MICRO-STRUCTURED FUNCTIONAL CATALYTIC
CERAMIC HOLLOW FIBRE MEMBRANE REACTOR
FOR METHANE CONVERSION

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

December 2014
DECLARATION OF ORIGINALITY

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 Information derived from published and unpublished results of others has been acknowledged in the text and in the relevant references included within the thesis.

Nur Hidayati Othman

Imperial College London,

December 2014

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ABSTRACT

The most significant issue associated with the oxidative methane conversion processes is the use of pure oxygen, which is extremely expensive. By using a dense oxygen permeable membrane reactor, a possible decrease in the air separation cost can be expected due to the elimination of oxygen plants. Besides, higher reaction yields can be attained due to the selective dosing of oxygen into the reaction zone. This thesis focuses on the development and potential application of functional micro-structured catalytic ceramic hollow fibre membrane reactor (CHFMR) in oxidative methane conversion to syngas (known as partial oxidation of methane (POM)) and to ethane and ethylene (known as oxidative coupling of methane (OCM)).

As the membrane reactor performance is crucially dependant on the oxygen permeation rate and good contact between oxygen and methane, two types of membrane reactor designs were proposed in this study. The first design involves the development of CHFMR that consists of two layers i.e.: an outer oxygen separation layer and an inner catalytic substrate layer, known as dual-layer catalytic hollow fibre membrane reactor (DL-CHFMR). The DL-CHFMR was fabricated via a novel single-step co-extrusion and co-sintering technique, in which the thickness and the composition of each functional layer can be controlled in order to improve reactor performance.

The second design involves the development of CHFMR with an outer dense separation layer integrated with conical-shaped microchannels open at the inner surface, created via a viscous fingering induced phase inversion technique. Besides substantially reducing resistance across
the membrane, the microchannels can also act as a structured substrate where catalyst can be deposited for the catalytic reaction to take place, forming a catalytic hollow fibre membrane microreactor (CHFMMR). Although the CHFMRs discussed in this study are designed particularly for POM and OCM, there are general advantages of such membrane structures and reactor designs for improving the overall reaction performance. Therefore, these reactor designs can be transferred to other important catalytic reactions.
ACKNOWLEDGEMENTS

First and above all, I praise to Almighty Allah SWT who gave me patience, courage and persistence throughout this PhD study and granting me the capability to proceed successfully. This doctoral thesis would not have been possible without assistance, guidance, and support of several peoples around me. Therefore, I would like to offer my sincere thank you to all of them.

I would like to express my deep gratitude towards my PhD supervisor, Professor Kang Li for valuable advice, insightful discussions, invaluable support, and encouragement given since I express my interest to be his PhD student until the day I completed my PhD study.

I would also like to thank my post-doctoral fellow, Dr. Wu Zhentao for constant help, guidance and countless hours of discussion throughout my study.

To my special colleague and my best friend Ana Gouveia Gil; thank you for being there through every coffee sessions, every laugh, every tears and for the endless moments of helping hand and supporting shoulder during my time in London.

Thanks also to all the members of Prof. Li’s group: Dr. Benjamin F.K Kingsbury, Dr. Bo Wang, Tao Li, Farah Diyana Aba, Melanie Lee, Ji Jing, Nilay Kesir Demir and Jeng Yi for providing such a good atmosphere in our lab. Joao Burgal, thank you for all the funny jokes and good office environment. Not forgetting, Suhaiza Hanim Hanipah, thanks for always listening to me even though you are far away.
I appreciate the support of Patricia Carry, Dr. Ardakani, Dr. Ecaterina Ware and Richard Sweeney for your excellent technical assistance and your kind answers to all my queries. I would like to express appreciation to the safety officer, academic and postgraduate administrators in our department, Dr. Severine Toson, Alicia Lithgow, Jessica Baldock and Susi Underwood.

Acknowledgement is due to the Ministry of Education Malaysia as well as Universiti Teknologi Mara (UiTM) for providing financial support during the course of my study. I would also like to acknowledge the research funding provided by EPSRC in the United Kingdom.

Special thanks to my parents (Othman and Siti Rohana), brother, sister and beloved friends who give relentlessly morale support. Thank you to my two lovely princesses, Aleesya Arissa and Aira Batrisya, who are the inspiration for my PhD journey. Finally and most importantly, I would like to thank my husband, Muhamad Nazif for his support, encouragement, and great patience during my PhD study and above all for believing my potential. Thank you for your high regard on my ambition and willingness to sacrifice your career just to be with our children and me.
LIST OF PUBLICATIONS

Publications


2. **N.H. Othman**, Z. Wu, K. Li, Bi$_{0.5}$Y$_{0.3}$Sm$_{0.2}$O$_{3-\delta}$-based ceramic hollow fibre membranes for oxygen separation and chemical reactions, Journal of Membrane Science 432 (2013), 58-65.

3. **N.H. Othman**, Z. Wu, K. Li, Fabrication of Bi$_{0.5}$Y$_{0.3}$Sm$_{0.2}$O$_{3-\delta}$-based dual-layer ceramic hollow fibre membranes for catalytic reactions. Journal of Applied Membrane Science & Technology 15 (2013), 43-51.

4. Z. Wu, **N.H. Othman**, G. Zhang, Z. Liu, W. Jin, K. Li, Effects of fabrication processes on oxygen permeation of Nb$_2$O$_5$-Doped SrCo$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ micro-tubular membranes, Journal of Membrane Science 442 (2013), 1-7.

5. **N.H. Othman**, Z. Wu, K. Li, A micro-structured La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3-\delta}$ hollow fibre membrane reactor for oxidative coupling of methane, Journal of Membrane Science 468 (2014), 31-41.

6. **N.H. Othman**, Z. Wu, K. Li, Micro-Structured Bi$_{0.5}$Y$_{0.3}$Sm$_{0.2}$O$_{3-5}$ Catalysts for Oxidative Coupling of Methane, submitted to AIChE Journal, 2014.
7. **N.H. Othman**, Z. Wu, K. Li, An oxygen permeable membrane microreactor with an in-situ deposited $\text{Bi}_{1.5}\text{Y}_{0.3}\text{Sm}_{0.2}\text{O}_{3-\delta}$ catalyst for oxidative coupling of methane, submitted to Journal of Membrane Science, 2014.

**Conference Oral Presentation**

1. **N.H. Othman**, Z. Wu, K. Li, Fabrication of $\text{Bi}_{0.5}\text{Y}_{0.3}\text{Sm}_{0.2}\text{O}_{3-\delta}$-based dual-layer ceramic hollow fibre membranes for catalytic reactions. Presented at 10$^{th}$ International Conference on Membrane Science & Technology, 22$^{nd}$ – 24$^{th}$ August 2012, Bangkok, Thailand.


**Conference Poster Presentation**

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CHAPTER 1

Introduction

1.1 Research background

Natural gas, which primarily consists of methane is frequently produced during oil production. Previously it was considered as a by-product in oil fields and was usually burned off. This causes wastage of raw materials as well as release of carbon dioxide into the atmosphere, which can contribute to global warming. However, the utilization of methane has grown rapidly since 1990s due to its ample supply and relatively cheaper price when compared with petroleum. Apart from that, the increase in the desire for cleaner energy sources also helps to expand the application of methane. It is currently commonly used for heating and sometimes in electrical power generation. As methane burns in a cleaner way (less CO\textsubscript{2} emissions) than other fossil fuels, it has also been used for transportation. However, most natural gas deposits have not yet been exploited to the same extent as oil deposits. One of the main issues limiting its utilizations is the remote location of the natural gas deposits. Thus, the recovered gas needs to be transported over a very long distance in order to reach to market. Such transportation process is both energy and cost intensive, unless it is physically liquefied (LNG) or economically converted to more value added liquid chemicals [1-3]. Methane is a very stable, symmetrical molecule; the C–H bonds are strong (425 kJ/mol) and it contains no functional groups, magnetic moment or polar distribution to facilitate chemical attacks.
Therefore, an activation of methane by splitting of the C–H bond will require high temperatures and/or the use of oxidation agents [4]. In addition, catalysis is also very important in most methane conversion processes. The conversion of methane into other more valuable chemical products can be carried out in two ways: direct and indirect, as shown in Fig. 1. 1.

![Fig. 1. 1 Routes for methane conversion](image)

Direct methane conversion route offers one-step transformation to final chemical products such as olefins (ethylene), oxygenates and aromatic. In most cases, the activation and conversion of CH₄ and CH₃O species into desired products is carried out within a single vessel. The non-oxidative coupling of methane known as thermal coupling, require a high operating temperature (>1000°C). In compared to that, the oxidative coupling does not require an external energy supply and has no thermodynamic limitations. One of the interesting oxidative coupling reactions is the conversion of methane into C₂ (olefins) products as shown below:
The direct conversion of methane has been recognized as a highly challenging process, kinetically and thermodynamically. Other than the high temperatures required for methane activation, the strength of C-H bond in methane is also stronger than the possible products [6], which make the desired products more reactive than methane. As the reaction is thermodynamically favourable to the products rather than methane, low product conversion is normally encountered [7]. Although much works on the direct conversion of methane into value added chemical products has been carried out in the past few decades, no feasible cost effective process has been developed [3]. Thus, at present, only indirect conversion processes are implemented in industrial scale.

The indirect route (e.g. Fischer-Tropsch, Mobil Process and Shell Middle Distillate Synthesis) involves transformation of methane into an intermediate compound known as synthesis gas (syngas), which consists of a mixture of CO and H₂. The production of syngas can be carried out through three principal processes or combinations thereof: steam reforming, dry reforming and partial oxidation of methane. The methane reforming reactions are given as below [8]:

\[
2\text{CH}_4 + \text{O}_2 \rightarrow \text{C}_2\text{H}_4 + 2\text{H}_2\text{O} \quad \Delta H_{298K}^0 = -280.8 \text{kJ} / \text{mol} \quad (1.1)
\]

Both of these reforming reactions are highly endothermic and involve extensive heat treatment. The steam reforming method is widely used in the production of methanol from
syngas compared to dry reforming. However, there are two main issues with the steam reforming process, which are: (1) the requirement of high temperatures and high steam pressure to favour \( \text{H}_2 \) and \( \text{CO} \) at equilibrium, and (2) the high amount of coke formation especially when nickel catalyst is used. Therefore, at present, partial oxidation of methane (POM) is more preferable in the production of synthesis gas owing to several advantages such as higher energy efficiency, higher selectivity to \( \text{CO} \) and \( \text{H}_2 \), and a ratio of \( \text{H}_2/\text{CO} \) of 2 in the ideal reaction [9].

\[
\text{CH}_4 + \frac{1}{2} \text{O}_2 \rightleftharpoons \text{CO} + 2 \text{H}_2 \quad \Delta H_{298K}^0 = -35 \text{kJ/mol} \tag{1.4}
\]

For methane conversion processes that require oxygen, the most significant issue is associated with the separation process of oxygen from air. Pure oxygen is usually obtained from either pressure swing adsorption or cryogenic distillation process that are extremely expensive [10]. There is also an issue with hazard handling for the oxygen separation process especially when it involves large quantities of undiluted oxygen and \( \text{O}_2/\text{CH}_4 \) mixtures [8]. For example, in 1997, an explosion in the air separation unit at the Shell F-T plant in Bintulu, Malaysia occurred. In this context, alternative technologies, such as membrane reactors, which eliminate the need for an oxygen plant, represent the opportunity to reduce the costs as well as to enhance the safety of the methane conversion process.

**Membrane reactor for methane conversion processes.**

A membrane reactor can be defined as a chemical device that simultaneously performs a reaction combined with a membrane based separation in a single physical unit [11]. Such
concepts of integration processes have been widely discussed since 1960’s [12] and the fundamental concept of membranes reactors has been pioneered by the application of palladium membrane for dehydrogenation processes [13]. Membranes for membrane reactors can be classified according to their function, geometry, type and materials, as shown in Fig. 1.2. The selection of a suitable membrane for each process application is dependant largely on parameters such as separation selectivity, permeation rate, and reaction conditions. The following discussion will concentrate on membrane function and geometry, while details on membrane types, cross-section and materials will be discussed in the literature review.

**Fig. 1.2 Classification of membranes for use in membrane reactors**
The concept of combining membrane and reactor has been explored in various configurations and can be classified into three groups depending on the membrane functions in the process as shown in Fig. 1. 3. The membrane can act as (1) an extractor, (2) a distributor and (3) an active contactor. The membranes that are used as extractors and distributors usually do not have catalytic properties and are combined with a fixed bed catalyst placed on one of the membrane surfaces. In general, a membrane reactor that acts as an extractor will selectively remove product (s) from reaction zone, thus high conversion rate can be achieved due to the shifting of reaction equilibriums. It has been widely applied to increase the conversion of a number of limited reactions such as dehydrogenation of alkane by selectively removing the produced hydrogen, resulting in a high product yield even at lower temperatures. Other reactions that are producing H₂ such as water gas shift and steam reforming of methane have also been successfully investigated [14-20]. The efficiency of this extractor type membrane depends on the H₂ permselectivity and its permeability.

A distributor membrane reactor is also known as a selective reactant addition. This type of membrane is used to control the reaction pathways by introduce/ distribute the reactant(s) along the reactor wall, which can limit side reactions. This type of membrane mode has been mainly studied in consecutive parallel reaction systems such as partial oxidation, oxy-dehydrogenation of hydrocarbons or oxidative coupling of methane [21]. This is due to its ability to control the supply of oxygen to the reactant, to bypass the flammability area and to optimize the O₂ profile concentration along the reactor. Furthermore, direct pre-mixing of oxygen and reactant can be avoided, maximizing the selectivity of the desired oxygenate product [22]. In such reactor type, the O₂ permselectivity of the membrane is an important economic factor because air can be used instead of pure O₂. An active contactor membrane
is used when intensification of contact between reactant and catalyst is required. The perm-selective property is not an important requirement for this type of membrane, as it functions only as a diffusion barrier. However, the membrane needs to be catalytically active in order to achieve intensification.

The potential applications of membrane reactors especially in refinery processes have been extensively studied as shown in Table 1.1, and the number of applications continue to grow due to the development of new inorganic membrane materials, in particular, ceramic-based membranes. Improvement in manufacturing techniques of ceramic materials (i.e., sol-gel, pyrolysis of polymeric precursors, phase separation and leaching) have aided the production of more permselective membranes whilst maintaining the permeability rate.
Table 1.1. Membrane reactor application in refinery process

<table>
<thead>
<tr>
<th>Processes</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane steam reforming</td>
<td>[16, 23]</td>
</tr>
<tr>
<td>Ethane dehydrogenation</td>
<td>[24, 25]</td>
</tr>
<tr>
<td>Water-gas shift reaction</td>
<td>[26, 27]</td>
</tr>
<tr>
<td>Oxidative coupling of methane</td>
<td>[28-30]</td>
</tr>
<tr>
<td>Partial oxidation of methane</td>
<td>[31-33]</td>
</tr>
</tbody>
</table>

Membranes used in membrane reactors can be divided into three different geometries i.e. (1) disc, (2) tubular and (3) hollow fibre (Fig. 1. 4). The disc-shaped membranes are usually preferred due to their low cost and ease of fabrication and quality control. However, it often delivers low production rates due to the limited membrane surface area. In order to overcome the problem, tubular membrane with higher surface area were developed through an extrusion process followed by high temperature sintering. Nonetheless, the membrane thickness and limited surface area/volume ratio are still considered to be unfavourable for industrial purposes. Besides, this type of membrane usually consists of a symmetric structure due to the membrane fabrication process. Since the membrane surface area is a very important element in a membrane reactor system to ensure high production rate, hollow fibre membranes with smaller diameters and thicknesses have been developed. Besides possessing a higher surface area, an ease in membrane sealing and great membrane uniformity for large-scaled production can also be achieved.
One of the main challenges in methane conversion processes involves the production and distribution of oxygen inside the reactor, in which the use of membrane reactors can help address this challenge. Therefore, the main aim of this study is to develop micro-structured functional catalytic ceramic hollow fibre membranes for methane conversion, in which improvement in oxygen permeation rate and better contact between oxygen and reactant (methane) are very crucial. In order to obtain a reasonably high oxygen permeation flux, two different membrane microstructures designs are proposed as shown in Fig. 1. 5.
Fig. 1.5 Schematic diagram of the multifunctional catalytic reactors proposed for this study: (i) a dual-layer catalytic hollow fibre membrane reactor (DL-CHFMR) and (ii) a catalytic hollow fibre membrane microreactor (CHFMMR)

The first design involves the development of catalytic hollow fibre membranes with dual functional layers, i.e. an outer oxygen separation layer and an inner catalytic substrate layer (DL-CHFMR) using a novel single step membrane fabrication, i.e. a co-extrusion and co-sintering process (Fig. 1.5 (i)). The pure oxygen generated by the membrane outer layer can simultaneously react with methane at the catalytic inner layer. The second design involves the development of functional ceramic hollow fibre membranes with an outer dense oxygen separation and conical-shaped microchannels open at the inner surface using a viscous fingering induced phase inversion process. These microchannels can act as a structured substrate into which catalysts can be deposited to form a catalytic hollow fibre membrane microreactor (CHFMMR) (Fig. 1.5 (ii)).

Among the main advantages offered by these types of reactors are extraordinarily high surface areas per unit volume, tuneable macrostructure and most importantly, cost effectiveness on account of their compact design. Partial oxidation of methane (POM) and oxidative coupling
of methane (OCM) were chosen as the application in order to demonstrate the advantages of using the micro-structured functional catalytic ceramic hollow fibre membrane reactor. The main objective was achieved by completing the following specific objectives:

(i) To develop a dual-layer catalytic hollow fibre membrane reactor (DL-CHFMR) for methane catalytic reactions (OCM and POM)

A micro-structured catalytic hollow fibre membrane reactor with two functional layers, i.e. an outer oxygen separation layer and an inner catalytic substrate layer was developed and used for oxidative methane conversion processes such as OCM and POM. The DL-CHFMR was fabricated via a single-step co-extrusion and co-sintering technique, in which the thickness and the composition of each functional layer can be controlled in order for a better reactor performance. In order to promote oxygen permeation, since this is considered to be the controlling step in the use of DL-CHFMR for methane conversion [34], Bi$_{1.5}$Y$_{0.3}$Sm$_{0.2}$O$_{3-δ}$ (BYS) was used both in the outer oxygen separation layer and in the inner catalytic substrate layer due to its high ionic conductivity. Prior to this, the compatibility between the materials of each layer was investigated, since a mismatch of material shrinkage during high temperature sintering could lead to delamination of the membrane layers.
(ii) **To develop a new micro-structured BYS catalyst ring for OCM**

BYS, a ceramic material showing great activity and selectivity to oxidative coupling of methane (OCM), was fabricated into catalyst rings (i.e. capillary tubes) with a plurality of self-organised radial microchannels. A modified combined phase inversion and sintering process also known as a viscous fingering induced phase inversion, was employed in the fabrication of the micro-structured BYS catalyst rings. This work aims to highlight the advantages of the micro-structured design.

(iii) **To fabricate micro-structured LSCF hollow fibre as a membrane reactor for OCM**

La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3-\delta}$ (LSCF) has been studied extensively and proven stable under oxygen separation conditions. Thus, it was selected in the development of micro-structured catalytic hollow fibre membrane reactor. The main aim of this work was to enhance oxygen permeation flux of the membrane by modifying the membrane microstructure. Asymmetric membranes, which consist of conical-shaped microchannels open at the inner surface and an outer dense oxygen separation layer, were developed via a viscous fingering induced phase inversion technique, using different types of bore fluids. Beside substantially reduced resistance across the membrane, the microchannels can act as a structured substrate where catalysts can be deposited so that the catalytic oxidative coupling of methane (OCM) can take place.
(iv) To evaluate the performance of the LSCF catalytic hollow fibre membrane micro
reactor (CHFMMR) for OCM

Further investigation on the fabricated micro-structured LSCF hollow fibre prepared was
carried out to ensure that the membranes were defect free. A defect free membrane is very
important to ensure infinite selectivity of oxygen supply. Commercial BYS powders were then
incorporated inside the membrane microchannels by using a washcoating technique to form
CHFMMR. In order to address the advantages of such microreactor design, the OCM
performance of CHFMMR was then compared with a packed bed membrane reactor
(PBHFMR) using a similar hollow fibre membrane.

(v) To investigate on the effects of catalyst deposition approaches in the fabrication of
CHFMMR

The final focus on the development of LSCF CHFMMR was to investigate the effects of BYS
catalyst preparation and deposition techniques on the OCM performance. In this work, the
BYS catalyst was synthesized and deposited into the membrane microchannels using an in-
situ sol-gel technique. The differences in the OCM performances between the in-situ sol-gel
prepared and washcoated CHFMMR were highlighted.
1.3 Thesis arrangement

The thesis consists of seven (7) chapters in total including introduction, literature review overall conclusions and suggestions for future work. Each chapter addresses different aspects on the development of micro-structured catalyst, micro-structured hollow fibre membrane and the combination of both, which is the functional ceramic hollow fibre membrane reactor. Every chapter begins with an abstract followed by a brief introduction, capturing fundamental findings in the sub-research and building up connections with previous chapters. The overall arrangement of the thesis is shown in Fig. 1.6.

