless plating [118]. Therefore, by implementing the asymmetric hollow fibres prepared in this work for hydrogen production by water-gas-shift as a test reaction, the advantages of this microreactor concept can be demonstrated and the technology can be applied to steam reforming of ethanol for onboard hydrogen production in future work.

The reactor integrates both a catalytic membrane microreactor (CMMR) and a Pd membrane in the same unit, Figure 6.5, and offers several advantages over existing H₂ production systems. Firstly, the CMMR reduces the pressure drop, increases the catalytic
surface to volume ratio and improves the heat and mass transfer as well as the mixing of gases during the reaction. Secondly, this reactor works at significantly lower temperature and/or using lower quantities of catalyst than conventional reactors. Finally, this reactor combines the processes of generating and separating H$_2$ in a single step by the integration of an hydrogen selective Pd layer.

Figure 6.5: SEM images of a hollow fibre microreactor for H$_2$ production. (a): Hollow fibre cross section, (b): hollow fibre cross section at increased magnification, (c): surface of palladium separation layer.

The asymmetric structure shown in Figure 6.5(a) allows for the use of the alumina hollow fibres as a single support for both the Pd layer and 30%CuO/CeO$_2$ catalyst in the development of the ceramic hollow fibre membrane microreactor (CHFMMR). Figure 6.5(b) clearly shows that the finger-like region is made up of many micro-channels which
are perpendicularly distributed around the fibre lumen. This unique structure allows for 
Al₂O₃ hollow fibres to be used as an extremely efficient support in a catalytic 
microreactor. Finally, the relationship between the thickness of the finger-like and the 
sponge-like regions imparts the Al₂O₃ hollow fibres with sufficient mechanical strength 
while retaining a high permeability.

Results show that the maximum conversion obtained in a fixed-bed reactor configuration 
is 23% lower than that obtained in the CHFMMR shown in Figure 6.5 under the same 
reaction conditions. This increase in the catalytic activity can be explained by the 
presence of micro-channels in the finger-like region where the catalyst is dispersed, 
which improves the catalytic surface to volume ratio and the heat and mass transfer as 
well as the mixing of gases during the reaction.

6.3 The dehydrogenation of propane to propene

Hollow fibres have been prepared consisting of finger-like voids and a sponge-like 
structure in order that the finger-like voids generated during the fibre preparation process 
may be impregnated with catalyst and the sponge-like region of the fibre may serve as a 
substrate for a hydrogen permselective membrane. Inorganic hollow fibre membrane 
reactors iHFMR-I [105] and iHFMR-II [113] were designed, bases on this principal, for 
the dehydrogenation of propane to propene.

Two methods of catalyst deposition have been used to impregnate the alumina hollow 
fibre substrate with catalyst: (1) Sub-micron sized Pt(0.5wt.%)/γ-alumina catalyst 
particles were prepared and deposited into the substrate of the hollow fibre membrane
reactor (iHFMR-I) prior to the deposition of a Pd/Ag hydrogen permselective membrane on the outer fibre surface. Prior to catalyst deposition, the catalyst particles were dispersed in an aqueous medium using Arlacel P135 as dispersant. Only the catalyst particles suspended evenly in the aqueous medium were used for subsequent catalyst deposition and as a result, a very small amount of the catalyst is deposited uniformly in the finger-like voids of the asymmetric alumina substrates. It can be seen from Figures 6.6(a) and 6.6(b) that the surfaces of the finger-like voids in iHFMR-I are covered by a thin layer of sub-micron sized catalyst particles, while the sponge-like regions of the substrate remain unaffected.

![Figure 6.6](image_url)

Figure 6.6: SEM images of catalyst deposition in a hollow fibre substrate. (a): Catalyst particles deposited within the finger-like voids and (b): the surface of the finger-like voids at increased magnification.
Figure 6.6(b) shows the finger-like void surface at high magnification and indicates that the catalyst particles are sparsely deposited. This agrees with the result that, after catalyst deposition, the average weight gain of the asymmetric alumina hollow fibre substrates (30 cm in length) is approximately only 0.74%.

As a consequence of the limited weight gain associated with this method, a second method of catalyst impregnation was investigated: (2) The asymmetric alumina hollow fire substrates are functionalized by depositing SBA-15 mesoporous silica inside the finger-like voids using a sol-gel technique, followed by treatment with a solution containing Pt catalyst precursors. It can be seen from Figures 6.7(a-d) that SBA-15 has been successfully deposited within the alumina hollow fibre substrates and instead of blocking the finger-like voids completely, there is a gap between the deposited SBA-15 and the walls of the finger-like voids after calcination.
In this case a pure Pd hydrogen permselective membrane was deposited on the shell side of the fibre to form a catalytic hollow fibre membrane reactor (iHFMR-II).