Chapter 1 briefly introduces the background and main objectives of the research. A systematic literature review in Chapter 2 gives an insight into the current knowledge of mixed ionic electronic conducting (MIEC) membranes for oxygen separation, POM and OCM, as well as the membrane fabrication process and related membrane reactor designs.

Chapter 3 involves development of micro-structured dual-layer catalytic hollow fibre membrane reactor (DL-CHFMR) using a new single step membrane fabrication process, i.e. a co-extrusion ad co-sintering process. For this purpose, BYS is not only used as a membrane material but also as part of the catalyst for methane conversion processes.

Chapter 4 investigates the technical feasibility of using a combined phase inversion and sintering process to fabricate micro-structured BYS hollow fibre that can be used as OCM catalysts, addressing more on the advantages of the micro-structured design.
Chapter 5 investigates the effects of membrane macrostructure such as dimensions of the conical-shaped microchannels and thickness ratios between the inner layer with such microchannels and the outer dense separation layer. The performance of OCM was investigated in two forms of membrane reactor: (1) PBHFM – whereby BYS catalyst is packed outside and (2) CHFMMR – whereby BYS catalyst is packed inside the microchannels of the hollow fibre. The performances of the membrane reactors were then compared with a traditional fixed bed reactor of BYS catalyst (FBR) and a blank LSCF hollow fibre membrane reactor in order to address the advantages of having uniform catalyst deposition inside the micro-structured membrane reactor.

Chapter 6 investigates the use of in-situ sol-gel technique in order to improve the homogeneity of BYS deposited inside the ceramic hollow fibre membrane microchannels. The performance of CHFMMR formed using sol-gel technique was then compared with washcoated CHFMMR prepared in Chapter 5.

Chapter 7 provides general conclusions of the whole study and recommendations for future work.
1.4 References


Chapter 1

38

Introduction


CHAPTER 2

Literature Review

2.1 Membranes for oxygen separation

Cryogenic air separation is a well-established technology that has been used to produce oxygen with high purity for various application. However, this technology is rather complex, costly and energy intensive. Therefore, membrane separation has been increasingly viewed as one of the promising technology as an alternative to the cryogenic air distillation. The membrane separation technique for purified oxygen production from air is based on the use of a dense functional ceramic membrane which, is only permselective to oxygen at elevated temperatures (>800 °C). This enables a pure permeate product to be achieved, thereby eliminating the need for any post-treatment of the products.

There are two main types of ceramic membranes that have been used as a dense oxygen permeable membrane: (1) pure oxygen conducting and (2) mixed ionic and electronic conductor (MIEC). Fig. 2. 1 illustrates the transportation of oxygen ions and electrons through the two different types of membranes. Membranes fabricated from pure oxygen ionic conductors require an external electrode to allow for the circulation of electrons in order to fulfil the electric neutrality criteria. The main advantage of this type of membrane is the ability to
control the amount of oxygen generated via the electric current. However, such membranes tend to have lower permeation rate due to the poor contact between the external electrode and the membrane [1]. In contrast, MIEC membranes do not require external electrodes, as the oxygen ions transport to the methane side via an ionic conduction phase while the electrons return via the electronic conduction phase.

![Transportation of oxygen and electrons through membranes](image)

**Fig. 2.1** Transportation of oxygen and electrons through membranes fabricated from (a) an ionic conductive material, (b) mixed ionic and electronic conductive materials

Over the last decade, extensive research has been carried out to investigate the potential of MIEC materials. This research is broadly supportive of the idea that membranes developed using these materials have potential applications for pure oxygen production, ranging from medical purposes to large scale combustion processes, provided the technical challenges of membrane stability and durability can be overcome [2-7].
MIEC ceramic materials usually possess a defined crystal structure that can be derived from perovskite (ABO₃), fluorite, brownmillerite (A₂B₂O₅), pyrochlore (A₃B₂O₇), Ruddlesden-Popper series (Aₙ₊₁BₙO₃ₙ₊₁), orthorhombic K₂NiF₄ and etc. [8-12]. In addition, a pure ionic conducting ceramic can also be a MIEC material by incorporating metallic materials. For example, a pure oxygen ionic conductor such as zirconia is known to be not suitable for oxygen separation applications due to its lack of electronic conduction. Instead of using external electrodes, incorporation of an electronic conductive material, such as TiO₂, is one way to provide this electronic conductivity [13, 14]. Since this work was undertaken, several groups have proposed the dispersal of electronic conductive metallic materials into a predominantly ionic conductive ceramic as a way to obtain MIEC membranes [1, 12, 15, 16].

Perovskite-type and fluorite-type oxides are among the most studied MIEC ceramic membranes and have been found to give the best oxygen permeation. The perovskite solid oxides with chemical formula of ABO₃ is originally named after the mineral oxide of CaTiO₃. The ideal perovskite structure with an ABO₃ stoichiometry is shown in Fig. 2. 2. The simplest way to describe the perovskite structure is a cubic cell with A atoms at the centre of the cell, B atoms at the corners and oxygen atoms at the midpoints of the cubic cell edges. Each A atom is surrounded by twelve equidistant oxygen atoms [17]. An ideal perovskite structure is not capable of conducting oxide ions. Therefore, there is a need for imperfections or defects within the structure. Such imperfections can be introduced using a doping technique. The oxygen permeation flux of a doped defect perovskite is determined by its ionic conductivity. The perovskite is usually formed by combining lanthanide or group II element cations (A-site cation), which are responsible for the oxygen vacancy and typically first row transition metal
cations (B-site cation), responsible for electronic conductivity. Some other common combination of perovskite structures are: $\text{A}^{1+}\text{B}^{5+}\text{O}_3$, $\text{A}^{2+}\text{B}^{3+}\text{O}_3$ and $\text{A}^{3+}\text{B}^{3+}\text{O}_3$ [18]. This structure possesses rich defect chemistry that is created by doping suitable cations into the structure. The defects are evidenced by the creation of oxygen vacancies within the oxygen sub-lattice, $V_0^{\bullet\bullet}$ that can be represented in Kroger-Vink notation and the formation of electronic n- and p-type conductivity at high temperatures under appropriate gas atmosphere conditions [19]. The creation of lattice oxygen vacancies is indicated by the 3-δ oxygen non-stoichiometry.

![ Ideal perovskite structure](image)

The first oxygen permeable dense MIEC perovskites membranes is $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1+y}\text{Fe}_y\text{O}_{3-\delta}$, reported by Teraoka et al. [20, 21]. Since then, this material has attracted considerable attention [6, 22-26] as it exhibits a remarkable oxygen permeation flux that is much higher than that of stabilized zirconia. The main characteristic of LSCF is that it desorbs a large amount of oxygen from its crystal lattice while still keeping the fundamental crystal structure intact when heated at elevated temperatures under low oxygen partial pressure. In addition, the oxygen uptake into thermally reduced oxygen (oxygen desorb) oxides proceeds fast and facile [27,
This oxygen sorption and desorption (OSD) property of LSCF is a result of the principle of pressure-driven oxygen permeation since this OSD involves both the bulk migration of oxide ions and the association and dissociation reactions of oxygen on the surface [27]. In addition to the LSCF oxides, a number of other perovskite-based membranes has been developed such as BaBi$_x$Co$_{0.2}$Fe$_{0.8-x}$O$_{3-\delta}$ [29], Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ [8, 30-33]. More than 25 years after the first work, there is still no industrial application of these perovskite-based membranes due to issues such as their stability at elevated temperatures.

An ideal fluorite structure is based on ZrO$_2$ as illustrated in Fig. 2. 3. This structure consists of anions in a simple cubic packing with half of the interstices occupied by cations. It has face centred cubic (fcc) packing, in which the empty interstice is located in a space at the centre of the cubic anion lattice [3]. This structure is attractive due to the high number of mobile oxygen ions that results in high ionic conductivity. This type of structure also tends to have cations occupying all cation sites, while leaving many of the oxygen anion sites empty, which leads to high oxygen deficiency [34, 35]. This material is usually doped with MgO, CaO, U$_2$O$_3$ and CeO$_2$ in order to stabilize the cubic structure [3]. Fluorite structure materials that have been doped with alkaline earth or rare earth oxides usually have higher oxygen conductivity than commonly used electrolyte materials such as YSZ, especially at lower temperatures [36].
Bismuth oxide (Bi$_2$O$_3$) in δ form is one of the fluorite structure materials that is receiving particularly great attention due to its high ionic conductivity, which reaches 1 S·cm$^{-1}$ at 800 °C. This is attributed to a high concentration of oxygen vacancy due to the occupancy of only three out of four oxygen sites in the fluorite lattice [37, 38]. Nevertheless, the major problem facing by this material is the relatively low melting temperature, at around 850 °C. In order to stabilize the structure of δ phase at much higher temperatures, cation doping has been considered. A number of studies have proved that doping bismuth oxide with CaO, BaO and SrO compounds can stabilize the structure, thus giving a more stable material with high ionic conductivity [39, 40]. Yttria stabilized bismuth oxide ((Bi$_2$O$_3$)$_{0.75}$(Y$_2$O$_3$)$_{0.25}$) has proved to be one of the best ionic conductors as it exhibits the δ phase for a wide range of temperatures. A further study has been carried out by incorporating samarium oxide (Sm$_2$O$_3$) into bismuth yttrium oxide to further stabilize the δ-phase [41]. This study was successful, in that the melting temperature increased significantly up to 1100 °C, making it a potential material for use in the fabrication of oxygen permeable membranes for catalytic membrane reactors.
In general, the dense MIEC oxygen separation membrane should ideally have: (1) high ionic conductivity for a high oxygen permeation rate, (2) stability during oxidizing and reducing operations, (3) high mechanical strength and (4) low cost for large scale industrial applications [42]. However, it is a challenging task to find a single-phase MIEC material that can meet all of the above requirements since improving one aspect of the single-phase membranes often simultaneously reduces other aspects of the membrane’s performance. For example, a thinner membrane is often preferred in order to ensure a higher oxygen permeation rate. However, this thinner membrane usually possesses lower mechanical strength. A new group of membrane materials known as dual phase or composite MIEC membranes was introduced by Mazanec [1] to overcome these problems. The dual phase membrane was composed of yttria stabilized zirconia (YSZ) and a metal of Ag/Au to improve the electronic conduction. These types of dual-phase MIEC membranes can be developed through a series of ceramic material combinations such as perovskite-perovskite, fluorite-fluorite, and perovskite-fluorite [43]. Promising results have been observed by using the dual phase membrane not only for oxygen separation but also for other chemical applications [16, 44-46]. The main advantage of these membranes over homogeneous single-phase MIEC membranes is the ability to tailor the membranes properties for specific applications by adjusting the fraction of materials.

Still, there is an additional problem arising in the development of the dual phase membranes. The interdiffusion and chemical reaction between the materials is sometimes observable during sintering and this interaction is usually depending on the sintering activity [47]. In addition, there is a high chance of surface cracking due to the different thermal expansion coefficient of each material. Both of these issues have given a rise to a great number of research opportunities, especially in the selection of suitable materials, membrane
geometries, fabrication methods, and sintering cycles in order to obtain stable membranes with outstanding performance [48-50].

2.1.1 Mechanism of oxygen permeation through dense MIEC membranes

A dense mixed ionic and electronic conducting ceramic (MIEC) membrane is permeable only to \( \text{O}_2 \) at high temperatures under oxygen chemical potential difference. This membrane is considered 100% selective to oxygen, resulting in production of oxygen with very high purity. The oxygen permeation through this type of membrane is limited by surface exchange resistance, bulk diffusion limitations, or both [23]. In the case of where the membrane is relatively thick, bulk diffusion is known to be the controlling step. Fig. 2. 4 shows the mechanism of oxygen permeation through the dense membrane. The oxygen is first adsorbed onto the membrane surface with higher oxygen partial pressure, then dissociation (reduction) of molecular oxygen into oxygen ions \((\text{O}^{2-})\) take place. The oxygen ions then diffuse across the ceramic membrane towards the oxygen lean side under the partial pressure difference rather than the absolute pressure on each respective side. The oxygen ions are then converted back to oxygen gas at the oxidizing surface. At the same time, electrons flow in the opposite direction forming a short-circuited electrochemical device without the need of an external circuit. Only oxygen ions will pass through the membrane to the permeate side as they are the only species that mobile within the ceramic membrane, thus, all other gasses such as nitrogen, methane, CO and \( \text{CO}_2 \) are excluded.
2.2 Partial oxidation of methane (POM) into syngas

The remote locations of many sources of natural gas has led to a demand for converting methane into liquid products that are easily transportable. Most methane conversion processes currently involve converting methane into syngas (CO+H₂), which is then being converted into chemical products through the Fisher-Tropsch process. The steam reforming process has been widely established for the production of syngas compared to the partial oxidation of methane approach. However, due to its endothermic nature, the steam reforming process is energy intensive. In addition, the reaction produces syngas with a high H₂/CO ratio of 3.0 that is unsuitable for methanol or Fisher–Tropsch (F–T) synthesis [51]. For these
reasons, the use of slightly exothermic partial oxidation of methane (POM) to produce syngas has been the focus of much scholarly attention [52-57]. The other advantages of this POM reaction is its \( \text{H}_2/\text{CO} \) ratio of about 2, which makes it ideal for the production of syngas for methanol or F–T synthesis.

The POM conversion can be carried out in two ways; either at a high operating temperature (>1127 °C) or at an intermediate operating temperature with the help of a catalyst/reduce metal surface [58]. One example of an existing plant that is operating without any catalyst presence is in Sarawak, Malaysia. This plant has been successfully operated by Shell using the high temperature selective process [59]. Although the reaction is achievable at high temperatures, it is not always a feasible way of producing syngas since this energy extensive process means higher operating costs. As such, the introduction of a catalyst into the reactor is more preferable, as the POM reaction can be facilitated at lower temperatures [60]. The pioneering work in the field of catalytic partial oxidation was carried out by Liander [61] in the 1970’s, which achieved a high product yield at much lower temperatures (727-927 °C) and at atmospheric pressure. Since then, developments in the field of catalysts in particular for partial oxidation of methane has received much attention.

In general, there are three groups of catalysts that are widely studied for POM, which are: (1) Ni, Co and Fe; (2) noble materials and (3) any other transition metal carbide. Nickel based catalysts have been proven to have excellent catalytic performance and are currently widely applied in industrial processes. However, this type of catalyst tends to promote carbon formation, which in time, causes severe deactivation of catalyst by blocking the catalyst pores [62]. A number of modifications have been proposed in order to improve the catalytic
performance and to overcome the drawbacks associated with the poor stability of the nickel-based catalysts. Among the modifications that have been carried out is the introduction of a catalyst support [63-66]. The introduction of catalyst support for nickel-based catalyst has been found to significantly improve its cokes-resistance and overall performance [58]. In addition, the use of excess water and high operating temperature (> 800 °C) can also decreased the formation of carbon due to the thermodynamically unfavourable operating conditions.

Noble metal catalysts are known to have high yields and conversions that are close to thermodynamic equilibrium. The examples of noble metal catalysts are palladium, silver and rhodium. Claridge et al. [67] has systematically investigated the effects of catalyst types toward the carbon deposition and found that the noble catalyst tend to have the lowest carbon deposition. Early transition metals such as molybdenum and tungsten are known to have high catalytic performances [58] but their main disadvantage is their tendency to deactivate at ambient pressure [60]. Therefore, in overall, nickel has proved to be the most cost effective and suitable for industrial purposes when compared to other types of catalyst.

In addition to the limitation of the catalyst itself, the use of air as a source of oxidant can also cause a problem in the POM process, since nitrogen cannot be tolerated in the downstream product. Pure oxygen can be used as an oxidant to eliminate the post-separation of nitrogen [68], but the cost of oxygen separation is extremely high, since either cryogenic distillation or a pressure swing absorption process is required to carry it out [69]. This issue has led to the application of oxygen permeable dense membrane reactors in the POM process.
2.2.1 Membrane reactor for POM

Fig. 2. 5 illustrates steps that are involved in gas to liquid technology using POM, particularly for the Fischer-Tropsch process. Prior to the production of syngas, the separation of pure oxygen from air and the purification of natural gas (methane) must be carried out. By employing a membrane reactor, the air separation and partial oxidation of methane (POM) processes can be integrated into one operational unit, which significantly reduces both the capital and production costs.

A membrane reactor for POM is based on dense oxygen permeable membranes to ensure that the syngas product is free of nitrogen. There are several other advantages of utilizing the
dense oxygen permeable membrane reactor: (1) the achievement of high product selectivity, (2) the circumvention of flammability limits due to the diffusion limited operation, and (3) the avoidance of the formation of NO\textsubscript{x} during the high temperature reaction [69]. Fig. 2. 6 shows the schematic representation of POM using a membrane reactor.

During the POM process, air and methane are introduced into opposite sides of the membranes, where oxygen permeates through the membrane into the methane side under an oxygen partial pressure difference. Oxygen is dissociated into oxygen ions (O\textsuperscript{2-}) on the membrane surface, these oxygen ions then selectively transfer through the membrane towards the methane side due to the oxygen partial pressure difference across the membrane. The reaction then takes place with the presence of a catalyst. The POM catalyst can be packed on an inert membrane substrate (an inert membrane packed reactor, IMPBR) or it can be fluidized in the reactor (an inert membrane fluidized bed reactor, IMFBR). In contrast, if the membranes have been coated or impregnated with a catalyst, the membrane reactor is known as a catalytic membrane reactor (CMR) [70].
Fig. 2.6 Schematic diagram of the dense membrane reactor for POM reaction

The supply of oxygen is known to have a great effect on the final POM performances. The use of highly oxygen permeable membranes have been systematically studied and it has been verified that an improvement in product selectivity depends on the membrane properties [71-73]. It is believed that the key to success in the development of MIEC membrane-based syngas production is by fabricating a ceramic membrane that combines high oxygen flux with long-term mechanical stability in the strong reducing syngas environment [74]. Membranes made from LSCF have been widely investigated due to their high ionic and electronic conductivity and hence high oxygen permeation flux [75]. However, this type of membrane experiences phase transition under low oxygen pressure or low temperature and decomposes under reforming conditions. Consequently, several MIEC materials such as Sr-Co-Fe oxides (SCFO)[55], La_{0.2}Ba_{0.8}Co_{0.2}Fe_{0.8}O_{3-δ}(LBCFO)[69] and Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} (BSCFO) [76], which have better stabilities, have been successfully applied for POM in the presence of a catalyst, particularly nickel-based catalysts. The development of MIEC membrane reactors for syngas production is still considered to be at an elementary level due to the embryonic of the
membrane itself. In light of this, section 2.4 will discuss the overall challenges in the development of dense oxygen permeable membrane reactors for methane conversion processes, specifically POM and OCM.

2.3 Oxidative coupling of methane (OCM) to ethane \((C_2H_6)\) and ethylene \((C_2H_4)\)

Oxidative coupling of methane (OCM) is a direct process of converting methane into more valuable \(C_2+\) products (ethylene and ethane), which is from an economic point of view, are more beneficial over indirect routes such as steam methane reforming (SMR) and partial oxidation of methane (POM). Most OCM studies have revealed that the major barrier in the commercialization of the OCM process is the decrease of \(C_2+\) selectivity with the increase in methane conversion. This is due to the competitive nature of the oxidation of methane and ethane. The overall OCM reactions for \(C_2+\) formation are shown below:

\[
\begin{align*}
2CH_4 + 0.5O_2 & \rightarrow C_2H_6 + H_2O & \Delta H^\circ_{298K} &= -175.6 \text{ kJ/mol} \quad (2.1) \\
2CH_4 + O_2 & \rightarrow C_2H_4 + 2H_2O & \Delta H^\circ_{298K} &= -280.8 \text{ kJ/mol} \quad (2.2)
\end{align*}
\]

Besides the two selective reactions above, the following non-selective oxidation reactions to \(CO_x\) can also take place, reducing the \(C_2+\) yields.

\[
\begin{align*}
CH_4 + 2O_2 & \rightarrow CO_2 + 2H_2O & \Delta H^\circ_{298K} &= -890.4 \text{ kJ/mol} \quad (2.3) \\
C_2H_4 + 3O_2 & \rightarrow 2CO_2 + 2H_2O & \Delta H^\circ_{298K} &= -1411.17 \text{ kJ/mol} \quad (2.4)
\end{align*}
\]
In principal, hundreds of elementary steps could be involved in the conversion of methane and oxygen. However, it has been widely accepted that the OCM reaction proceeds in a combination of heterogeneous and homogeneous mechanisms [77-80]. The reaction proceeds with the activation of methane into methyl radical (●CH₃) on the catalyst surface, which is considered as the rate-limiting step. This methyl radical will subsequently couple in the gas phase to form ethane, which can then be converted to ethylene via heterogeneous (oxidative) dehydrogenation and/or homogeneous (thermal) dehydrogenation. Typically, the C₂⁺ selectivity decreases when CH₄ conversion is increased due to the oxidation of C₂⁺ products into COₓ, as favoured by the kinetics within the reaction network. These pathways account for the inherently limited yield of the overall OCM process [35, 36, 41, 42]. The minimum required yield to make this process industrially viable has been estimated to be around 20 to 25% [43].

Fig. 2. 7 shows the simplest homogeneous-heterogeneous mechanism of the OCM reaction for a La₂O₃/CaO catalyst as suggested by Mleczko and Baerns [79]. This is applicable for a broad range of reaction conditions, such as a temperature range of 700-950 °C and a methane to oxygen ratio (CH₄/O₂) of 2.5 to 10. Methane reacts via different pathways, in which it can suffer undesired total oxidation to carbon dioxide (Eq. 1). It might also form ethane via OCM (Eq. 2), or it can form carbon monoxide by partial oxidation (Eq. 3) with subsequent oxidation of the carbon monoxide to carbon dioxide (Eq. 4). Ethane can heterogeneously react to form ethylene via its oxidative dehydrogenation (ODH, Eq. 5) or can follow the homogeneous non-catalytic thermal dehydrogenation to ethylene (Eq. 8). Ethylene can undergo oxidation to carbon monoxide (Eq. 6) or steam reforming (Eq. 7). Carbon monoxide can also be oxidized to carbon dioxide or vice versa via the water-gas shift reaction (Eqs. 9 and 10). All these
reaction pathways are heterogeneously catalyzed, except the thermal dehydrogenation of ethane.

Although the principal reaction details of OCM are well established, there are still more investigations need to be done with regards to the catalyst design [78, 81], reaction kinetics [82], reactor design [83, 84] and reaction conditions [79], with the ultimate goal of fully understanding the OCM reaction and to make it attractive for industrial applications.

1: \( CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \)
2: \( 2CH_4 + 0.5O_2 \rightarrow C_2H_6 + H_2O \)
3: \( CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \)
4: \( CO + 0.5O_2 \rightarrow CO_2 \)
5: \( C_2H_6 + 0.5O_2 \rightarrow C_2H_4 + H_2O \)
6: \( C_2H_4 + 2O_2 \rightarrow 2CO + 2H_2O \)
7: \[ C_2H_4 + 2H_2O \rightarrow 2CO + 4H_2 \]

8: \[ C_2H_6 \rightarrow C_2H_4 + H_2 \]

9/10: \[ CO + H_2O \rightleftharpoons CO_2 + H_2 \]

*Fig. 2. 7 Reaction scheme of OCM [79]*

### 2.3.1 Membrane reactor for OCM

Since the pioneering work by Kellers and Bhasin [85], extensive research on developing highly efficient and selective OCM catalysts and understanding the reaction mechanism has been carried out to elevate the \( C_2+ \) yield and reduce the formation of \( CO_x \), in order to justify the commercial potentials of OCM reaction [80, 86]. Despite that, the performance of catalysts operated in conventional fixed bed reactor is still below the industrial expectations. As a result, there is a continuing interest in developing new type of reactors, such as fluidised bed [87], reverse flow reactors [88] and membrane reactors [83, 89] for obtaining more \( C_2+ \) products.

Previous researches have proved that a membrane reactor can offers a higher \( C_2+ \) selectivity over conventional co-feed reactor, particularly when an oxygen permeable membrane takes the role of supplying, controlling and distributing oxygen. This is because the oxygen is added discretely into the catalyst bed along the length of the reactor, which enables the local hydrocarbon to oxygen ratio in the reaction to be kept high. *Fig. 2. 8* shows the schematic representation of dense MIEC membrane employed for OCM. This membrane acts as a barrier between two compartments; one side is exposed to air (upstream) and the other side
to methane (downstream). Only the ionic conducting species (dissociated and ionized oxygen) can pass through the membrane under oxygen partial pressure difference and then react with the methane. As such, this type of membrane lead to an improvement in the oxidation process as air can be used as an oxidant without the need of subsequent products stream purification. This elimination, which is often regarded as the difficult separation can lead to process cost savings [90]. Furthermore, reaction selectivity can be improved as direct contact between gaseous oxygen (O_2) and methane can be avoided, which results in less deep oxidation of C_{2+} hydrocarbons as gas phase oxygen is no longer present on the reaction side.

\[
\frac{1}{2} O_2 + V^{**} \rightarrow O_o^x + 2 h^* 
\]

![Diagram](Fig. 2. 8 Schematic diagram of the dense membrane reactor for OCM reaction)

The OCM reaction in a dense oxygen permeable membrane can be explained by the following mechanism in Kroger-Vink notation (Fig. 2. 8). The reaction occurs on the membrane surface exposed to air is expressed as below:
\[ O_2 (g) \leftrightarrow 2O_{ads} \quad (2.5) \]
\[ 2O_{ads} + V_o^{**} \leftrightarrow O_o^x + 2h^* \quad (2.6) \]

At high temperatures, lattice oxygen \( O_o^x \) and electron holes \( h^* \) may be transported through the membrane to the reaction side. The local charge neutrality is maintained by joint diffusion of oxygen vacancies and electrons on the surface exposed to air. On the membrane surface exposed to CH\(_4\) during the OCM, following reactions can occur.

\[ CH_4 (g) \leftrightarrow CH_4 (s) \quad (2.7) \]
\[ 2CH_4 (s) + O_o^x + 2h^* \rightarrow 2CH_3 + H_2O + V_o^{**} \quad (2.8) \]
\[ 2CH_3 \rightarrow C_2H_6 \quad (2.9) \]

In an integral form:

\[ 2CH_4 (g) + O_o^x + 2h^* \rightarrow C_2H_6 + H_2O + V_o^{**} \quad (2.10) \]

Therefore, the ethane formation rate can be expressed by

\[ r_{C_2H_6} = k_c [CH_4]^2 h^{**2} \quad (2.11) \]

where \([CH_4]\) is the methane concentration in the gas phase and \( P \) is the electron hole on the membrane surface exposed to methane. Since reaction (2.9) is fast and irreversible, the
constant of reaction, \( k_c \) is determined by reactions (2.7) and (2.8). At the same time, the ethane produced will be further converted into ethylene following a similar mechanism:

\[
C_2H_6 + O_\text{O}^x + 2h^+ \rightarrow C_2H_4 + H_2O + V_O^{**} \quad (2.12)
\]

If reaction (2.8) and (2.12) cannot completely consume all the lattice oxygen (\( O_\text{O}^x \)) or the reaction rates of both reactions are not fast enough to consume all the lattice oxygen in time, the following reaction can occur.

\[
2O_\text{O}^x + 4h^+ \rightarrow O_2 + 2V_O^{**} \quad (2.13)
\]

Thus, the lattice oxygen (\( O_\text{O}^x \)) on the membrane surface exposed on methane side is competitively consumed by three reactions: methane activation (2.8), ethane activation (2.12) and recombination of oxygen ions (2.13). As the gaseous oxygen produced in (2.13) can further react with methyl radicals (2.14) and \( C_2 \) to form \( CO_x \), a high oxygen flux does not necessarily improve the \( C_2^+ \) selectivity, although the OCM activity can be increased.

\[
\bullet CH_3 + xO_2 \rightarrow CO_x + H_2O \quad (2.14)
\]
2.3.2 Research developments in dense oxygen permeable MIEC membranes for OCM

The main issue that hinders the commercialization of OCM is its low \( \text{C}_2^+ \) yield. In order to achieve the target \( \text{C}_2^+ \) yield, it is important to obtain a high \( \text{C}_2^+ \) selectivity, without affecting the methane conversion. One of the possible ways to overcome this limitation is using a dense oxygen permeable catalytic membrane reactor, in which better control of oxygen with reactants can be achieved. A great deal of effort has been devoted to the use of dense oxygen permeable MIEC membranes for OCM. Beside their oxygen permeability properties, most MIEC membranes have also been observed to be catalytically active and selective for OCM.

\( \text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta} \) (LSCF) is one of the MIEC materials that show catalytic activities towards OCM. Its catalytic activities are closely related to the nature of B-site cation, while A-site cation, which is generally not catalytically active, strongly affect the oxygen nonstoichiometry of the oxide and the mobility of oxygen ions in the bulk phase [22, 91]. Consequently, this can affects the ability of solid phase oxygen species to participate in the oxidation reaction. Besides this, the type of the conductivity oxides is also found to affect the catalytic properties, in which p-type or ion conducting oxides in general are more selective for methane coupling reactions while n-type conductors are more selective for \( \text{CO}_x \) formations [92-94].

Elshof et al.[95] has investigated the use of disc LSCF membranes in OCM reactions. They reported that \( \text{C}_2^+ \) selectivity up to 70% could be achieved at higher temperatures, but the methane conversion was low: in a range of 1-3%. Xu and Thomson [96] have also analysed the performance of several disc-shaped perovskite-based membranes including LSCF and have reported a \( \text{C}_2^+ \) selectivity between 10-50 % at methane conversion of about 3%, when
pure methane was used as the reactant. It is believed that one of the main reasons for the low performances achieved in the above experiments is due to the undesired membrane reactor configuration. Several works have shown that membrane configurations have significant effects on reaction results and oxygen permeation flux during the OCM reaction. An increased in OCM activity is usually observed when tubular or hollow fibre membranes are used in compared with disc-shaped membrane due to their thin membrane wall, consequently, giving higher O$_2$ flux [97, 98].

In addition, Lin and Zeng [99] also found that the catalytic properties of perovskite-based membranes can vary with the oxygen partial pressure in the surrounding atmosphere. The membrane surface of the perovskite-type ceramic with good OCM catalytic activities under normal conditions can become non-selective for OCM in lower oxygen partial pressure atmospheres. This is due to a p-type to n-type switch of the electronic conduction mechanism of this material with respect to oxygen partial pressure, which can lead to unsatisfactory OCM performances.

Besides the perovskite-based membranes, promoted bismuth oxide based MIEC membranes with fluorite structure have been studied by Zeng and Lin [92, 100-102] for OCM reactions. They found that by doping yttrium into bismuth oxide, the overall C$_2^+$ yields can be increased, although the C$_2^+$ selectivity decreased slightly. Furthermore, in their subsequent studies, they found that the stability properties of bismuth yttrium oxide (BYO) could be further improved by doping the BYO with samarium oxide (Sm$_2$O$_3$). By using Bi$_{1.5}$Y$_{0.3}$Sm$_{0.2}$O$_{3-δ}$ (BYS) disc, a C$_2^+$ yield of 20-27% with C$_2^+$ selectivities of 50-62% could be achieved [103]. They also found that when a BYS dense tubular membrane was used at 900 °C, overall C$_2^+$ yield can be improved
to 35%, with a C$_2$ selectivity of 54% [104, 105]. This suggests that other than the catalytic properties of the metal oxides, OCM performance can be improved by designing the membrane geometry [97]. In addition, BYS is found to be mechanically and chemically stable for OCM reaction, making it suitable to be used as a membrane reactor [104].

In spite of extensive research on membrane reactors for OCM, the currently achieved C$_{2+}$ yields are still below the values needed for industrial commercialization. From the reaction kinetics, it is possible to increase the C$_2$ yield by matching the oxygen permeation rate across the membrane with surface catalytic activation of methane on the membrane surface, as the overall C$_2$ yield is determined by the combined effects of both important factors. In addition, when the oxygen permeation rate is greater than the rate consumed in the methane coupling, deep oxidation of methyl radical and C$_{2+}$ products to CO$_x$ will occur and thus, the C$_{2+}$ yield will be reduced. Therefore, it is essential to improve the surface catalytic activation of methane in parallel with the increase of the oxygen permeation rate. One way to achieve this is by fixing a catalyst onto the membrane surface to form a catalytic membrane reactor (CMR). Many attempts have been made to develop CMR using different MIEC membranes.

Tan et al. [83] compared the OCM performance of LSCF hollow fibre membrane reactor with and without additional catalyst (SrTi$_{0.9}$Li$_{0.1}$O$_3$). The methane conversion and oxygen permeation rate was remarkably improved with the use of catalyst but a decrease in C$_{2+}$ selectivity was observed. This is likely due to the mismatched of oxygen flux and catalytic activity of the membrane. Haag et al. [106] investigated the use of three catalytic disc membranes reactors (BSCFO, BSMFO and BaBiFeO with Pt/MgO catalyst), each of which possess different oxygen permeation rates. They found that the formulation of the catalyst
should be determined by the permeability of the membrane, in which insufficient oxygen supply can lead to poor methane conversion/C2+ selectivity even though a catalyst with high catalytic activity was used. Thus, a highly permeable membrane needs a highly active catalyst to avoid poor C2+ selectivity.

Bhatia et al. [107] compared the performance of other catalytic reactors with a catalytic Ba0.5Ce0.4Gd0.1Co0.8Fe0.2O3−δ dense membrane on porous alumina support with a Na-W-Mn/SiO₂ catalyst. The performance of the CMR was observed to be the best in compared with other types of reactor. However, similarly to Haag et al. [106], they found that the oxygen supply in the reactor need to be regulated to fit the amount required by the reaction to further increase the CMR performances. This is because higher oxygen flux does not guarantee higher yield of C2+ products due to recombination of oxygen ions into gaseous oxygen in the methane-enriched side, which then react with intermediates to form carbon oxides.

If a stable and high performance catalytic membrane reactor (CMR) is to be developed, further enhancements in the catalytic activity of the membrane are clearly required other than just improvements in the oxygen permeation rate. The past few decades have seen a determined effort to develop a selective catalyst for OCM, which for industrial purposes would ideally require a catalyst allowing a high initiation rate of methyl radical. This process usually occurs on the catalyst surface and, most importantly, can suppress the non-selective oxidation of CH₄ and C₂⁺ products to COₓ[78]. Initial catalyst screening was carried out by Keller and Bhasin, in which 25 different catalysts such as α-Al₂O₃ supported metal oxides, and the oxides of Mn, Cd, Sn, Sb, Tl, Pb and Bi were tested and found to be active for the OCM reaction. This was followed by a number of studies by Carreriro and Baerns [108], DeBoy et al.[86], Zhang
et al. [93], Baidikova et al. [109] and Voskresenkaya et al. [110]. Recent work by Zavyalova et al. [78] has used statistical analysis in order to obtain a new insight into the composition of high performance OCM catalysts. In general, the OCM catalyst formulations are divided into formulations operating at (i) low temperature, such as tungsten [111] and zirconia [112]-based systems (around 400-530 °) and (ii) high temperature, e.g. nickel calcium oxide, lanthanum calcium oxide or lithium magnesium oxide based systems [81]. Based on the above mentioned researches, mixed metal oxides with adjustable solid-state properties have been demonstrated to have impressive catalytic properties towards OCM, when compared to the single metal oxide catalysts [78]. From many studies reported in literature, the C$_2$+ yields obtained were usually below 20%, since they were mainly conducted using a packed bed reactor configuration.

### 2.4 Challenges in the development of dense oxygen permeable catalytic membrane reactors

Over the past few decades, there has been substantial progress in the application of dense oxygen permeable catalytic membrane reactors for refinery products. The idea of integrating the separation and reaction processes into one unit is attractive but also complex, which hindering the widespread use of its applications. There is still a need for major substantial progress in the field of membrane materials, catalysts, and chemical engineering in order to fully exploit the potential of membrane reactor at an industrial scale [113]. Table 2. 1 lists some of critical issues that limiting the development of membrane reactors.
**Table 2.1 Critical issues in membrane reactor development**

### Membrane

1. Discovering membrane materials that have better properties (i.e. usually there is a trade-off between oxygen permeation and the chemical stability of membranes.)
2. Fabricating uniform and defect-free thin oxygen permselective membranes using simple and cost effective techniques.
3. Improving the chemical stability of membrane materials in a reducing atmosphere.
4. Improving the membrane resistance to temperature and thermal fatigue [113]
5. Developing a reliable and cost effective high temperature sealing method.
6. Reproducing membrane reactors on a large scale.

### Catalyst

1. Developing a new membrane catalyst that is less sensitive to poisoning and coking.
2. Finding ways to position the catalyst, either on the membrane surface or impregnating it into the membrane macrostructure.
3. Understanding the control mechanism for catalytic activation [114].

### Chemical Engineering

1. Designing a method for the large-scale production of uniform oxygen permselective membranes.
2. Finding a way to increase the membrane area per unit volume.
(3) Developing membrane reactor systems complete with heat supply and temperature control.

(4) Finding alternatives ways to replace the usage of sweep gas as a carrier gas.

(5) Developing optimal membrane reactor designs.

Therefore, it can be concluded that the main challenges towards the widespread application of ceramic membrane reactors is the membrane itself. However, by a proper selection of membrane materials, material composition, and membrane properties (structure and thickness), it is expected that both the oxygen separation and membrane stability can be significantly improved.

On the other hand, by having a highly oxygen permeable membrane, enhancements in the catalytic activity of the membrane are obviously required. Or else, the most promising membranes would also suffer a decrease in selectivity if the oxygen supply rate is too high compared to the catalyst activity. Similarly, a detrimental effect on \( \text{C}_2 \text{H}_4 \) selectivity could also occur if a low oxygen permeable membrane is used with a high catalytic activity of catalyst. Therefore, the selection of catalyst should be matched with the amount of oxygen supply delivered by the membrane.

Besides the selection of the membrane materials and catalyst, membrane morphologies and geometries also play a very important role in increasing the oxygen flux. Membrane morphologies can be either symmetric or asymmetric. For membrane reactor applications, membranes with asymmetric structures are more preferable in order to obtain a higher oxygen permeation rate without affecting the permselectivity [25, 26, 98, 115-118].
In term of membrane geometry, most research has involved the use of a small disc membrane, since this is relatively easy and cheap to prepare. However, such disc membranes are usually very thick and provide only a limited surface area for oxygen to permeate. Tubular membrane reactors with a higher surface area were then developed to overcome the problem, but due to its symmetric structure, the transport resistance of this membrane is very high. In addition, the limited surface area/volume ratio of tubular designs is unfavourable for industrial purposes. Since membrane area is a very important element in a membrane system in order to ensure high production \( \text{O}_2 \) flux, it is necessary to develop a technique to fabricate a thin membrane. Therefore, hollow fibre configurations with smaller diameter and reduced thickness can be considered as a good alternative to the above configurations.

To date, ceramic hollow fibre membranes are not commercially available since there is no technique available to produce membranes with a thin and dense separation layer in a hollow fibre form. These configurations also suffer from poor mechanical strength, which limits their use as ceramic membranes. Several attempts have been made to establish a proper technique to make ceramic hollow fibres, but most of these have failed, since the membranes are usually porous and symmetric. Many additional steps are therefore required in order to obtain the asymmetric structures, which are both time and cost intensive [119-121]. In addition, the mismatch of the ceramic materials and the porous substrates has also being an issue.

A new single step technique based on combinations of phase inversion and sintering process has recently been developed and has been successfully used to fabricate several ceramic hollow fibres with different MIEC materials [6, 122-128]. The membranes prepared using this
technique are typically in asymmetric structures and possess a thin top layer integrated onto a porous support, which is due to the phase inversion process of the same material. This process is currently receiving wide attention compared to other membrane fabrication techniques such as deposit technique, since it is a relatively simple and fast method [75]. Besides that, the technique allows variety of membrane morphologies to be obtained by simply varying the fabrication conditions.

2.5 Fabrication of ceramic hollow fibre membrane

There are three main steps in the fabrication of ceramic hollow fibre membranes using a combined phase inversion and sintering technique as shown in Fig. 2. 9: (1) preparation of a spinning suspension, (2) spinning of hollow fibre precursors and finally (3) sintering of hollow fibre membranes. Each of the steps has controlling factors that will affect the final membrane structures.
2.5.1 Preparation of spinning suspension

In general, a spinning suspension consists of four main components: ceramic powders, a polymer binder, an additive and a solvent. Each of these components has a specific role in the fabrication of hollow fibre membranes. The spinning suspension preparation consists of a few steps: (1) mixing a dispersant with a selected solvent, (2) adding the ceramic particles into the suspension, and (3) adding polymer binders and additives. The most important components in the spinning suspension are the ceramic powders themselves, as these are the only components left after the sintering / burn-out process. The appropriate selection of
ceramic powders in relation to their particle size and distribution are vital since this affects the porosity and pore size of the final membrane product.

The other three components are usually used to pre-design the membrane morphology (pore size, porosity, cross-sectional structures, etc.) and to facilitate the spinning and sintering process. A polymer binder is used to bind the ceramic particles for ease of extrusion. Polyethersulfone (PESf) is one of the small numbers of polymer binders that are widely used in the fabrication of ceramic hollow fibre membranes. The main criterion for the polymer binder is that it should be able to be fully removed without leaving any ash and tar during the sintering process. Additives can be dispersants, anti-foaming agents, pore formers, antistatic, chelating and bactericide, depending on the required function in the spinning suspension. The introduction of additives is considered to be the easiest method to directly tailor the membrane structures as it can directly adjust the phase inversion rate. One of the additives that has been widely used with PESf is polyvinylpyrrolidone (PVP). PVP is a well-known additive that helps to improve the viscosity of spinning suspension. However, it also tends to increase the formation of macrovoids, therefore giving higher permeation rates [129]. The formation of macrovoids is considered an advantage for a porous membrane. This however, is not preferable for dense membranes. PVP has proved to possess different effects at different loading contents. Although it functions as a pore former, surprisingly at a higher content, the formation of macrovoids seems to be reduced due to the fact that the de-mixing process is delayed because of the high viscosity of the spinning solution [130].