A comparison of the surface area increase and weight gain for the two methods for catalyst impregnation can be seen in Figure 6.8.
In comparison with Method (1) in which the catalyst was first deposited on γ-alumina particles before impregnation into the finger-like voids of the hollow fibre support, Method (2) is much more efficient and achieves greater loading of catalyst with a higher surface area, and as a result yields a significantly higher catalyst surface area in the functionalized substrates. The increase in the surface area of the reaction zone (5 cm in length) in iHFMR-II, which is calculated based on the amount of SBA-15 deposited, is approximately 5.19 m², which is much higher than the value of 0.22 m² obtained for iHFMR-I.

A comparison of the performance of iHFMR-I and iHFMR-II was undertaken and the performance was compared with a fixed bed reactor (FBR) in which 0.1 g of
Pt(0.5wt.%)/γ-alumina catalyst was packed into the centre of a dense ceramic tube, 9 mm in diameter. The results clearly demonstrated the advantages of the asymmetric hollow fibre membrane microreactor concept, particularly in terms of the space time yield for the reaction. Detailed operational data can be found elsewhere [113,119].

6.4 Conclusions

The hollow fibre membrane microreactor concept is applicable to a wide range of applications such as the dehydrogenation of propane and hydrogen production by water-gas-shift so the ability to manipulate the fibre morphology to maximize performance for each application or situation is essential. By studying the preparation of fibres from raw materials through to fibre precursors and finally the sintered product, it is possible to vary the fibre morphology and a high level of control over the final product properties can be achieved. For fibres to be prepared with the desired properties, adequate control over the processes involved at each stage of fibre preparation is required, from the preparation of the spinning suspension to the formation of the fibre precursor and the effect of heat treatment. By using alumina/PESf/NMP systems to study the formation mechanisms for finger-like void structures and determining a generic mechanism (viscous fingering), the formation of finger-like and sponge-like structures can be predicted and controlled when preparing hollow fibres for a wide range of applications. The asymmetric structures consisting of finger-like voids and a sponge-like structure allow hollow fibres prepared using the combined phase inversion and sintering technique to function as both a substrate for catalyst and a substrate for a separation layer such as a palladium or palladium alloy membrane. The advantages of this reactor configuration have been
demonstrated by comparison with a traditional fixed bed reactor design and increased efficiencies have been observed, resulting from the implementation of novel asymmetric hollow fibre structures.

**6.5 References**


Chapter 7

Conclusions and Future Work

7.1 General conclusions

This thesis has demonstrated that with proper control over the properties of ceramic suspensions used for the fabrication of ceramic hollow fibres and over the many relevant variables during fibre spinning, a wide range of morphologies can be obtained. Despite the complexity introduced by the large number of parameters involved, with a good understanding of how they interact to affect the fibre structure, this can be seen as an advantage. By understanding the relationship between the composition and properties of the spinning suspension, the spinning parameters and the fibre structure, it is possible to design hollow fibres with a wide range of structures.

7.1.1 Suspension preparation

The viscosity of the spinning suspension is critical in determining the range over which the spinning parameters can be varied and consequently the range of fibre morphologies that can be generated in fibres prepared from a certain suspension. The design of the spinneret is also critical in determining the range of extrusion rates that can be used for a given suspension, a parameter that has a huge impact on the degree of control that can be achieved over fibre morphology.

Alumina/polymer/solvent systems have complex rheologies that are not observed for more simple two phase systems and the rheology can be unpredictable for this reason,
often exhibiting shear thinning as well as shear thickening rheology over a range of shear rates. The particle size distribution plays a key role in determining the suspension rheology and can be varied not only to control fibre properties such as mechanical strength, pore size and porosity but also to change the suspension viscosity and rheology so that the desired combination of spinning parameters can be achieved. In addition, the milling time plays a crucial role in determining the suspension rheology and viscosity. Initially, an increase in milling time causes a reduction in suspension viscosity after which the viscosity is seen to increase after extended milling. Therefore, milling time can be used to impart suspensions with identical compositions with very different rheologies and therefore has a strong effect on the morphology of the resulting hollow fibre. The alumina/polymer/solvent suspensions prepared in this study exhibit hysteresis as the shear rate is increased and then decreased with relaxation times of over 2 hours. Therefore, the treatment of the suspension with respect to degassing/stirring and pumping must be considered in order to achieve suspensions with reproducible properties.

7.1.2 Morphology

Fibres prepared using the combined phase inversion and sintering technique consist of regions of finger-like voids and a sponge-like structure in varying ratios, ranging from a symmetric sponge-like structure to a structure in which finger-like voids extend across 90% of the fibre cross section. Sandwich-like structures consisting of finger-like voids extending from both the inner and outer fibre surfaces with a central sponge-like region can also be prepared. The formation of finger-like structures results from hydrodynamically unstable viscous fingering which is a well know phenomenon that
occurs when a less viscous phase intrudes into a more viscous phase. The extent of
viscous fingering is determined by the suspension viscosity and the precipitation rate of
the polymer phase and can be controlled prior to spinning by varying the suspension
viscosity by such means as changing the particle size distribution, the milling time or by
the addition of non-solvent or poor solvent additives. During spinning, parameters such
as the air-gap, extrusion rate and internal precipitant flow rate determine how the
viscosity changes during this process which affects the nature of the viscous fingering
phenomenon.