Apart from additives, dispersants are also sometimes added to the spinning suspension. This is due to the tendency of ceramic powders to form soft agglomerates when dispersed in the
solvent, due to the proximity of individual primary particles. These soft agglomerates can usually be broken down by adding a dispersion, which will disperse the primary particles and hold them in a homogeneous suspension. The amount of dispersion needs to be maintained to ensure the stability of the suspension.

The solvents used in the spinning suspension must be able to dissolve the additive and polymer binders. They must also possess a high exchange rate with non-solvent/coagulant since the exchange rate has a significant effect on the hollow fibre precursor structure and hence the final membrane structure [131]. For a low viscosity spinning suspension, dimethyl sulfoxide (DMSO) is more preferable as a solvent due to its low boiling point and freezing effects. This freezing effect helps to increase the spinning suspension’s viscosity, allowing for an easy spinning process and the formation of a dense membrane structure.

In some cases, a non-solvent is introduced to the spinning suspension in order to change the de-mixing behaviour and precipitation path, simultaneously giving a denser structure. A few types of non-solvents can be considered such as water, glycerol, methanol, etc. The effects of non-solvent additions have been widely investigated in polymeric membranes [129, 132], but it is still a rather new addition for ceramic membranes. An extensive study has been carried out to understand the formation of asymmetric structures, with the authors showing that a finger void structure occurs when the local viscosity of the nascent fibre is larger than the local viscosity of the coagulants [127]. Further studies have also shown that the addition of non-solvents into the ceramic spinning suspension can significantly reduce, and sometimes eliminate, finger void structures [133]. This is due to the introduction of the non-solvent into the system serving to alter the viscosity of the spinning suspension, making it nearer to the
precipitation point and thus reducing the finger like void structure. In light of this, the addition of non-solvents during dense membrane fabrication can be considered in the future.

Spinning suspension homogeneity plays an important role in determining the mechanical strength of the membrane. A homogenous spinning suspension is a vital requirement during the formation of ceramic hollow fibre precursors since it can eliminate structural defects and thereby improve the membrane's mechanical strength. A spinning suspension with different particle sizes is usually preferred so that the smaller particles can fill in the voids between the bigger particles, thus increasing the packing density. The ratio of polymer binder to the ceramic/catalyst content is also important and the value should be minimised, since during the sintering process, the polymer binder is removed.

2.5.2 Spinning of precursors hollow fibre

Phase inversion is a process in which a thermodynamically stable polymer suspension is transformed into two phases; a polymer rich phase (membrane matrix) and a polymer poor phase (membrane pores). This method was developed by Loeb and Sourirajan in the 1960’s to produce an asymmetrically structured membrane that possesses a high selectivity and water flux. A typical phase inversion in a polymeric system involves the interaction of three components: polymer, solvent and non-solvent. In general, the polymer is dissolved in a solvent to form a homogeneous polymer suspension solution. Then, the polymer solution is immersed into a non-solvent coagulation bath in which the solvent will diffuse out of the polymer solution while the non-solvent diffuses into the solution. The exchange of the solvent
and the non-solvent results in the solidification of the polymer solution and the formation of a polymeric membrane. This exchange rate is an important aspect that needs to be carefully controlled, since it is the step that determines the membrane’s overall morphology.

The phase inversion mechanism for ceramic hollow fibre membranes is usually quite different and more complex than with polymeric membranes. The ceramic particles in the suspension system will affect the solidification mechanism such that, instead of only the exchange rate governing the membrane structure, the movement of the ceramic particles also has a direct effect on membrane morphology. A number of research studies have been conducted to give a better understanding of the ceramic membrane fabrication process [127, 134-137]. It has been concluded that various parameters such as ceramic particle sizes, ceramic particle compositions, spinning solution composition, solvent selection, spinning parameters, etc. could affect the membrane properties. In light of this, a comprehensive study of the fabrication process is important. The spinning process of hollow fibre precursors can be based on the principles of dry/wet/dry-wet phase inversion. The hollow fibres are spun through a tube in an orifice or a triple orifice spinneret, which consists of a central bore and either one or two annulus. Fig. 2. 10 shows a schematic representation of spinnerets used for single layer and dual layer hollow fibre membranes spinning.
Fig. 2. 10 Schematic representation of spinnerets (a) tube in orifice for single layer membrane (b) triple orifice for dual layer membrane

Fig. 2. 11 illustrates the co-extrusion process of the dual layer hollow fibre precursors. The outer layer spinning suspension and bore fluid are introduced at the annulus side of the spinneret and a gear pump is used to control the rate of the suspension through a tube to the spinneret. A non-solvent, typically deionised water is used as a bore fluid. The inner layer spinning suspension is pumped through the syringe into the bore side of the spinneret. The
spinneret is then positioned outside of the coagulation bath, containing tap water, with the membrane allowed to fall freely from the spinneret into the bath. Alternatively, the spinneret can also be positioned inside the coagulation bath, depending on the required membrane structure. The exchange between solvent and non-solvent will cause instability of the spinning suspension, which leads to the solidification of the polymer phase, entrapping the ceramic and inorganic particles. Since ceramic particles are immobilized once the precipitation occurs, macrostructure tailoring must be carried out before precipitation of the fibre, by manipulating and adjusting various parameters during the spinning. The developed precursor fibres are then transferred into a small tank containing deionised water in order to complete the phase inversion. The polymer matrix from the precursors is removed using a heat treatment and the ceramic particles will be sintered, therefore changing the precursor fibre to the rigid ceramic body.

The spinning process involves a few parameters that directly correlate with the structure and membrane performances. The selection of both the internal coagulant (bore fluid) and external coagulant is very important as it affects the phase exchange and simultaneously the formation of membrane voids. Finger like voids occur when a less viscous fluid (non-solvent) penetrates into more viscous fluid (spinning suspension). This void formation is dependent on the viscosity of two phases, and by varying the air-gap, bore fluid flow rate, and the precipitation rate of polymer during the spinning, the membrane structure can be tailored.
Fig. 2. 11 Co-extrusion of dual-layer hollow fibre precursors[121]

Fig. 2. 12 illustrates the two main membrane structures that can be observed in ceramic membranes. A sandwich structure consists of a central dense layer and two surface skin dense layers integrated with two finger voids from inner and outer fibre surfaces. This kind of structure would not be suitable for separation applications as it has higher diffusion resistance but would be suitable for certain membrane catalytic reactors, especially for catalyst impregnation [136]. An asymmetric membrane structure, consisting of a finger like structure on the substrate layer and a sponge structure on the top layer is more preferable for oxygen separation, since the dense sponge top structure is not only responsible for the oxygen separation layer but also for providing the mechanical strength of the membrane. The mechanical strength of the sandwich-like membrane structure is usually quite low since the middle sponge layer is sandwiched by the finger-like porous substrates.
2.5.3 Sintering of hollow fibre

After the spinning process, the membrane precursors need to undergo a high temperature treatment known as sintering. Sintering is a process of transforming a ceramic powder into a solid body using heat, but without melting them. The process is usually carried out between approximately 50 to 80% of the melting temperature of the ceramic particles. During this process, all spinning suspension components except the ceramic particles are burned out. A number of parameters such as sintering temperature, dwelling time, heating rate and cooling rate need to be considered during the sintering process. An optimum sintering condition is favourable to ensure that the membrane precursor survives the sintering process without any cracks being formed. The sintering process consists of three stages: (1) pre-sinter, (2) thermolysis and (3) final sintering, with this last stage in turn consisting of three further stages (initial, intermediate and final) [139]. Pre-sintering usually begins when the temperature is around one half to two thirds of the melting temperature of the materials. At this temperature, vaporization of chemically combined water and crystallization water occurs in organic
particles. A lower heating rate (1°C/min) is preferable in order to prevent the membranes from cracking or fractures arising from the pressures produced as vapour evolves or from differential thermal expansion phases.

Thermolysis is an important process in sintering prior to densification. During this stage, organic components such as the polymer binder, dispersant and additive are burnt out. A proper selection of heating rate and thermolysis atmosphere (gas surrounding the pre-cursor fibres) are vital to avoid membrane defects such as deformation, distortion, formation of cracks and expanded pores [140]. Any membrane defects will significantly affect the membrane performance. Precursors containing low amounts of organic components would be able to open pore channels sufficient to allow for the transport of vapour and gases between the reaction zone and the membrane surface, allowing complete burn out to occur.

The final sintering phase occurs in three stages: initial, intermediate and final [139]. Each stage has different particle movement attributes, from grain coarsening to pore closing. Different materials require a different sintering profile. During the initial stage of sintering, ceramic particles rearrange and neck growth at contact points between particles is observed. The neck growth between particles is led by at least six different mechanisms, including surface diffusion, lattice diffusion from the surface, vapour transport, grain boundary diffusion, lattice diffusion from the grain boundary and plastic flow [133]. Then, the grain boundaries start to develop, bonding ceramic particles and forming pore channels. During this time, a significant shrinkage of the ceramic membrane occurs. As the pores continue to shrink, some of the pores pinch off and become isolated at the grain corners. Then at the end, the pores are gradually eliminated from the membrane surface and the grain growth continues (Fig. 2.13).
For the development of dual layer hollow fibre membranes, membrane delamination or membrane cracking during sintering is a present issue due to the mismatch in shrinking behaviour of each layer. The introduction of at least one identical material in the inner and outer layer would be expected to reduce these differences. The sintering process of ceramic hollow fibre membranes is still more of an art than a science, since it is difficult to predict the real mechanism even with the help of a dilatometer. Study with a dilatometer would, however, probably provide a better explanation for the thermal behaviour of disk membranes compared to hollow fibre membranes, due to the latter’s larger surface area and a more curved form. A number of factors, such as membrane thickness, membrane structure, and the adhesion
between the inner and outer layers, may cause significant dissimilarities between the thermal
behaviours given by the dilatometer study compared with real membranes. Therefore, the only
option to further understand the effects of sintering conditions on the properties of dual layer
hollow fibre membranes is to employ a trial-and-error approach.

2.6 Microreactors technology

In recent years, micro-technology has grown rapidly in many areas of application, including in
chemical processes. Micro-structured reactors have demonstrated substantial advantages
compared to conventional chemical reactors in intensifying mass and heat transport, as well
as in improving flow patterns. Micro-structured reactors are generally defined as reactors with
three-dimensional structures, in which the inner dimensions are between ten and a hundred
micrometres) [141, 142]. This miniaturisation brings significant advantages compared to
conventional chemical reactors [141]:

a) *Increase of surface to volume ratio (SA/V):* the specific surface areas of
microstructures lie between 10 000-50 0000 m²·m⁻³, while those of traditional reactors
are generally about 100 m²·m⁻³, only in rare cases reaching 1000 m²·m⁻³. In addition,
the increase in specific vessel surface can be further utilized, e.g., in catalytic gas
phase reactors coated with the active material on the inner walls.

b) *Better heat transport:* since the heat transfer coefficient is inversely proportional to a
channel diameter, values in the order of 10 kW·m⁻²·K⁻² can be obtained. This high heat-
exchanging efficiency allows for fast heating and cooling in reaction mixtures within the microstructures.

c) **Suitable for strong exothermic or endothermic reactions:** due to better heat transport, the development of hot spots or the accumulation of reaction heat can be suppressed so that undesirable side reactions are hindered. As a result, higher product selectivity, yield and quality can be achieved.

d) **Improvement in mass transport:** the influence of mass transport on the speed of reaction is less since the mixing times are generally shorter and the diffusion time is very short.

e) **Better hydrodynamic flow:** the flow inside the microchannels is mostly laminar, directed and highly symmetric. The Reynold numbers lie between 1 to 1000, depending on velocity and channel dimensions.

f) **Better control of process parameters:** the process parameters such as pressure, temperature, residence time and flow-rate are easily controlled due to the small reaction volumes.

g) **Better technical safety:** the small reaction volume of micro-reactors minimises the hazards associated with strong exothermic and endothermic reactions. The smaller inner dimensions not only function to assist heat removal but also can mechanistically control a reaction where radical chains are suppressed.

Metal, silicone, glass and a few polymers are among the materials that can be used in micro process engineering, and a comprehensive knowledge of structuring techniques has been established for most of these materials [143]. However, these materials are typically ill-suited for chemical reactions at high temperatures and/or where corrosive reactants are involved.
Furthermore, the diffusion of metallic atoms can occur in metal-based reactors, if a metal that is commonly used as active sites for a catalyst, such as nickel and copper, is also used as a microreactor substrate [144]. Ceramic materials should therefore be used, due to their high thermal and chemical stability. On the other hand, their material properties such as high hardness and high melting point making the moulding process that has been used for other materials, could not be transferred to ceramic materials due to the economic reason, which is the main drawbacks that have limited the development of ceramic-based microreactors [143]. In this context, one of the greatest achievements in respect to ceramic-based microreactors is the development of a gas-tight ceramic microreactor by Knitter and Liauw [145] for heterogeneously catalysed gas-phase reactions (oxidative coupling of methane (OCM) and selective oxidation of isoprene to citraconic anhydride). They reported that the reactor can be operated to temperatures of at least 1000 °C without any contamination from the ceramic materials, thus confirming the suitability of ceramic materials for microreactor development.

2.6.1 Catalytic hollow fibre membrane microreactors (CHFMMRs) for chemical reactions

MMR is a unit that combines membrane-based separation and a chemical reaction with the advantages of a microreactor, leading to a significant intensification of the production process. This design allows the reactor to work under improved reaction conditions due to rapid mass and heat transfer rates as well as significantly lower operating temperatures, and/or use of less catalyst than in conventional reactors. In addition to this, the problem of deformation and cracks due to accumulated stresses during processing and reaction can be avoided due to
the miniaturization [146]. Moreover, the selectivity and permeability of miniature membranes can be enhanced compared with conventional membrane units [147].

In recent years, considerable research has been carried out on the use of membrane microreactors for catalytic reactions, especially in strong exothermic/endothermic environments. Since the membranes possess small channel dimensions, they facilitate heat transport and minimise the formation of hot spots. In addition, explosive gas mixtures can be handled safely. MMRs can be fabricated either from catalytic materials themselves or by impregnating the microchannels with the catalytic material after membrane fabrication.

In general, MMRs can be divided into two categories: plate-type and tubular-type, depending on the configuration and geometry of the reactor. However, only tubular MMRs will be discussed in this section. In tubular MMRs, the microchannels for fluid flow may be formed due to the small size of the tube or distributed within the tube wall, while the membrane is usually coated on the outer surface of the tube [146]. A simple palladium (Pd)-MMR has been developed by Yamamoto et al. [148] for the dehydrogenation of cyclohexane to benzene. They placed different sizes of stainless steel rod inside the tubular membrane reactor to investigate the effects of microchannel sizes and found that the product yield doubles compared to where no rods are present due to the increase in the surface area per volume ratio of the membrane.

Recently, Li’s group has developed several Pd-based MMRs for the production of high purity hydrogen using porous asymmetric ceramic hollow fibre membranes made from Al₂O₃ and YSZ [149-152]. The ceramic hollow fibres were fabricated using a modified phase inversion and sintering technique (viscous fingering induced phase inversion) that leads to the formation
of open finger-like microchannels at the inner surface side, making it suitable as a substrate for catalyst deposition [116, 150]. Fig. 2. 14 shows the CHFMMR developed by Rahman et al. [153] for ethanol steam reforming, in which the catalyst was impregnated into the finger-like structure of YSZ hollow fibre substrate. A Pd/Ag membrane was then deposited on the outer surface of the hollow fibre by the electroless plating method. According to their study, the open finger-like structure can be viewed as microchannels with a 0.1 µm diameter, although the fabrication technique is different compared to the conventional micro-technique. Furthermore, each catalyst-impregnated hollow fibre can actually act as a catalytic microreactor made up of hundreds of microchannels that are perpendicularly distributed around the lumen of the fibre [146].

Although CHFMMR offers significant advantages, there are still a number of technological challenges limiting its application. Among the main issues that need to be addressed are (1) mechanical stability, which limits the maximum pressure differentials for driving mass transfer across the membrane and (2) the introduction of a catalytic phase in the CHFMMR.
Fig. 2. 14 Schematic representation of CHFMMR developed by Li’s group for high-purity hydrogen production using ESR reaction [153]

2.6.2 Deposition of catalysts for catalytic microreactor

Microreactor usually requires a solid catalyst to catalyse the gas phase reaction and the progress of this reactor is crucially depends on the development of the catalyst layer [154]. One of the easiest ways to introduce catalytic materials is by filling or packing the microchannels with catalyst powder. This method allows the use of commercial catalysts that have already been optimized. The catalyst beds in micro-structured reactors, however, could lead to a large pressure drop and a change of fluid flow, which could result in a non-uniform
temperature distribution. As a result, the deposition of thin catalyst layers onto the reactor wall is preferable. Such an approach not only increases the catalytic activity of the micro-structured reactor but consequently allows better heat transfer and isothermal conditions to be achieved as well. The coating of the catalyst onto the reactor walls can be carried out by wash coating, such as is applied either in exhaust gas cleaning or through wet-chemical impregnation.

The wash-coating technique is among the easiest available and has been widely used to deposit catalysts onto the inner surface of microreactors [155, 156]. This technique generally includes four main steps: (1) preparation of catalyst slurry, in which the catalyst powder is mixed with a binder such as acetic acid and a solvent such as ethanol; (2) pre-treatment of the support includes cleaning and annealing; (3) coating / deposition of catalyst and (4) drying and calcination at higher temperatures. The dispersion of catalyst powder can then be enhanced by stirring or by using an ultra-sonic bath. Stefanescu et al. [155] found that by optimizing the catalyst slurry preparation in term of particle size, solid loading, binder content and viscosity, different thicknesses of catalyst layer and improvements in adhesion and uniformity can be achieved. Germani et al. [154] have systematically studied the nature of binders used for the coating of Cu/Zn/Al catalyst into microchannels and concluded that the binders play a major role on: (i) slurry viscosity (through their chemical structure and molecular weight); (ii) coating adhesion, and; (iii) catalytic activity (through the re-dispersion of the active phase because of the formation of metal complexes).

Incipient wetness is one of the methods used in wet-chemical impregnation. This approach requires the fixing of an oxide support in the walls of the microchannels before an active metal precursor in nitrate form can be impregnated. Although this method is relatively
straightforward, it produces large catalyst particles that can significantly reduce the performance of the microreactor.

The sol-gel technique has also been used to impregnate catalyst inside the microchannels [153, 157]. This approach offers great advantages in that the catalyst preparation and impregnation processes are combined into a single step. In this method, a solution of catalyst precursor is first prepared and allowed to age until the gelation (peptisation) of sol occurs. The aging time can be from a few minutes to several weeks, depending on the concentrations of the sol. This step is very crucial since it determines the properties of the catalytic layer inside the microchannels. Typically, a long aging time will lead to a highly viscous catalyst sol, allowing a thicker layer of catalyst to be deposited. This thick catalyst layer is more likely to crack, however, which leads to a reduction in reactor performance [158]. Therefore, ways of introducing a catalytic active phase into the microchannels without affecting its activity remains a key challenge in development of catalytic microreactor.

2.7 Review conclusion

The main problem faced in the oxidative conversion of methane is the use of air as the oxidant, which usually needs to be followed by another separation unit to allow for nitrogen removal from the product stream. Benefiting from significant development of membrane technology, the concept of integrating catalytic reaction and membrane separation into one unit has been proposed. By using a dense MIEC oxygen permeable membrane, air can be directly utilized as the source of oxygen in the catalytic membrane reactor. Furthermore, the use of
membranes to control the reaction pathways by distributing the oxygen into the reactor could also increase the reaction yield. Although significant progress has been achieved experimentally and theoretically to demonstrate the feasibility as well as the advantages of using a membrane reactor for methane conversion processes, there are still a number of technological challenges limiting the application of this technology. These include:

1. A lack of reliable techniques for the fabrication of uniform and defect free thin oxygen permselective film on a stable substrate; which could lead to an increase in oxygen flux and reduce membrane cost.
2. The trade-off between oxygen permeation and the chemical and mechanical stabilities of membrane materials.
3. The need to develop catalytic membrane reactor designs with higher volume productivity.

By using a phase inversion and sintering technique in the development of compact micro-structured functional ceramic hollow fibre membrane reactors (CHFMR), it is possible to simplify the fabrication process significantly as well as to allow full control of the hollow fibre membrane structures. The hollow fibre configuration itself offers significant advantages in terms of oxygen permeation flux and catalytic reaction due to the increase in the surface area to volume ratio. Since the micro-structured CHFMR design proposed in this study is relatively new, more work is needed to develop a membrane reactor with high oxygen permeation rate, high catalytic activity, better membrane stability and greater efficiency.
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CHAPTER 3

Fabrication of Bi$_{1.5}$Y$_{0.3}$Sm$_{0.2}$O$_{3-\delta}$ Based Dual-Layer Membrane Reactor for Oxygen Separation and Chemical Reactions

Abstract

The indirect routes of methane conversion involve formation of an intermediate product known as syngas (a mixture of CO and H$_2$). Currently, the syngas is obtained from the methane steam reforming processes, which is energy and capital intensive. For these reasons, partial oxidation of methane (POM) is considered as the promising alternative to the reforming process as it possesses higher energy efficiency and higher selectivity to CO and H$_2$. The production of syngas through POM can be enhanced by the use of membrane reactor due to the integration of oxygen separation (from ambient air) and methane conversion processes into a single unit operation (Fig. 3. 1). In this study, a ceramic hollow fibre membrane reactor consisting of two functional layers was developed, which can significantly reduce the reactor volume due to the extremely high surface area/volume of the hollow fibre configuration. The dual-layer catalytic hollow fibre membrane reactor (DL-CHFMR) was fabricated using a new single step membrane fabrication process, i.e. a co-extrusion and co-sintering process, in which the thickness and the composition of each functional layer can be controlled for a better reactor performance. Bi$_{1.5}$Y$_{0.3}$Sm$_{0.2}$O$_{3-\delta}$ (BYS), an oxide of great ionic conductivity was used to develop the BYS- La$_{0.8}$Sr$_{0.2}$MnO$_{3-\delta}$ (LSM) dual-phase membranes in an objective of promoting oxygen permeation that has been considered as the controlling step of our recent DL-CHFMR
for methane conversion. As a result, the temperature needed for both oxygen separation and catalytic reaction can be lowered. Although the oxygen permeation obtained was significantly higher than the previous counter-part, the stability of BYS based DL-CHFMR was observed to be greatly hampered in the strong reducing atmosphere of POM. However, the advantages of such reactor design have been proved and can be transferred to other important catalytic reactions, such as oxidative coupling of methane (OCM) where no strong reducing environment is required. Besides the high oxygen permeation of BYS, it also shows a great catalytic activity for OCM.

![Diagram of DL-CHFMR](image)

**Fig. 3.1 Schematic diagram of DL-CHFMR**

### 3.1 Introduction

Ceramic membranes composed of a separation layer supported on a porous substrate layer have shown a number of important advantages [1-3], especially in escalating permeation flux by reducing the thickness of separation layer. However, such a membrane structure is currently achieved via a multi-step fabrication process that consists of repeated coating and sintering steps, which is complicated, and time and energy consuming. Combining the multi-
step processes into a single step process would significantly reduce the fabrication costs, besides additional benefits such as good adhesion between layers and consistent quality control. Our previous studies have demonstrated that a dual-layer ceramic hollow fibre membrane consisting of an outer separation layer supported on an inner catalytic substrate layer can be prepared using a reliable single-step co-extrusion and co-sintering process. When different membrane materials are used in each layer, certain functions can be integrated into such unique membrane design. Membranes of this type have been utilized as a compact membrane reactor for partial oxidation of methane (POM) \([4, 5]\) and micro-tubular solid oxide fuel cells (SOFCs) \([6-10]\).

In our previously designed dual-layer ceramic hollow fibre membrane reactor (DL-CHFMR) for POM reaction, the outer thin dense layer \((\text{ZrO}_2)_{0.90}(\text{Sc}_2\text{O}_3)_{0.10}(\text{ScSZ})-\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3-\delta\) (LSM) or LSM-YSZ) for oxygen separation was supported on the inner porous catalytic substrate layer (Ni-ScSZ or Ni-YSZ)\([4, 5]\). Oxygen permeation is always the slowest or controlling step even if the thickness of separation layer can be reduced to less than 10 \(\mu\)m. High operating temperatures are thus needed for proper oxygen permeation flux, good methane conversion and suppressed coke formation, which addresses the importance of oxygen permeation of the outer separation layer to the performance of such DL-CHFMR design.

Mixed ionic and electronic conducting (MIEC) membranes have received great attentions for several decades due to their unique mechanism for oxygen separation. Such membranes have also shown many potential applications related to pure oxygen production, from medical treatments to large scale combustion processes, as long as the technical challenges of
permeation flux, membrane sealing and durability can be overcome [11]. Similar to MIEC materials (single phase) with typically a perovskite type structure, dual-phase materials with ionic conducting and electronic conducting in two separate phases show mixed conducting behaviour as well. As a result, oxygen permeation of dual-phase materials should also be affected by two factors, i.e. the thickness of separation layer [12] and its mixed ionic-electronic conductivity. Based on Wagner theory, oxygen permeation of MIEC membrane is proportional to $\frac{\sigma_i \sigma_e}{\sigma_i + \sigma_e}$ [13]. Thus, dual-phase materials with higher ionic conductivity and electronic conductivity are always preferred. Since LSM is a great electronic conducting ceramic, improving the ionic conductivity of the LSM based dual-phase separation layer is the key to higher oxygen permeation. According to Singhal and Kendall [14], bismuth yttrium oxide (BY) exhibits higher ionic conductivity than ScSZ and YSZ, especially between 600 and 800 °C. However, because it is thermodynamically unstable, doping technique is implemented to fine-tune its stability and conductivity. Bismuth yttrium oxide doped with samarium (Sm$_2$O$_3$) gives much higher oxygen permeation and greater chemical stability over a wide range of temperatures [15]. In a recent study [16], BYS was mixed with LSM to fabricate dual-phase hollow fibre membranes for oxygen separation, with the oxygen permeation flux of 0.52 ml·min$^{-1}$·cm$^{-2}$ ($3.9 \times 10^{-7}$ mol·s$^{-1}$·cm$^{-2}$) at 850 °C using helium as sweep gas.

As a result, BYS is used to replace ScSZ or YSZ in this study as the ionic conducting phase in the oxygen separation layer, in order to improve the oxygen permeation of DL-CHFMR for a better reactor performance at possibly lower temperatures. Such a reactor design offers a more structured catalytic interface when compared to the conventional method of packing catalyst particles inside membrane reactor, therefore allowing more efficient use of catalytic
surface area. For the purpose of comparison, oxygen permeations of both single-layer BYS-LSM hollow fibre membranes and BYS-LSM/BYS-Ni dual-layer counterparts are investigated, and linked to the changes in membrane micro-structures during oxygen permeation and catalytic reactions. Although the stability of BYS in strong reducing atmosphere hampers the use of BYS-LSM/BYS-Ni DL-CHFMR for partial oxidation of methane (POM), it shows potentials to oxidative coupling methane (OCM) due to the great catalytic activity of BYS [17].

3.2 Experimental

3.2.1 Chemicals and materials

BYS (Bi$_{1.5}$Y$_{0.3}$Sm$_{0.2}$O$_{3-\delta}$) with a surface area of 4.4 m$^2$/g was purchased from PraxAir Surface Technologies, USA. LSM (La$_{0.8}$Sr$_{0.2}$MnO$_3$) with a surface area of 5.8 m$^2$/g and NiO with a surface area of 3.7 m$^2$/g were commercially available from Fuel Cell Materials, USA, and were used as supplied. Dimethyl sulfoxide, (DMSO, VWR), Polyvinylpyrrolidone (PVP-K30, Fluka) and polyethersulfone (PESf, Radal A300, Ameco Performance) were used as a solvent, an additive and a polymer binder in spinning suspension, respectively. Deionized water and tap water were used as an internal- and external-coagulations, respectively, during the preparation of hollow fibre membranes.
3.2.2 Preparation of BYS-LSM single-layer and BYS based dual-layer hollow fibre membrane reactor

Received BYS powder was calcined in static air at 800 °C for 2 hours, followed by ball milling for at least 8 hours prior to the preparation of spinning suspension. Generally, spinning suspensions were prepared by dispersing a pre-determined amount of ceramic powders into a solution of DMSO and additive. The mixture was roll milled (G 91, Gladstone Engineering) for at least 24 hours before adding PESf. The milling was continued for another 2-3 days to ensure a homogeneous spinning suspension. Table 3.1 lists the compositions of spinning suspensions used in this study.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Single-layer membrane (wt %)</th>
<th>Dual-layer membrane Outer layer (wt %)</th>
<th>Inner layer (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BYS</td>
<td>43.69</td>
<td>34.16</td>
<td>41.90</td>
</tr>
<tr>
<td>LSM</td>
<td>23.74</td>
<td>27.84</td>
<td>-</td>
</tr>
<tr>
<td>NiO</td>
<td>-</td>
<td>-</td>
<td>23.10</td>
</tr>
<tr>
<td>Polymer binder,</td>
<td>6.75</td>
<td>6.20</td>
<td>6.50</td>
</tr>
<tr>
<td>PESf</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Additive, PVP 30</td>
<td>2.08</td>
<td>1.00</td>
<td>-</td>
</tr>
<tr>
<td>Solvent, DMSO</td>
<td>23.74</td>
<td>30.80</td>
<td>28.50</td>
</tr>
</tbody>
</table>

Density: BYS = 8.10 g/cm³, LSM = 6.6 g/cm³ and NiO = 6.7 g/cm³

The fabrications of single- and dual-layer ceramic hollow fibres have been introduced elsewhere [5, 18]. Generally, the spinning suspension needs to be degassed by stirring under vacuum prior to the spinning, in order to remove air bubbles. After degassing, the spinning
suspension was transferred into a 200 ml stainless steel syringe controlled by a syringe pump (Harvard PHD 22/2000 Hpsi), extruded through a spinneret and passing through an air gap before entering into the external coagulant bath. In the meantime, a stream of internal coagulant controlled by another syringe pump flowed through the central bore of the spinneret, forming the hollow fibre configuration. A tube in orifice spinneret and a triple-orifice spinneret were used for the fabrication of single- and dual-layer hollow fibre membranes, respectively, as shown schematically in Fig. 3. 2.

Spinning parameters of both the single- and dual-layer hollow fibres are listed in Table 3. 2. The air gap for single-layer fibres was different from the dual-layer fibres, due to different in viscosities of the spinning suspensions. The formed precursor fibres were left overnight in a water bath filled with deionised (DI) water, to complete the phase inversion process. The precursor fibres were then cut to a specific length and dried at room temperature prior to sintering in a CARBOLITE furnace. The furnace was heated up from room temperature to 600 °C at a rate of 2 °C/min and dwelled for 2 hours to remove the organic components. Then, the furnace temperature was increased to the target temperature (1040-1100 °C) at 5-10 °C/min and dwelled for another 5-12 hours. Finally, the furnace was cooled down to room temperature at 3 °C/min to complete the sintering process.
Chapter 3  Fabrication of $\text{Bi}_{1.5}\text{Y}_{0.3}\text{Sm}_{0.2}\text{O}_3$ Based Dual-Layer Membrane Reactor for Oxygen Separation and Chemical Reactions

![Diagram of spinneret for (a) single-layer (b) dual-layer hollow fibre membranes](image)

**Fig. 3.2** Schematic diagram of spinneret for (a) single-layer (b) dual-layer hollow fibre membranes

**Table 3.2** Spinning parameters for single- and dual-layer hollow fibre membranes

<table>
<thead>
<tr>
<th></th>
<th>Single-layer</th>
<th>Dual-layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air gap (cm)</td>
<td>2</td>
<td>25</td>
</tr>
<tr>
<td>Single layer extrusion rate (ml/min)</td>
<td>10</td>
<td>-</td>
</tr>
<tr>
<td>Inner layer extrusion rate (ml/min)</td>
<td>-</td>
<td>11</td>
</tr>
<tr>
<td>Outer layer extrusion rate (ml/min)</td>
<td>-</td>
<td>0.2-5.0</td>
</tr>
<tr>
<td>Bore fluid extrusion rate (ml/min)</td>
<td>10-13</td>
<td>10</td>
</tr>
</tbody>
</table>
3.2.3 Characterizations

**X-ray diffraction (XRD)**

The X-ray diffraction patterns were obtained with an X'celerator detector (X'Pert PRO model) using Cu- Kα as the radiation source. The XRD scans were carried out in a 2θ range from 5° to 80° using a step width of 0.05°. The equipment voltage and current were set at 40 kV and 40 mA, respectively.

**Sintering behaviour**

The sintering behaviour of membrane materials was analysed using a dilatometer (NETZCH, DIL 402 C) in static air. Ceramic powders were uniformly packed into a square-shaped stainless steel mold (6mm x 6mm x 6mm) and compressed vertically using a hydraulic pressure of 1 tonne. A 30 kN force was applied to the compacted sample by a ceramic push rod in the dilatometer during the tests.

**Membrane morphologies**

A JEOL JSM-5610 scanning electron microscope (SEM) was used to investigate membrane structures. Samples were cut carefully to ensure a clean break for a clear observation. The samples were then mounted onto sample stubs with the surface to view facing up. These samples were then spur-coated with gold using an SEM sputter coater before being viewed with the scanning electron microscope.
3.2.4 Experimental set-up for oxygen permeation, POM and OCM reaction

Oxygen permeation of BYS-LSM single layer membrane was measured between 650 °C and 900 °C, using the system shown schematically in Fig. 3. 3(a) [19]. Prior to testing, the membrane was sealed between two dense alumina tubes using high temperature ceramic sealant (Resbond 940 LE) as shown in Fig. 3. 4. The furnace was heated up at a rate of 5 °C/min from room temperature to target temperatures. Ambient air was used as the source of oxygen and pure argon was used as a sweep gas feeding into the lumen of BYS-LSM hollow fibre membrane. The oxygen concentration in the permeate stream was measured using an oxygen analyzer (Model 572 with ± 0.01 % resolution, Servomex). Possible gas leakage can be detected by co-monitoring the flow rate of permeates and abnormal changes in oxygen concentrations. The oxygen concentration data were collected 10 minutes after the setting temperature was stable. The oxygen permeation flux of single-layer membrane was calculated using the following equation:

\[ J_{O_2} = \frac{V_t \times x_{O_2}}{A_t} \]  \hspace{1cm} (3.1)

where \( J_{O_2} \) is the permeation flux of oxygen (ml·min\(^{-1}\)·cm\(^{-2}\)), \( V_t \) is the flow rate of the effluent stream (ml·min\(^{-1}\)), \( x_{O_2}(\%) \) is the oxygen concentration obtained from the oxygen analyzer and \( A_t \) is the effective membrane area (cm\(^2\)).

Similar to the single-layer counterpart, the dual-layer membranes were tested at the temperature range of 600 to 900 °C, using ambient air as the source of oxygen Fig. 3. 3 (b).
The inlet gases were controlled using mass flow controllers (Model 0154, Brooks Instrument). Prior to the performance tests, argon was replaced by diluted hydrogen (50 % in Ar) at 400 °C to reduce NiO to Ni. This reduction process was required in order to make the inner layer porous and allow the permeation of oxygen. After 15 minutes of reduction, the dilute hydrogen was replaced by carbon monoxide (10 % in argon) to start the oxygen permeation process for dual layer membranes. CO was used to avoid re-oxidation of Ni into NiO. The gas flowrate from the outlet of the hollow fibre was measured using a bubble flowmeter. The permeate stream was on-line analysed using a gas chromatograph (Varian 3900). The oxygen permeation flux was calculated based on mass balance of oxygen species, i.e. the amount of CO consumed and the amount of CO₂ produced.

For catalytic reactions, CH₄, instead of CO, was used after the reduction. Oxygen analyzer was also used to monitor possible leaking from sealing and system. The conversion of methane ($X_{CH₄}$) and selectivity ($S_i$) are calculated using the following equations:

$$X_{CH₄} = \frac{F_{CH₄, inlet} - F_{CH₄, outlet}}{F_{CH₄, inlet}} \times 100\% \quad (3.2)$$

$$S_i = \frac{n_i F_{i, outlet}}{F_{CH₄, inlet} - F_{CH₄, outlet}} \times 100\% \quad (3.3)$$

where $n_i$ is the number of carbon atoms in species $i$. 
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Fig. 3. 3 Schematic diagram of (a) oxygen permeation system for single-layer membrane, and (b) oxygen permeation and catalytic reaction system for dual-layer membrane

Fig. 3. 4 Photograph of membrane reactor preparation
3.3 Results and discussion

3.3.1 Macrostructures of BYS-LSM single- and BYS-LSM/BYS-NIO dual-layer membranes

Fig. 3. 5 shows SEM images of the sintered BYS-LSM single-layer hollow fibre membrane. A sandwich-like structure that consists of a central sponge-like layer and finger-like structures on both sides was formed, due to the short air gap used. The outer diameter of the fibre is approximately 1.4 mm, with a wall thickness about 220 µm. The thickness of the sponge layer in the central part of the fibre is around 63 µm, which is about 1/3 of the fibre wall thickness. In general, the formation of finger-like void is attributed to the viscous-fingering phenomenon occurred from membrane surfaces where more viscous spinning suspension is in contact with less viscous coagulants [20]. The growth of finger-like voids proceeds with solvent-non-solvent exchange that leads to the precipitation of polymer binder, until the central region where the local viscosity increases (due to the flow-out of solvent to both sides) to a level that further growth of finger-like voids cannot proceed.

Fig. 3. 5 SEM images of BYS-LSM single-layer membrane: a) whole view b) cross-section
Fig. 3.6 illustrates SEM images of dual-layer membrane. The outer and inner diameters of the dual layer-fibre are about 1.04 mm and 0.68 mm, respectively. It can be seen that, due to the longer air gap used, finger-like structure can only be formed from the inner surface. However, due to the high co-sintering temperature that is quite close to the melting point of BYS, such finger-like structure is not reserved very well. The thickness of the BYS-LSM separation layer is about 32 µm, while the inner layer is around 150 µm. A thinner separation layer is preferred in order for a higher oxygen permeation flux, when bulk diffusion still affects oxygen permeation. In Fig. 3.6 (c), there is no observable gap at the interface between the inner and outer layers, indicating good adhesion between the two layers. In addition, a clear dual-phase structure of the inner layer can be seen in Fig. 3.6(d), indicating good dispersion of the two phases (BYS and NiO).

**Fig. 3.6** SEM images of dual-layer membrane: a) whole view  b) cross section  c) interface between two layers  d) inner surface
3.3.2 Oxygen permeation of BYS-LSM single layer membrane

Fig. 3. 7 illustrates oxygen permeation of the single-layer membrane, using 35 ml·min⁻¹ of argon as the sweep gas. It can be seen that the oxygen permeation flux increases linearly with temperatures especially above 750 °C due to enhancement in the concentration of oxygen vacancy. The oxygen permeation at 850 °C is approximately 1.0 ml·min⁻¹·cm⁻², which is slightly higher than the previous study [16] (0.52 ml·min⁻¹·cm⁻²) at the same operating temperature, and is much higher than ScSZ-LSM and YSZ-LSM (less than 0.2 ml·min⁻¹·cm⁻²). This demonstrates the advantage of using BYS as a more ionic conductive phase in this study to promote oxygen permeation, besides better chemical compatibility with LSM when compared with ScSZ and YSZ [4, 5], as no additional impurity phase was observed.

![Graph showing oxygen permeation vs temperature](image-url)

**Fig. 3. 7 Oxygen permeation of single-layer hollow fibre membrane**


3.3.3 Sintering behaviour of BYS-LSM/BYS-Ni DL-CHFMR

Sintering is a crucial step in the fabrication of ceramic membranes, as it affects the final structure and performance of the membranes. The sintering of ceramic hollow fibre membranes is more difficult due to the higher surface area and curvity when compared to other membrane geometries (planar and tubular). A number of parameters such as sintering temperature, dwelling time, heating and cooling rates need to be considered, especially for the membranes with a dual-layer structure. Each of the membrane materials has a different sintering behaviour and thermal expansion when subjected to a heat treatment; therefore the understanding of thermal behaviours of each material is important. An optimum sintering condition is favoured to ensure that the dual-layer membranes can survive the co-sintering process without the formation of cracks or delamination of the outer separation layer.

Fig. 3. 8 illustrates sintering curves of the membrane materials at 1100 °C. The temperature of 1100 °C was selected because it is close to the melting point of BYS. In general, a sintering process consists of three different regions. The first (I) region is from room temperature to 600 °C, in which ceramic materials expand slightly and no significant shrinking phenomenon is observable. In region (II), BYS and NiO start to shrink at a much lower temperature (around 650 °C) than that of LSM. The final shrinkage increases in the order of LSM (5.6 %), NiO (14.2 %) and BYS (15.5 %). The rate of shrinking slows down in dwelling (30 min) and cooling stage for all the materials (region III).
In term of correlating the shrinking behaviour analysis with the co-sintering of dual-layer membranes, the gap in final shrinkage between the inner layer and outer layer should be minimised in order to avoid the formation of cracks or defects. This means that, for the BYS-LSM/NiO-BYS system, less BYS should be used in both two layers to match the sintering behaviours in a better way, as long as the functions of each layer, such as oxygen separation of the outer layer and catalytic activity of the inner layer are not affected. The importance of selecting appropriate material compositions has been highlighted in previous study [5], as it is one of the factors that governs the co-sintering process of the dual-layer membrane. In this study, the outer separation layer of the membrane is composed of a dual-phase material (BYS-LSM), while the inner layer consists of BYS-NiO. BYS used in both layers can be considered as the medium that facilitated the matching of the sintering behaviours between two layers, which is similar to the role of YSZ and ScSZ employed in our previous studies [4, 5].