7.1.3 Characterization

The asymmetric fibres prepared using the combined phase inversion and sintering method
exhibit a bi-modal pore size distribution with separate peaks for both the finger-like and
sponge-like regions of the fibre. While the pore size distribution of the sponge-like region
is determined by the composition of the spinning suspension, the pore size of the
entrances to the finger-like voids is determined by the spinning parameters and the
polymer precipitation rate. By varying certain parameters in combination, the pore size of
these entrances and the length of the finger-like voids can be varied independently. It has
been found that an increase in calcination temperature leads to a gradual reduction in
porosity of the sponge-like region and a gradual increase in pore size, however, the
entrances to the finger-like voids resist change during the calcination process and retain
their function.
7.1.4 Applications

It has been demonstrated in this work that the combined phase inversion and sintering technique can be used to prepare hollow fibres for a wide range of applications and increases in performance can be achieved by the implementation of novel hollow fibre structures. Asymmetric hollow fibres prepared for use in catalytic membrane reactors for the dehydrogenation of propane and hydrogen production by water-gas-shift have been developed in which a region of finger-like voids functions as a series of micro-channels in which catalyst has been deposited and a sponge-like structure forms the substrate for the deposition of a palladium or palladium alloy hydrogen permselective membrane. For both reactions, substantial improvements in reactor efficiency have been achieved as a result of the asymmetric hollow fibre structure.

7.2 Future work

7.2.1 Suspension rheology

It has been shown in this work that there is a strong relationship between the properties of the suspension and the morphology of the fibres. Therefore, a greater understanding of how the composition of the suspension affects the rheology would be beneficial in predicting the range of structures that can be achieved for suspensions with different compositions. Therefore, a rheological study that would allow the prediction of suspension rheology without the need to prepare suspensions and test them would be extremely beneficial.
7.2.2 Shear rate within the spinneret

A number of studies have been undertaken to establish the relationship between the shear rate that exists within the spinneret during fibre spinning and the properties of polymeric membranes [120-122]. For polymeric membranes, the existence of shear has been shown to affect the alignment of polymer molecules which affects the properties of the separation layer in terms of flux and selectivity. For ceramic systems it is likely that the viscosity of the suspension will be substantially affected by the shear experienced within the spinneret. As the dominating factor in the formation of different fibre morphologies and in determining the pore size of the entrances to finger-like voids in asymmetric fibres is the viscosity, control and variation of shear during fibre spinning may provide an additional means of predicting and controlling fibre morphology.

7.2.3 Viscous fingering

As discussed in the previous chapters, milling time and the precipitation rate of the polymer phase can be used to control the initial and dynamic viscosity of the suspension during fibre spinning. Although suspension viscosity has been shown to be the dominating factor in the extent of viscous fingering during the phase inversion process, the exact nature of this process is unclear for these ceramic systems. A fundamental study on viscous fingering in ceramic systems used for fibre preparation would be beneficial to determine the driving forces for finger-like void formation and the effect of other parameters such as the composition and nature of the internal and external precipitants.
7.2.4 Morphology and applications

The concept of finger-like voids functioning as a series of micro-channels in a microreactor has been introduced, however, the structures formed in this work are not optimal. An increase in pore size of the entrances to the finger-like voids and a reduction in the width of finger-like structures would be beneficial both in terms of reactor performance and mechanical strength. Finger-like void formation results from hydrodynamically unstable viscous fingering and the dimensions of the finger-like structures are determined predominantly by the interfacial tensions and relative viscosities of the two phases. Although the dynamic nature of the phase inversion process makes the study of these parameters extremely difficult, an empirical study in which additives such as surfactants are used to modify these parameters may allow for greater control over the shape of finger-like voids as well as the pore size of their entrances.

It has been demonstrated in Chapter 6 that with the variation in hollow fibre properties that can be achieved using the combined phase inversion and sintering technique a wide range of applications may benefit from this technology. Following a successful demonstration of hydrogen production by water-gas-shift, a ceramic hollow fibre membrane microreactor can be developed for steam reforming of ethanol for onboard and small scale hydrogen production.

7.3 References


Publications, Presentations and Collaborative Work

Publications:


Collaborative work:

1. Fabrication of asymmetric hollow fibres for use in a membrane contactor for the absorption of CO₂ at the Central Glass and Ceramic Research Institute, Kolkata.

2. Development and fabrication of asymmetric hollow fibres for use in a membrane bio-reactor for the synthesis of red blood cells from stem cells, undertaken by a group led by Dr. Athanasios Mantalaris at Imperial College London.

3. Preparation of composite ceramic/polyimide membranes at Hyflux Ceparation, the Netherlands.

Conferences:

1. NanoMemPro (Zaragoza, Spain, November 2007).


4. European Membrane Summer School (Leuven, Belgium, September 2008)


7. International Conference on Catalysis in Membrane Reactors (Lyon, France, July 2009).


Presentations:


5. Euromembrane 2009 (Montpellier, France): Structural Diversity in Asymmetric Ceramic Hollow Fibres (September 2009).