Fig. 3. 8 Sintering behaviour of membrane materials (--- represents sintering profile)
Fig. 3. 9 illustrates sintering curves of the outer and inner layer materials at selected compositions (volume %). It can be seen that the inner and outer layers start to shrink at similar temperatures. However, final shrinkages of the inner layer were approximately 4-5 % higher than that of the outer layer. Since the difference in sintering behaviour between 40 % BYS-60 % NiO and 60 % BYS-40 % NiO is not significant, and more NiO in the inner layer may lead to two potential issues after being reduced into Ni, i.e. more coke formation during methane conversion and lower mechanical strength, the latter one was used as the inner layer composition. In addition, a larger amount of BYS leads to a higher final shrinkage of the inner layer, which is opposite to the outer layer. Such a difference can be a net result of several factors, such as green density, phase ratio, particle size and shape and interactions between the two phases etc.. As a result, a mixture of 50 % BYS-50 % LSM and 60 % BYS-40 % NiO was used for membrane fabrication. Composition of the corresponding suspension needs to be further adjusted based on viscosity (Table 3. 1), as an appropriate viscosity of spinning suspension is essential to ensure a proper co-extrusion process.

The XRD patterns of BYS-LSM single-layer fibre and BYS-LSM/ BYS-NiO dual-layer fibre (crushed into powder) are compared as shown in Fig. 3. 10. No additional peaks are observed in single layer fibre, apart from the one of BYS and LSM (the membrane was sintered at 1100 °C) that is in good agreement with the structure of membrane materials. This indicates a high level of chemical compatibility between BYS and LSM, which is another advantage over ScSZ and YSZ as they react slightly with LSM at high temperatures. It is the same to the dual-layer membrane where no additional peaks are present apart from the membrane materials (BYS, LSM and NiO), when subjected to the sintering at 1040 °C.
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**Fig. 3.9** Sintering behaviour of outer and inner layer materials (- - - represents sintering profile)

**Fig. 3.10** XRD patterns of single- and dual-layer hollow fibre membranes
3.3.4 Oxygen permeation, POM and OCM performance of BYS-LSM/BYS-Ni DL-CHFMR

Oxygen permeation measurement of the dual-layer membrane was carried out using CO as the sweep gas to avoid re-oxidation of nickel. The dual-layer membrane cannot survive testing temperatures higher than 850 °C, which may be related to the destabilization of BYS at higher temperatures after reduction. As can be seen in Fig. 3. 11, the oxygen permeation flux increases with increasing temperatures, the value of which is very close to the single layer membrane. For example at 850 °C, the oxygen permeation fluxes of both single-layer (Fig. 3. 7) and dual-layer membranes are approximately 1.0 ml·min⁻¹·cm⁻², although the separation layer of dual-layer membranes is thinner. One of the possible reasons for this can be the different of membrane structures. For dual-layer membranes, although its separation layer is thinner, and CO was used as the sweep gas that should lead to higher permeation flux due to lower oxygen partial pressure on the permeate side, NiO in the inner layer may not be fully reduced into Ni at 400 °C (50 % H₂ for 15 min). This would generate additional mass transfer resistance in the inner layer for oxygen permeation, and consequently lower oxygen permeation flux. Another possible reason can be due to the instability of BYS when it is in contact with strong reducing gas, which will be discussed later. The possible change in BYS structure during the reduction (prior to oxygen permeation measurement) may affect its ionic conductivity, and subsequently lowering the oxygen permeation flux.

Concerning the catalytic reactions in the DL-CHMR, methane is used as the reactant with the operating temperature no higher than 750 °C, above which the dual-layer membrane starts to fracture. This fracture may be related to a number of factors, such as thermal and chemical...
stability of membrane materials at certain reaction conditions and temperature difference across the membrane layers due to catalytic reactions, and will be further investigated. As can be seen in Fig. 3. 11, the methane conversion is around 14 % in the temperature range of 600-750 °C. The calculated oxygen permeation due to methane conversion is significantly lower than the oxygen permeation discussed above. This indicates a significant change of membrane materials under the reaction conditions.

![Graph showing oxygen permeation and catalytic reaction of dual-layer hollow fibre membrane](image)

**Fig. 3. 11** Oxygen permeation and catalytic reaction of dual-layer hollow fibre membrane

A further XRD analysis was carried out to investigate the stability of BYS in inert (argon) and reducing atmosphere (hydrogen) to understand the changes of BYS in the oxygen permeation and catalytic reaction (dual-layer membranes). In Fig. 3. 12, it can be seen that there is no evident change when BYS is exposed to Argon (800 °C). In contrast, there is a significant change when BYS was exposed to H₂ at 400 °C. In general, the exposure of BYS to H₂ can
cause distortion of the ideal BYS fluorite structure, although diluted hydrogen and a short reduction period were used. This suggests relatively low chemical stability of BYS in H$_2$, and further in contact with CH$_4$ or CO. This is very similar to 25 mol% yttria-doped bismuth oxide (BY25), where its fluorite structure and catalytic activity can be maintained as long as stoichiometric oxygen is not consumed. Otherwise, its fluorite structure will be destroyed because of the reduction of metallic ions [21]. Due to the chemical instability of BYS in DL-CHFMR, CO$_2$ is the major product of methane conversion, as Ni in the inner layer cannot work together with an ionic conducting phase to produce syngas (CO + H$_2$), although both Ni and NiO exist in the inner layer (Fig. 3.12). Previous study on oxidative coupling methane (OCM) reaction by Akin [22] showed that, the bismuth element migrated towards membrane surface that was exposed to the reactants, although such bismuth migration did not affect the structure and catalytic properties of the BYS membrane. In our study, the bismuth destabilization and migration due to the contact with H$_2$ resulted in the deactivation of the inner catalytic layer. As a result, it is believed that the CH$_4$ conversion of less than 15 % is mainly due to combustion, which is also the major reason for lower oxygen permeation in catalytic reactions (Fig. 3.11).

All these indicate that strong reducing atmospheres need to be avoided when BYS is used as a membrane material. But due to the great ionic conductivity and oxygen permeation of BYS at intermediate operating temperatures, similar reactor design can be used for other catalytic reactions of great importance, such as OCM where BYS shows great catalytic activity [23, 24]. The use of BYS as membrane material is expected not only to improve the membrane reactor performances, but eliminates the requirement of additional catalyst such as Ni because BYS itself is a catalyst for OCM. The conversion of methane into valuable C$_2$ products (ethane and
ethylene) through OCM has been widely studies since 1980s. Although it has been demonstrated that the catalytic membrane reactor can improve the methane coupling reaction, research in this area is progressing slowly, hampered by membrane materials and reactor performance issues.

An early investigation of the catalytic activity of BYS towards OCM reaction was carried out using the BYS-based DL-CHFMR. Since H₂ reduction cannot be used, the inner layer maintains a dense structure, which stops the permeation of oxygen from the outer layer. As a result, a mixture of CH₄ and O₂ (2:1) was fed into the lumen of the dual-layer fibre and tested between 800-900 °C, without the reduction step. This time, the fibre can withstand

**Fig. 3.** 12 XRD patterns of BYS powders and BYS-NiO inner layer in inert and reducing environments
temperatures up to 900 °C, much higher than POM (750 °C) as the fibre was not exposed to strong reducing atmosphere (H₂). The C₂⁺ yield obtained after 2 hours of stabilization at 900 °C is about 0.75 %, with a C₂⁺ selectivity of 9.40 %. The performance can be further improved when the inner layer is porous or sintered at a lower temperature, as a fixed bed reactor packed with BYS powder gave a much higher C₂⁺ yield (11.3%) and C₂⁺ selectivity (41.4%) under the same operating conditions. This indicates that such BYS-based DL-CHFMR design can be used for catalytic reactions where no strong reducing gas is involved, although the membrane material for the outer oxygen separation layer needs to be changed accordingly, in order to match sintering temperatures and operating temperature for both oxygen permeation and OCM reaction. For catalytic reactions that require pure oxygen, this DL-CHFMR with thin separation layer and porous catalytic layer is preferred to ensure a great membrane reactor performance.

3.4 Conclusions

BYS, a great ionic conducting ceramic at intermediate temperatures, has been employed in this study to replace ScSZ and YSZ and fabricate dual-layer ceramic hollow fibre membranes for catalytic reactions, resulting in better chemical compatibility with LSM and significantly higher oxygen permeation. This demonstrates the advantages of using BYS in fabricating DL-CHFMR, especially in terms of supplying more oxygen for possibly better reactor performance at lower operating temperatures. The insufficient chemical stability of BYS in strong reducing atmosphere changes its structure and consequently catalytic activity of the inner layer, and
affects the reactor performance for methane conversion. However, the advantages of such reactor design have been proved and can be transferred to other important catalytic reactions, such as OCM where no strong reducing environment is required.

3.5 References


[16] C. Yang, Q. Xu, C. Liu, J. Liu, C. Chen, W. Liu, Bi_{1.5}Y_{0.3}Sm_{0.2}O_{3}–La_{0.8}Sr_{0.2}MnO_{3-δ} dual-phase composite hollow fiber membrane for oxygen separation, Materials Letters, 65 (2011) 3365-3367.


CHAPTER 4

Micro-Structured $\text{Bi}_{1.5} \text{Y}_{0.3} \text{Sm}_{0.2} \text{O}_{3-\delta}$ Catalysts for Oxidative Coupling of Methane

Abstract

This chapter addresses the advantages of using catalyst with micro-structured properties for exothermic reaction, particularly oxidative coupling of methane (OCM). In this study, $\text{Bi}_{0.5} \text{Y}_{0.3} \text{Sm}_{0.2} \text{O}_{3-\delta}$ (BYS), a ceramic material showing great activity and selectivity to oxidative coupling of methane (OCM), has been fabricated into catalyst rings (i.e. capillary tubes) with a plurality of self-organised radial microchannels. The unique microchannels inside such BYS catalyst rings allow easier access of reactants, as well as increased the surface area, which potentially contributes to higher reaction efficiencies due to improved mass transfer. The micro-structured BYS catalyst rings were investigated systematically via two types of reactors; (1) randomly packed fixed bed reactor and (2) monolithic-like structured reactor. These two reactor designs have different flow patterns of reactants, i.e. non-ideal and ideal flows, which can significantly affect the final OCM performance. A remarkable improvement in $\text{C}_2^+$ yield ($Y_{\text{C}_2^+} > 20\%$) was obtained in the monolith-like structured reactor, in contrast to randomly packed powder and micro-structured rings ($Y_{\text{C}_2^+} < 15\%$), which proves the advantages of using a micro-structured catalyst with an ideal flow in the feed for OCM.
4.1 Introduction

Recent developments in shale gas are generating much excitement around the world, as it has been foreseen as an opportunity to gradually shift towards the use of natural gas (methane) as the feedstock producing a wide range of valuable chemicals due to its abundant supply at a lower price over petroleum [1-3]. The state-of-the-art process of methane conversion can be roughly divided into direct and indirect routes [4]. Among those methane conversion processes available, oxidative coupling of methane (OCM) has been considered as an attractive route for more efficient utilization of natural gas, as it offers a direct conversion of methane to C$_2$+ products (ethane (C$_2$H$_6$) and ethylene (C$_2$H$_4$)). However, due to a number of scientific and technique challenges, indirect conversions of methane via syngas are more widely considered for industrial applications. Major challenges that still constrain the commercial exploitations of OCM include (i) high operating temperatures (700–900 °C) in order to achieve high C$_2$+ yield; (ii) C$_2$+ products are more reactive than methane, resulting in deep oxidation of the C$_2$+ products to CO$_x$ especially at high temperatures and (iii) higher conversion is normally accompanied with lowered selectivity, making the achievement of high C$_2$+ yield extremely difficult. However, with the recent soaring exploration of shale gas, once again, OCM is becoming an interest research topic, which has been well reflected by the increasing number of related publications since 2010. The OCM reactions for C$_2$+ formation are shown below:

$$2CH_4 + 0.5O_2 \rightarrow C_2H_6 + H_2O \quad (\Delta H=-175.6 \text{ kJ/mol}) \quad (4.1)$$

$$2CH_4 + O_2 \rightarrow C_2H_4 + 2H_2O \quad (\Delta H=-280.8 \text{ kJ/mol}) \quad (4.2)$$
Besides the two selective reactions above, following non-selective oxidation reactions to CO\textsubscript{x} can take place and reduce the C\textsubscript{2+} yields.

\[ CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \quad (\Delta H=-890.4 \text{ kJ/mol}) \]  
(4. 3)

\[ C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O \quad (\Delta H=-1411.17 \text{ kJ/mol}) \]  
(4. 4)

As a result, an ideal OCM catalyst should allow high initiation rate of methyl radical, which usually occurs on the catalyst surface, and most importantly can suppress the non-selective oxidation of CH\textsubscript{4} and C\textsubscript{2+} products to CO\textsubscript{x}[5]. Since the pioneering work on OCM catalyst by Kellers and Bhasin [6] in 1980s, remarkable progress in developing highly efficient and selective OCM catalysts have been achieved. Nevertheless, the C\textsubscript{2+} yields obtained are still below the 30% threshold value expected for the purpose of commercialization [7].

Mixed metal oxides with adjustable solid-state properties have been known with impressive catalytic properties toward OCM, when compared to the single metal oxide catalysts [5]. Among the mixed metal oxide catalysts investigated for OCM, Bi\textsubscript{1.5}Y\textsubscript{0.3}Sm\textsubscript{0.2}O\textsubscript{3-δ} (BYS) of a fluorite structure, which was reported by Zeng et. al [8] and Akin et. al [9], shows a promising performance. This material appears to be not only oxygen permeable but also catalytic active for OCM, a reaction with both heterogeneous and homogeneous reaction mechanisms [9-12]. In addition, BYS is mechanically and chemically stable for OCM reaction, making it suitable to be used as OCM catalyst. Interestingly, when this BYS powder was used to make a tubular dense membrane reactor, a 35 % of C\textsubscript{2+} yield was achieved at 900 °C [9], exceeding the C\textsubscript{2+} yield of its powder form (~20 %) [8]. This suggests that apart from the catalytic properties of the metal oxides, the OCM performance can be improved by designing the catalyst structure.
and reactor configuration. Most of the catalysts investigated in laboratory were in a powder form as it is much easier and faster to prepare. While for larger scale operations, catalyst pellets (or rings) are much preferred due to less clogging and great mechanical strength. Fixed bed reactor (FBR) is one of the established reactors that have been extensively used in industry as it generally shows low cost and easy maintenance [13]. The packing of catalyst inside the FBR is normally irregular and lack of ordered patterns, which can lead to a non-uniform flow of reactants and subsequently hot spots / thermal runaway, especially for a highly exothermic reaction such as OCM. In contrast to the FBR, a structured catalytic reactor offers a more organised flow of reactants (i.e. an ideal flow), which could reduce pressure drop across the reactor while maximizing the access to the active sites of catalysts. This type of catalytic reactor can contain either “normal’ catalyst particles that are in a structured arrangement or “structured catalyst” in which catalyst and reactor are in the same entities [14].

In this study, a new design of BYS catalyst rings, which have significant self-organised microchannels opening from the inner surface, has been developed using a viscous fingering induced phase inversion process. This technique has been widely used in the fabrication of micro-structured ceramic hollow fibre membrane as it offers great flexibility in tailoring both the macro- and micro-structures [15, 16]. In order to understand the role of catalyst structure in affecting OCM, a systematic comparison between BYS powder, micro-structured rings and micro-structured monolith was designed as shown in Fig. 4. 1. Two types of reactors, i.e. randomly packed reactor and structured reactor, have been used in this study in order to evaluate the performance of micro-structured BYS rings and monoliths. The use of BYS powder serves as a comparison on the OCM activity of this material.
Fig. 4.1 Schematic representation between BYS powder, micro-structured BYS rings and micro-structured BYS monoliths

4.2 Experimental

4.2.1 Chemicals and Materials

$Bi_{1.5}YO_{0.3}SmO_{3-d}$ (BYS) was purchased from PIDC, USA. Dimethyl sulfoxide (DMSO, VWR), Hypermer KD-1 (Croda), and polyethersulfone (PESf, Radal A300, Ameco Performance) were used as the solvent, dispersant and polymer binder for spinning suspensions, respectively. DMSO and tap water were used as a bore fluid and external coagulant, respectively.

4.2.2 Fabrication of micro-structured BYS catalyst rings for OCM

A BYS spinning suspension was first prepared by dispersing 68 wt.% of BYS powder into a mixture of solvent and dispersant. The mixture was then roll milled for at least 3 days before
adding the polymer binder. The milling was then continued for another 3-5 days to ensure a
homogeneous spinning suspension. Prior to the spinning process, the suspension was
degassed by stirring under vacuum to remove air bubbles. The degassed spinning suspension
was then transferred into a 200 ml stainless steel syringe controlled by Harvard PHD 22/2000
Hpsi syringe pump. The micro-structured BYS rings (or capillary tubes) were fabricated using
a viscous fingering induced phase inversion process, the details of which have been described
elsewhere [15, 17]. In this process, the spinning suspension was extruded through the
spinneret, which was positioned inside the coagulation bath, with a stream of solvent as the
bore fluid flowing through the central bore of spinneret, forming a capillary tube configuration
(Fig. 4. 2). The extruded tube precursors were rinsed with water and left in a water bath
overnight to complete the phase inversion process, before being cut into a specific length prior
to calcination. The calcination process was carried out between 920-1080 °C for 12 hours.
The calcined tubes are then cut into rings (short tubes) or assembled as monoliths (long tubes
and then bundled together) for OCM reaction. The fabrication conditions of the micro-
structured BYS catalysts are shown in Table 4. 1.

<table>
<thead>
<tr>
<th>Experimental parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition of spinning suspension:</td>
<td></td>
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<tr>
<td>Ceramic powder</td>
<td>68 wt%</td>
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<tr>
<td>Polymer, PESf</td>
<td>6.8 wt%</td>
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<tr>
<td>Solvent, DMSO</td>
<td>22.2 wt%</td>
</tr>
<tr>
<td>Dispersant, KD1</td>
<td>3 wt%</td>
</tr>
<tr>
<td>Spinning parameter:</td>
<td></td>
</tr>
<tr>
<td>Bore fluid</td>
<td>DMSO</td>
</tr>
<tr>
<td>Air gap</td>
<td>0 cm</td>
</tr>
</tbody>
</table>

Table 4. 1 Fabrication conditions of micro-structured BYS catalyst rings (capillary tubes)
### Flowrate of spinning suspension
7 ml/min

Flowrate of bore fluid
5 ml/min

External coagulant
Tap water

---

**Fig. 4.2** Schematic diagram of spinning process

---

### 4.2.3 Characterizations

X-ray diffraction (XRD) analysis was used to characterize the structure of BYS upon heat treatment. The XRD patterns were obtained with an X’celerator detector (X’Pert PRO) using Cu- Kα as the radiation source. The XRD scans were carried out in a 2θ range from 10° to 80° using a step width of 0.05°. The equipment voltage and current were set at 40 kV and 40 mA, respectively.
A JEOL JSM-5610LV scanning electron microscope (SEM) was used to observe the catalyst structures. The samples were coated with gold under vacuum using a SEM sputter coater before being viewed. Brunauer-Emmett-Teller (BET) analysis was performed using nitrogen in order to measure the specific surface areas of BYS powders upon different calcination temperatures. Prior to the analysis, the samples were dried and degassed at 120 °C for 4 h.

### 4.2.4 Oxidative coupling of methane

Two types of the reactor designs, i.e. randomly packed and structured (i.e. monolith-like) reactors were investigated in this study, as shown in Fig. 4. 3. A randomly packed fixed bed reactor (FBR) of BYS powder (2.0 g) was prepared by mixing a pre-determined amount of BYS powder with an inert support (silica carbide). The mixture was then placed at the centre of a dense ceramic tube (internal diameter = 6 mm), giving a catalyst zone of 5 cm in length (Fig. 2a). Quartz wool was used to fix the catalyst bed in the middle of the reactor. For the BYS rings, 2.0 g of the rings (0.5-0.7 cm in length) was randomly packed in the middle of the reactor using similar procedure as described for powder (Fig. 4. 3b), forming a fixed bed of 5 cm in length. For the structured reactor, four long BYS capillary tubes of 5 cm in length with a total weight of 2.0 g were arranged as a monolith (Fig. 4. 3c), with the gaps between the BYS tubes being sealed using ceramic sealant to provide organised reactant flows.
The experimental set-up for OCM reaction is shown in Fig. 4. The prepared reactor was positioned horizontally in a tubular furnace (uniform heating length of 5 cm) and heated up to the desired reaction temperature in argon. The setting temperature of the furnace was referred as the operating temperature of the reaction. The flow rates of the reactants were controlled using mass flow controllers (Brooks Instrument, model 0154) and monitored by a bubble flow meter. All gas flows were at the standard temperature and pressure. Once the furnace temperature reached 600 °C, argon was replaced with a mixture of 10% methane in argon to activate the catalyst. Then the furnace was further heated up to desired reaction temperatures (700-900 °C). The analyses of the reactor effluents were performed on-line by gas chromatography (GC), after the reaction temperature was stabilized for 1 hour. Before entering the GC, the effluent gas was passed through a silica gel for removal of water. Two types of GC (Varian 3900) detectors were used in the analysis; i.e. thermal conductivity detector (TCD).
for permanent gases (H₂, CO, CO₂, etc) and flame ionisation detector (FID) for light hydrocarbons (CH₄, C₂H₆, C₂H₄, etc.)

The OCM performance was evaluated based on the CH₄ conversion ($X_{CH₄}$) as well as selectivity ($S_j$) of C₂⁺ and COₓ using the equations below:

$$X_{CH₄} = \frac{F_{CH₄, inlet} - F_{CH₄, outlet}}{F_{CH₄, inlet}} \times 100\%$$  \hfill (4.5)

$$S_j = \frac{\sum n_j F_j}{F_{CH₄, inlet} - F_{CH₄, outlet}} \times 100\%$$  \hfill (4.6)

$$C₂⁺ \text{ Yield} = X_{CH₄} \times S_{C₂⁺}$$  \hfill (4.7)

where $n_j$ is the number of carbon atom in the carbon-containing product $j$, $F_{CH₄}$ and $F_j$ are the flow rates of methane and product $j$ in mol/min. The C₂⁺ yield was then calculated by
multiplying the methane conversion with selectivity. The productivity rate ($Y_j$) was calculated by taking into account the mass of BYS ($M_{cat}$) used in the reactor, as shown in the equation below:

$$Y_j = \frac{\sum n_j F_j}{M_{cat}}$$  \hspace{1cm} (4.8)

### 4.3 Results and discussion

#### 4.3.1 Physical properties of BYS catalyst powders

Fabrication of BYS capillary tubes and the subsequent OCM reactions involves high operating temperatures, which can cause the sintering of BYS that affects its activity. As a result, the effects of sintering temperature towards the OCM performance were first investigated. The BYS powder was heat-treated at various temperatures between the maximum operating temperatures of OCM (900 °C) and melting points of BYS (~1100 °C). Table 4.2 shows the BET surface area of BYS powder before and after heat treatment. It can be seen that in general, the surface area values of fresh and calcined BYS powders are relatively small (<1.0 m$^2$/g), similar to a previous study [18]. In addition, the effect of sintering temperature on the change of the specific surface area was noticeable, but was not significant. The effect of sintering temperature towards the change of BYS crystal structures is shown in Fig. 4.5. From the XRD patterns, it can be seen that the sintered BYS was still of the fluorite structure, which is consistent with the fresh powder, up to 1040 °C. At 1080 °C, a small amount of impurity phase (○) was observed, which is likely due to the change in BYS crystal structure when the
calcination temperature approached the melting point of BYS. The intensity of the XRD peaks was observed to increase with the heat treatment temperatures, which indicates the increase in crystal size of BYS.

Table 4.2 Specific surface areas of BYS powder at different calcination temperatures

<table>
<thead>
<tr>
<th>Calcination temperature</th>
<th>Specific surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh powder</td>
<td>0.22</td>
</tr>
<tr>
<td>920 °C</td>
<td>0.20</td>
</tr>
<tr>
<td>1040 °C</td>
<td>0.17</td>
</tr>
<tr>
<td>1080 °C</td>
<td>0.14</td>
</tr>
</tbody>
</table>

Fig. 4.5 XRD patterns of the heat-treated BYS powder; (○) indicate the presence of foreign phases
4.3.2 Fabrication of micro-structured BYS catalysts using a viscous fingering induced phase inversion

Fig. 4. 6 shows the SEM images of precursor of micro-structured BYS capillary tubes fabricated via a viscous fingering induced phase inversion process, using DMSO as the bore fluid. The outer diameter of the precursor is approximately 2.36 mm, with a wall thickness about 0.50 mm. From the SEM images, it can be seen that the use of DMSO as the bore fluid helps to delay the phase inversion at the inner surface, allowing the microchannels initiated from the outer surface to grow continuously across the tube wall, forming open microchannels at the inner surface of the tube. This type of microchannels offers great advantages in enhancing the accessible surface area, reducing the intra particle mass transfer resistance, and thus providing easier access of the reactant to the active sites of the catalyst.
Fig. 4. 6 SEM images of precursor micro-structured BYS capillary tubes; a) overall view, b) cross-section and c) higher magnification of the cross-section

Fig. 4. 7 shows the photograph and SEM images of micro-structured capillary tubes calcined at different temperatures. The outer diameter of the tube calcined at 920 °C is approximately at 2.25 mm, and decreases to 1.70 mm when the calcination temperature was increased to 1040 °C. It can be seen that lower calcination temperature gives a more porous tube (Fig. 4. 7(a)), while a denser tube (Fig. 4. 7(b)) was obtained when the calcination temperature of 1040 °C was used. It can also be seen from the SEM image of the inner surface of the tube as shown in Fig. 4. 7(c) that the microchannels opening on the inner surface are well retained even after the high calcination temperature was used.
Fig. 4. Photograph and SEM images of micro-structured BYS capillary tubes calcined at different temperatures; (a) cross-section at 920 °C, (b) cross-section at 1040 °C and c) inner surface at 1040 °C
4.3.3 Effects of catalyst designs in randomly fixed bed reactor on OCM performance

Fig. 4. 8 compares the effects of catalyst designs (i.e. micro-structured BYS rings) in a randomly fixed bed reactor with that of fresh BYS powder. The BYS rings were calcined at two temperatures; 920 °C and 1040 °C, in order to ensure that they remain in fcc fluorite structure. From Fig. 4. 8 (a-b), it can be seen that the methane conversion and C\textsubscript{2+} selectivity of the BYS micro-structured rings are higher than that of the powder. The improved methane conversion and C\textsubscript{2+} selectivity may be linked to better flow characteristics of the reactor packed with catalyst rings and less mass transfer resistance to the reactants within the catalyst due to the presence of the significant microchannels (Fig. 4. 6 and Fig. 4. 7)[17, 19, 20]. A C\textsubscript{2+} selectivity as high as 55.4% was achieved by micro-structured rings calcined at 1040°C at 850 °C, but as the OCM operating temperature was increased to 900 °C, the selectivity decreases, which is due to the deep oxidation of C\textsubscript{2+} products. The C\textsubscript{2+} yield obtained for the micro-structured rings were much higher than that of the powder form, as shown in Fig. 4. 8(c). It was also observed that the micro-structured BYS rings prepared in this study has not only benefited the selectivity, but also methane conversion and C\textsubscript{2+} yield. These results are in contrast to the study given by Zeng and Lin [21], where the C\textsubscript{2+} yield of pellets (without microchannels) was much lower than that of the powder catalyst, although the selectivity was improved due to low methane conversions from the pellets. The high methane conversion and C\textsubscript{2+} yield obtained in our study is thus more likely related with the unique microchannels inside the BYS rings, allowing easier access of reactants to the active sites of the catalysts and as well as less resistance for the heat transfer due to the existence of microchannels.
Fig. 4.8 Comparison of (a) methane conversion, (b) C\textsubscript{2+} selectivity and (c) C\textsubscript{2+} yield of powder catalyst (□), micro-structured rings calcined at 920 °C (△) and micro-structured rings calcined at 1040 °C (○)
4.3.4 Effects of reactor designs on OCM performance

Since OCM mechanism involves complex interactions between the gas phase and catalytic surface, catalyst geometries and packing are expected to affect the reactor performance. Fig. 4.9 compares the methane conversion, C$_2$+ selectivity, C$_2$+ yield, and C$_2$H$_4$/C$_2$H$_6$ ratio of different reactor designs as a function of operating temperature. From Fig. 4.9 (a), it is evident that methane conversion was strongly affected by the reactor design, in which the conversion of monolith-like structured reactor is far better than that of the randomly packed BYS rings, although the residence time of the monolith-like structured reactor is 7 times shorter. This is believed to be related to the more organised flow of the reactants inside the micro-structured monolith reactor, when compared to the fixed bed reactor, leading to more efficient interaction between the reactants and BYS catalyst at the presence of the microchannels. In addition, the irregular type of packing in the fixed bed reactor could increase the pressure drop inside the reactor and further abolishes the uniformity of temperature and concentration profile, thus, leading to a decrease in reactor performance.

Similarly to methane conversion, the C$_2$+ selectivity of monolith-like reactor was found to be considerably higher as shown in Fig. 4.9(b). Apart from higher methane conversion and C$_2$+ selectivity, the C$_2$+ yield obtained in monolith-like reactor was also better, achieving 20-25% at temperatures above 850 °C. Comparing the performances between the monoliths that were calcined at 920 °C and 1040 °C, it was observed that the C$_2$+ yield of both monolith reactors was similar, except at 850 °C (Fig. 4.8(c)). The small difference in C$_2$+ yield may be caused by the difference in C$_2$+ selectivity as methane conversion of these reactors were almost
identical. This seems to imply that the denser structure (i.e. sintered at 1040 °C) of monolith-like micro-structured reactor can contribute to a higher $C_2^+$ selectivity because of less non-selective oxidation of $C_2^+$ products into $CO_x$ in the catalyst.

There was no $C_2H_4$ observed at temperature below 750 °C, but the $C_2H_4/C_2H_6$ increased gradually from 750 °C to 800 °C as shown in Fig. 4. 9(d). The increase of $C_2H_4/C_2H_6$ ratio with the reaction temperature suggests that the conversion of ethane to ethylene is more favoured at higher temperatures. The formation of ethylene in this study is mostly due to the thermal cracking of ethane, which is consistent with the appearance of hydrogen after $C_2H_4$ was formed during the reaction. However, the high $C_2H_4/C_2H_6$ observed in the randomly packed rings reactor also indicates that the oxidative dehydrogenation of $C_2H_6$ on catalyst surface can occurs as a results of longer residence time. These results confirmed further that the OCM reaction in this study proceeds in combination of heterogeneous and homogeneous reaction. Moreover, the $C_2^+$ productivity rate of the monolith-like reactor design ($81.34 \, \mu mol \cdot min^{-1} \cdot g^{-1}$) is observed to be 130 % higher over the randomly packed configuration, which further proves the importance of organised flow in improving the efficiencies of catalytic reactions such as OCM.
Fig. 4.9 Comparison of (a) methane conversion, (b) \( \text{C}_2^+ \) selectivity, (c) \( \text{C}_2^+ \) yield and (d) \( \text{C}_2\text{H}_4/\text{C}_2\text{H}_6 \) of different micro-structured reactor designs (△ - rings calcined at 920 °C; ▲ - monoliths calcined at 920 °C; ○ - rings calcined at 1040 °C and ● - monoliths calcined at 1040 °C)
4.4 Conclusions

A catalyst ring (i.e. short capillary tube) with a plurality of self-organised radial microchannels has been developed in this study for OCM using a viscous fingering induced phase inversion process. An improvement in OCM performances was observed when the BYS powder was fabricated into micro-structured catalyst rings. This is linked to better mass and heat transfer in the catalyst rings, due to the presence of the significant and unique microchannels. In addition, higher C$_2$+ yield was obtained when monolith-like structured reactor was used compared to the randomly packed reactor, which proves the advantages of using a micro-structured catalyst with an ideal feed flow in the reactor for OCM.

4.5 References


Chapter 4  

Micro-Structured $\text{Bi}_{1.5} \text{Y}_{0.3} \text{Sm}_{0.2} \text{O}_{3-\delta}$ Catalysts for Oxidative Coupling of Methane


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CHAPTER 5

Fabrication of Micro-Structured La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} Hollow Fibre Membrane Reactor for Oxidative Coupling of Methane

Abstract

A mixed ionic-electronic conducting ceramic material, La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} (LSCF) has attracted a lot of interest as a dense oxygen separation membrane due to its capability to provide high oxygen permeation fluxes and excellent stability. In addition, it is commercially available, which is vital for the fabrication of hollow fibre membrane reactor. In this chapter, the importance of membrane microstructure towards OCM activity has been addressed. 2 types of asymmetric La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} (LSCF) hollow fibre membranes, which consist of conical-shaped microchannels open at the inner surface and an outer dense oxygen separation layer have been developed via a viscous fingering induced phase inversion technique, using different bore fluids such as dimethyl sulfoxide (DMSO)-(M1) and N-methylpyrrolidone (NMP)-ethanol-(M2). The use of these solvent-based bore fluids results in different membrane microstructures, such as dimensions of the conical-shaped microchannels and thickness ratios between the inner layer with such microchannels and the outer dense separation layer. Apart from the substantially reduced resistance across the membrane, the microchannels can act as a structured substrate where catalyst can be deposited for the catalytic reaction to take place. The oxidative coupling of methane (OCM) performance of the hollow fibre membrane reactor was investigated in two forms depending on the way BYS
catalyst is packed: (1) PBHFMRR - where BYS catalyst is packed outside and (2) CHFMMR – where BYS catalyst is packed inside the microchannels of the hollow fibre. The performances are then compared with a traditional fixed bed reactor of BYS catalyst (FBR) and a blank LSCF hollow fibre membrane reactor. It is found that the efficient route to improve the efficiencies of hollow fibre membrane reactors (HFMR) is by uniformly dispersing a small amount of BYS catalyst inside the micro-structured ceramic hollow fibre membranes. However, the $C_{2+}$ yield obtained in this study is significantly lower than the 30% threshold value for industrial commercialization. The improvement on $C_{2+}$ yield and productivity rate can be potentially achieved by matching the reaction conditions.

5.1 Introduction

Recent development in unconventional gases, especially shale gas, is generating much excitement as it is seen as an alternative rescue to petroleum in order to meet the worldwide energy demands [1]. Other than making fuels from petroleum, natural gas has also been used as a feedstock in the production of a wide range of valuable chemicals. The abundance of natural gas at a reasonable price has led to a renewed interest in methane conversion processes, especially oxidative coupling methane (OCM), which has been well reflected by the increasing number of related publications since 2010. Oxidative coupling of methane (OCM) is a direct process of converting methane into more valuable $C_{2+}$ products (ethylene and ethane), which is, from economic point of view, more beneficial over indirect routes such as steam methane reforming (SMR) and partial oxidation of methane (POM). Since the
pioneering work by Kellers and Bhasin [2], extensive research on developing highly efficient and selective OCM catalysts and understanding the reaction mechanism has been carried out to elevate the C$_{2+}$ yield and reduce the formation of CO$_x$, in order to justify commercial potentials of OCM reaction [3, 4]. Despite that, the performance of catalysts operated in conventional fixed bed reactor is still below the industrial expectations. One of the main reasons for this is the deep oxidation of C$_{2+}$ products at high operating temperatures, which occurs faster than the oxidation of CH$_4$. As a result, there is a continuing interest in developing new reactors, such as fluidised bed [5], reverse flow reactor [6] and membrane reactor [7, 8] for obtaining more C$_{2+}$ products.

Membrane reactor is a unit that integrates separation and catalytic reaction. It has a great potential to increase the yield of desired products, which is normally limited by thermodynamic equilibrium, product inhibition, or kinetic selectivity due to undesired parallel and/or-series reactions [9, 10]. Previous researches have proved that a membrane reactor offers a higher C$_{2+}$ selectivity over conventional co-feed reactor, particularly when an oxygen permeable membrane takes the role of supplying, controlling and distributing oxygen [7, 8, 11, 12]. The oxygen permeation through such a membrane can be in the form of ions that contains oxygen species such as O$^-$ and O$_2^-$, which is known to be more selective towards the formation of C$_{2+}$, rather than CO$_x$ [8]. Furthermore, direct contact between gaseous oxygen (O$_2$) and methane can be avoided (as methane and oxygen are fed from two different reactor compartments), which also contributes to lesser deep oxidation of C$_{2+}$ hydrocarbons.
Ceramic membranes in a hollow fibre configuration have been extensively studied for various applications [13-19] as it is a favourable membrane geometry due to its smaller diameter and thinner membrane wall when compared to the other membrane configurations, giving higher gas permeability and a larger surface area per unit volume of a membrane module. For oxygen separation membranes, an asymmetric hollow fibre structure consisting of a thin dense separation layer and porous substrates is usually preferred for oxygen permeation. The formation of such hollow fibres membranes is based on a viscous fingering induced phase inversion process which offers a great flexibility in tailoring the membrane structures by controlling the fabricating parameters such as air gap, type of bore fluid, composition and extrusion rates of suspensions.

In our previous studies [14, 15], an asymmetric hollow fibre membrane used as a multifunctional catalytic membrane reactor was developed using a dry-wet spinning process, using a long air gap (30 – 40 cm) for more significant microchannels where catalyst can be deposited. However, as the entrance to these microchannels is relatively small, it was difficult for depositing a sufficient amount of catalyst. It is known that the bore fluid has significant effects on the membrane structures, especially related to the formation of conical-shaped microchannels. According to earlier studies by Zydorczak et al. [20] and Tan et al., [21], the use of a solvent based bore fluid can leads to microchannels with bigger entrances at the inner surface of ceramic hollow fibre membranes. This was mainly due to the delayed precipitation rate at the inner surface, allowing microchannels initiated from the outer surface to develop towards and finally penetrate the inner surface. Such asymmetric structure offers great
advantages over the conventional asymmetric structure, especially for easier incorporation of catalyst in a more uniform and controllable way.

Various dense oxygen separation membranes made of mixed ionic electronic conducting (MIEC) materials, such as $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) [22], $Ba_{0.6}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) [8], and $BaCo_xFe_yZr_zO_{3-\delta}$ (BCFZ, $x + y + z = 1$) [23], have been developed and used as a membrane reactor. Since most of these membranes show little activity to $C_2^+$ formation, catalyst has to be involved. In the last 40 years, a range of heterogeneous catalysts, especially metal oxides based, have been investigated for OCM reaction [24]. Although there have been reports [25, 26] on the use of highly ionic conductive bismuth oxides ($Bi_2O_3$) as OCM catalyst, $Bi_{1.5}Y_{0.3}Sm_{0.2}O_{3-\delta}$ (BYS) of a fluorite structure which was discovered by Zeng et al. [27] and Akin et al. [28] was found to give great $C_2^+$ yield, especially when it is used as OCM catalytic membrane. This material appears to be not only oxygen permeable but also catalytic active for OCM, which has a heterogeneous and homogeneous reaction mechanism [17, 28-30]. In addition, BYS is also mechanically and chemically stable for OCM reaction, making it suitable to be used as both OCM catalyst and membrane materials.

In this study, LSCF hollow fibre membranes with designed structures facilitating catalyst deposition were developed first, using different bore fluids. Selected membranes were then investigated as a packed bed hollow fibre membrane reactor (PBHFMR) and catalytic hollow fibre membrane microreactor (CHFMMR) for OCM, using BYS as the catalyst (Fig. 5. 1) and compared with fixed bed reactor (FBR). The conical-shaped microchannels inside the LSCF hollow fibre membranes could significantly reduce mass transfer resistance and generate
huge geometrical surface area, which substantially improves the contact between reactants and BYS catalyst. Moreover, the direct delivery of dissociated and ionized oxygen from membrane towards the reaction sites could limit the non-selective oxidation reaction and therefore improves the $\text{C}_2+$ yield.

Fig. 5.1 Schematic diagram of a) micro-structured hollow fibre membrane used as PBHFMRe and b) CHFMMRe where catalyst (BYS) can be deposited in finger-like microchannels

5.2 Experimental

5.2.1 Chemicals and materials

La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3-\delta}$ (LSCF; Fuel Cell Materials, USA) and Bi$_{1.5}$Y$_{0.3}$Sm$_{0.2}$O$_{3-\delta}$ (BYS; PIDC, USA) were used as the membrane material and catalyst, respectively. Dimethyl sulfoxide (DMSO; VWR) or N-methylpyrrolidone (NMP; VWR), polyvinylpyrrolidone (PVP-K30) and polyethersulfone (PESf Radal A300, Ameco Performance) were used as a solvent, additive and polymer binder for spinning suspensions, respectively. In order to obtain the micro-
structured hollow fibre membranes, a mixture of solvent (DMSO or NMP) and ethanol was used as the bore fluid and tap water was used as the external coagulant. Bi₁₅ Y₀.₃ Sm₀.₂ O₃-δ (BYS) was purchased from PIDC, USA and used directly in the preparation of wash coating solution.

**5.2.2 Fabrication of micro-structured LSCF hollow fibre membranes**

The LSCF hollow fibre membranes were fabricated using a viscous fingering induced phase inversion process (Fig. 5. 2). Firstly, spinning suspension was prepared by dispersing a predetermined amount of ceramic powders into a solution of solvent and additive. The mixture was roll-milled (G 91, Gladstone Engineering) for at least 24 hours before adding PESf. The milling was continued for another 2-3 days to ensure a homogeneous spinning suspension. Table 5. 1 lists the compositions of spinning suspensions and conditions used for the fabrication of LSCF hollow fibres. After extrusion, the hollow fibre precursor membranes were immersed in a coagulation bath for 2 hours to complete the phase inversion process, before being cut into a specific length prior to sintering. The sintering process was carried out between 1280-1350 °C.
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**Fig. 5.2** Photograph of the fabrication of micro-structured LSCF hollow fibre membranes through phase inversion process

**Table 5.1** Fabrication conditions of micro-structured LSCF hollow fibre membranes

<table>
<thead>
<tr>
<th></th>
<th>Membrane 1 (M1)</th>
<th>Membrane 2 (M2)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Spinning suspension content (wt%)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ceramic powder</td>
<td>LSCF 70</td>
<td>LSCF 63</td>
</tr>
<tr>
<td>Polymer</td>
<td>PESf 7</td>
<td>PESf 6.3</td>
</tr>
<tr>
<td>Additive</td>
<td>PVP 0.5</td>
<td>PVP 3.67</td>
</tr>
<tr>
<td>Solvent</td>
<td>DMSO 22.5</td>
<td>NMP 25.18</td>
</tr>
<tr>
<td>Non-solvent</td>
<td>H$_2$O 1.85</td>
<td></td>
</tr>
<tr>
<td><strong>Bore fluid (wt%)</strong></td>
<td>100% DMSO</td>
<td>90%NMP-10%EtOH</td>
</tr>
<tr>
<td><strong>Extrusion rate (ml/min)</strong></td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td>Spinning suspension</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td>Bore fluid</td>
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<td>5</td>
</tr>
<tr>
<td><strong>Sintering temperature (°C)</strong></td>
<td>1300</td>
<td>1350</td>
</tr>
</tbody>
</table>
5.2.3 Preparation of LSCF CHFMMR via direct-wash coating of BYS

A direct-wash coating of commercial BYS powder was carried out by using a catalyst suspension that consists of 5 wt% BYS powder in a mixture of co-polymer (P-123) in ethanol and milled for several weeks to break the powder agglomeration and form homogeneous catalyst coating solution (Fig. 5. 3(a)). Prior to the deposition of BYS, the hollow fibres membranes were wrapped with PTFE tape to avoid any contamination on the outer surface of the hollow fibre. The hollow fibres were then inserted into a transparent tube and connected to the experimental setup as shown in Fig. 5. 3(b). The BYS catalyst was deposited inside the membrane microchannels using a vacuum technique to form the CHFMMR. The vacuum pump was used to aid the removal of air inside the fibre in order to obtain a uniform catalyst deposition inside the microchannels. After the air inside the hollow fibre was removed, the catalyst solution was introduced slowly inside the tube. After the coating process, excess catalyst slurry was blown from the lumen of hollow fibre membrane to avoid microchannels plugging. The fibres were then left to dry vertically overnight at 40 °C before being calcined at 600 °C to remove the organic binder. The coating and drying processes were repeated several times until desired coating weight or/thicker coatings layer was achieved. The amount of BYS deposited inside the microchannels was determined by weighing the membranes before and after the coating and calcination steps. The catalytic hollow fibre membranes was then inserted into a ceramic tube and sealed using epoxy resins to form the CHFMMR as shown in Fig. 5. 4.
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Fig. 5. 3 Photograph of BYS wash coating solution and apparatus used during the deposition of BYS via vacuum

Fig. 5. 4 Photograph of preparation of the CHFMMR
5.2.4 Characterizations

Gas tightness

Gas tightness of the prepared hollow fibre membranes was tested using a nitrogen (N\textsubscript{2}) gas permeation apparatus [31]. The hollow fibre was sealed and glued onto a stainless steel sample holder with an epoxy resin (UKR-135 resin with UKH-136 hardener; UK Epoxy Resins, Lancashire, UK) before being assembled into a compartment (Fig. 5. 5). The gas permeation test was carried out at 25°C using the system shown in Fig. 5. 6. The test gas, nitrogen, was pressurised into the membrane sample by opening the valve and then the valve was closed thus creating a sealed system. The pressure change with time was monitored and recorded. The gas permeance, \( P \) (mol·m\textsuperscript{-2}·s\textsuperscript{-1}·Pa\textsuperscript{-1}) was then calculated based on the cylinder pressure change with time using the equation below:

\[
P = \frac{V}{RTA_m} \ln\left(\frac{P_0}{P_t} - \frac{P_a}{P_t}\right) \tag{5.1}
\]

where

\[
A_m = \frac{2\pi(0.5R_o - 0.5R_i)L}{\ln\left(\frac{R_o}{R_i}\right)} \tag{5.2}
\]

where \( V \) is the volume of the test compartment (m\textsuperscript{3}); \( R \) is the gas constant (8.314 J·mol\textsuperscript{-1}·K\textsuperscript{-1}); \( T \) is the measured temperature (K). \( P_0 \) and \( P_t \) are the initial and final measured pressures in the test cylinder (Pa); \( P_a \) is the atmospheric pressure (Pa). \( A_m \) (m\textsuperscript{2}) is the membrane area calculated using the equation (5.2), where \( R_o \) is the outer radius of the hollow fibre (m), \( R_i \) is
the inner radius at the dense layer (m), \( L \) is the length of the hollow fibre membrane (m); and \( t \) is the measurement time (s).

**Fig. 5. 5** Photograph of the hollow fibre sample prepared for gas tightness test

**Fig. 5. 6** Experimental setup for gas tightness test
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Fabrication of Micro-Structured La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} Hollow Fibre Membrane Reactor for Oxidative Coupling of Methane

**Membrane morphology**

A JEOL JSM-5610LV scanning electron microscope with secondary electron (SE) and back-scattered electron (BSE) was used to observe the membrane structure and the deposition of BYS catalyst. The samples were coated with gold under vacuum before the observation.

**Crystal structure**

The X-ray diffraction patterns were obtained with an X'celerator detector (X'Pert PRO model) using Cu- Kα as the radiation source. The XRD scans were carried out in 2θ range from 10° to 80° using a step width of 0.05°. The equipment voltage and current were set at 40 kV and 40 mA, respectively.

**Membrane porosity and pore size distribution**

Mercury intrusion porosimetry (Autopore IV 9500, Micromeritics) was used to investigate pore structure of a membrane, before and after BYS deposition. Mercury intrusion data were collected under absolute the pressure ranging from 1.98-136.29 Psi.

5.2.5 Reactors set-up for OCM reaction

The schematic diagram and photograph of experimental setup for OCM reaction is shown in Fig. 5. 7 and Fig. 5. 8, respectively. A fixed bed reactor (FBR) was first used to investigate the catalytic activity of BYS powders sintered at different temperatures for OCM reaction. The FBR was prepared by diluting 0.2 g of BYS powder with 2 g of inert support (silica carbide). The mixture was then placed at the centre of a dense ceramic tube (internal diameter = 6 mm), giving a catalyst zone of 5 cm in length. Quartz wool was used to fix the catalyst in the middle of the reactor. Two types of membrane reactor configurations were then investigated in this
study depending on the way catalyst (BYS) was deposited. For PBHFMR configuration, 0.5 g of BYS was mixed with 2 g silica carbide and packed at the shell side of the membrane where methane was fed, while air was fed into the membrane lumen. For CHFMMR, in which 30 mg of BYS was deposited inside the conical-shaped microchannels, methane and air were fed in an opposite way from PBHFMR.

**Fig. 5.** Schematic diagram of OCM experimental setup where a) FBR: BYS catalyst was fixed in the centre of mullite tube with a mixture of methane and oxygen fed into the lumen; b) PBHFMR: BYS catalyst was packed outside the HF with methane fed from the shell and c) CHFMMR: BYS was deposited inside the micro-structured HF with methane fed into the lumen of HF
A hollow fibre membrane of 30 cm in length was used in the preparation of PBHFMR and CHFMMR for the ease of sealing. The membrane reactor was positioned horizontally in a tubular furnace (uniform heating length of 5 cm) and heated to the desired reaction temperature in argon. The setting temperature of the furnace was referred as the operating temperature. The flow rates of the reactants were controlled using mass flow controllers (Brooks Instrument, model 0154) and monitored by a bubble flow meter. All gas flows were at standard temperature and pressure. Once the furnace temperature reached 600 °C, argon was replaced with a mixture of 10% methane in argon. Then the furnace was further heated up to desired reaction temperatures (700-900 °C).

The analysis of the reactor effluents was performed on-line by gas chromatography (GC) once the reaction temperature was stabilized for 1 hour. Two types of GC (Varian 3900) detectors were used in the analysis; thermal conductivity detector (TCD) for permanent gasses (H₂, CO
and CO₂) and flame ionisation detector (FID) for light hydrocarbons (CH₄, C₂H₄, C₂H₆). The OCM performance was evaluated based on the CH₄ conversion (X₇CH₄) as well as selectivities (S) of C₂+ and COₓ using the equations shown below:

\[
X_{CH_4} = \frac{F_{CH_4 \text{ in}} - F_{CH_4 \text{ out}}}{F_{CH_4 \text{ in}}} \times 100\% \quad (5.3)
\]

\[
S_j = \frac{\sum n_j F_j}{F_{CH_4 \text{ in}} - F_{CH_4 \text{ out}}} \times 100\% \quad (5.4)
\]

where \( n_j \) is the number of carbon atom in the carbon-containing product \( j \), \( F_{CH_4} \) and \( F_j \) are the flow rates of methane and product \( j \) in mol/min. In order to compare the overall performance of different reactor configurations, the productivity rate (\( Y_j \)) taking into account of the mass of catalyst (\( M_{\text{cat}} \)) used in each reactor configuration was used. The \( Y_{C2+} \) is defined as the amount of C₂+, produced per unit time and per unit amount of catalyst as shown below:

\[
Y_j = \frac{\sum n_j F_j}{M_{\text{cat}}} \quad (5.5)
\]

## 5.3 Results and Discussion

### 5.3.1 Fabrication of micro-structured LSCF hollow fibre membranes

Fig. 5. 9 and Table 5. 2 show the SEM images and resulted properties of M1 and M2 hollow fibre membranes fabricated using different solvents as the bore fluid. In general, a micro-
structured LSCF hollow fibre membrane with conical-shaped microchannels open at the inner surface was obtained via the wet spinning process using a solvent-based bore fluid. The use of such bore fluid helps to delay the phase inversion at the inner surface of the membrane, allowing the microchannels initiated from the outer surface due to the hydrodynamically unstable viscous fingering, to grow continuously across the membrane cross-section and form close tailed microchannels [20]. However, each bore fluid resulted in conical-shaped microchannels of different dimensions and thickness ratios between the inner open microchannels and the outer dense separation layers. As can be observed in Fig. 5. 9, M1 spun using DMSO as a bore fluid possesses well-organized and narrow conical-shaped microchannels. Interestingly, short microchannels were also observed near to the outer surface of the membrane, which might be due to the possible back flow of the bore fluid (solvent) and viscosity of the suspension. Therefore, the dense separation layer of M1 was found to be between the conical-shaped open microchannels and short microchannels. However, the entrance to the inner microchannels was observed to be smaller than M2, which may limit the uniform deposition of catalyst particles into the microchannels. As a result, a less viscous spinning suspension and a stronger bore fluid consisting of a mixture of NMP and ethanol was used as a bore fluid for the fabrication of M2.

From Fig. 5. 9, it appears that M2 has bigger microchannel openings (~ 50 µm) packed in a denser way. In addition, the conical-shaped microchannels were also observed to elongate across the M2 membrane when compared with M1. The changes in the membrane structure might be due to solubility difference between the bore fluids. This was in agreement with previous studies [32, 33], in which it was found that the solvent dissolution power to PESf
decreased from NMP to DMSO. The higher dissolubility of NMP-based bore fluid has led to the slower precipitation at the inner surface, which allows the extension of conical-shaped micro-structure from the outer wall towards the inner side of the M2, forming a better and bigger conical-shaped microchannels. It should be noted that the use of less viscous spinning suspension and the nature of NMP in the spinning suspensions could also results in similar structure as M2. By adding water in the spinning suspension, the defects in the outer separation layer were eliminated due to the possible faster phase-inversion. It is also worth to note that, sedimentation at the membrane inner surface tend to happen when a strong bore fluid is used, which could partly blocks the entrance to the microchannels.

**Table 5.2 Properties of fabricated membranes**

<table>
<thead>
<tr>
<th>Specifications</th>
<th>M1</th>
<th>M2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Outer membrane diameter (D_{out}, mm)</td>
<td>1.96</td>
<td>1.80</td>
</tr>
<tr>
<td>Inner membrane diameter (D_{in}, mm)</td>
<td>1.19</td>
<td>1.14</td>
</tr>
<tr>
<td>Separation layer thickness, (t_{sl}, \mu m)</td>
<td>50</td>
<td>10</td>
</tr>
<tr>
<td>Effective membrane area( A_{m*}, cm²)</td>
<td>3.00</td>
<td>2.83</td>
</tr>
</tbody>
</table>

*Uniform furnace heating length = Effective membrane length = 5 cm*
**Fig. 5.** SEM images of the fabricated M1 and M2; (a) overall view of the HF, (b) cross-section of the HF and (c) inner surface of the HF

$\text{N}_2$ permeation analysis was carried out to evaluate gas tightness of the micro-structured LSCF hollow fibre membranes. Only gas-tight membranes were used to prepare the membrane reactors for OCM. From Table 5.3, it is apparent that M1 with a thicker dense separation layer possess better gas tightness, although the sintering temperature was 50 °C lower than
M2 (Table 5. 2). The dense separation layer of M1 and M2 was found to decrease from 50 to 10 μm. According to Tan et al. [31], hollow fibre membranes with nitrogen permeance value of 1x10⁻¹⁰ mol·m⁻²·s⁻¹·Pa⁻¹ could be considered as fully gas-tight. Although the permeance value of M2 was slightly above than the threshold value, the membrane was still considered gas tight due to formation of open microchannels and a thin dense separation layer. Furthermore, a close examination on SEM images confirmed that the outer layer of M2 was dense and free of defects; hence, it can be used for oxygen separation and OCM reaction.

**Table 5. 3 Gas tightness and separation layer thickness of M1 and M2**

<table>
<thead>
<tr>
<th>Membrane types</th>
<th>Nitrogen permeance (mol·m⁻²·s⁻¹·Pa⁻¹)</th>
<th>Separation layer thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>1.04 x10⁻¹⁰</td>
<td>50</td>
</tr>
<tr>
<td>M2</td>
<td>2.57 x10⁻⁹</td>
<td>10</td>
</tr>
</tbody>
</table>

Fig. 5. 10 shows the pore size and pore size distribution of the fabricated membranes using mercury intrusion measurements. The distribution curve shows a typical asymmetric structures with bigger pores \(D_p = 5\text{-}100 \mu\text{m}\) and smaller pores \(D_p = 0.1\text{-}5 \mu\text{m}\), representing entrance to the conical-shaped structures at the inner surface and possibly dead-pores throughout the sponge-like structure, respectively. M2 was found to have bigger microchannel opening (50 μm), which is about 5 times of M1 (10 μm). As a result, M2 can facilitate the catalyst deposition and further development of a catalytic hollow fibre membrane microreactor (CHFMMR).
5.3.2 Catalytic activity of BYS powder in the reaction of OCM

OCM usually takes place at a high temperature between 700 to 1000 °C, which might lead to catalyst sintering. It has been pointed out by Sehested [34] that many industrial catalyst lost their catalytic activity due to deactivation of active sites at high operating temperatures. A preliminary study was carried out for evaluating fresh and heat-treated BYS powders in a fixed bed reactor (FBR), in order to investigate the BYS activity at high operating temperatures. The BYS powder was subjected to a heat treatment at 1040 °C (the maximum temperature in this study before BYS started to melt and stick on the sintering tube) for 12 hours. The FBR was prepared by packing 0.2 g BYS powder mixed with 2.0 g of silica carbide in the middle of a dense ceramic tube, giving a 5 cm catalyst bed.

Fig. 5. 10 Pore size distribution of M1 and M2
Fig. 5. 11 compares the overall performance of fresh and heat-treated BYS powders as a function of temperature. In general, the overall performances were better at elevated operating temperatures due to enhancement in reaction rate. However, a decreased in C$_2$H$_4$ selectivity was observed for both powders when the operating temperature was above 850 °C. Fresh BYS was observed to have a similar conversion and selectivity to C$_2$H$_4$ and CO$_x$ as the heat-treated BYS. This means that the difference in OCM activity between the fresh and heat-treated BYS was insignificant, although the heat-treated BYS appears to be sintered (Fig. 5. 12). In addition, no obvious coke deposition in BYS powder was observed during the reaction.

Fig. 5. 13 compares the XRD patterns of fresh and heat-treated BYS powders. No additional peak was observed after the heat treatment, which further indicates that the fluorite structure of BYS remained the same. This preliminary fixed bed study also demonstrates the feasibility of using BYS as OCM catalyst up to operating temperature of 1040 °C as its crystal structure remains in fluorite structure until that temperature.
Fig. 5.11 Comparison of (a) methane conversion, (b) $C_{2+}$ selectivity, (c) $C_{2+}$ yield, (d) $CO_x$ selectivity and (e) $C_2H_4/C_2H_6$ ratio of fresh (■) and heat treated BYS (●) with a mixture of $CH_4$ (5.93 ml·min⁻¹), Argon (52.61 ml·min⁻¹) and oxygen (6 ml·min⁻¹) into the lumen side.
Fig. 5.12 SEM images of the (a) fresh BYS and (b) heat treated BYS.

Fig. 5.13 XRD patterns of fresh and heat treated BYS.
5.3.3 OCM performance of packed bed hollow fibre membrane reactor (PBHFMR)

The use of a dense membrane as a membrane reactor for OCM offers unique advantages, such as uniform distribution of oxygen from air and reduced risks of explosion (no pre-mixing of reactants). Oxygen permeation is known to affect the performance of such membrane reactor designs [22, 23, 35]. Over supply of oxygen could increase the methane conversion at the expense of \( \text{C}_2^+ \) selectivity, and vice versa. In this study, M1 and M2 with different separation layer thicknesses and microchannels characteristics were used for oxygen separation and distribution in packed bed configuration. The OCM catalyst, which is a mixture of 0.5 g of BYS and 2.0 g of silica carbide, was packed on the outer surface of the membranes (shell side).

Fig. 5. 14(a) shows the methane conversion of M1 and M2 as a function of temperature. Apparently, methane conversion was observed to increase in a slow manner at lower temperature (700 °C to 800 °C). However, once the temperature was above 800 °C, a sharp increase of methane conversion was observed, which is likely due to the sudden increase in oxygen permeation across the membrane. According to Zeng et al. [11], the phenomenon of sharp increase in oxygen flux of LSCF membrane was due to the order-disorder transition of oxygen vacancies, which has also been observed in other MIEC membranes [36]. Meanwhile, the high reaction temperature can also affect oxygen permeation across the membrane due to the enhancements in both bulk diffusion and surface exchange, but at different rates [37]. In addition, the driving force for oxygen permeation will also increase with respect to faster consumption of permeated oxygen at higher temperature, due to more significant reactions.
Therefore, due to the outstanding conical-shaped microchannels and thinner oxygen separation layer (approximately 10 µm) of M2, which allow more oxygen to permeate across the membrane, it shows better methane conversion (33.0 %) compared to M1 (20.1 %),

The selectivities of OCM reaction products (C$_2$+ and CO$_x$), C$_2$+ yield, and the C$_2$H$_4$/C$_2$H$_6$ are shown in Fig. 5. (b-e). In general, it was found that the C$_2$+ selectivity, C$_2$+ yield and the C$_2$H$_4$/C$_2$H$_6$ increased as a function of temperature, which is in contrast with that of CO$_x$. From the C$_2$+ selectivity plot, it appears that the selectivity increased with temperature until 850 °C and then started to decrease when the temperature rose to 900 °C. M2 was observed to have the better C$_2$+ selectivity compared to M1. The decreased of C$_2$+ selectivity at 900 °C, which is accompanied by the increased of CO$_x$ reveals that the C$_2$+ products can undergo deep oxidation to CO$_x$, if the temperature is too high. However, the increase in the C$_2$+ yield and C$_2$H$_4$/C$_2$H$_6$ with reaction temperature suggests that the OCM reaction is favoured at high temperature.
Fabrication of Micro-Structured \(La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}\) Hollow Fibre Membrane Reactor for Oxidative Coupling of Methane

**Fig. 5.14** Comparison of (a) methane conversion, (b) \(C_2^+\) selectivity, (c) \(C_2^+\) yield, (d) \(CO_x\) selectivity and (e) \(C_2H_4/C_2H_6\) ratio of various membrane structures (\(\bullet\) - M1 and \(\diamond\) - M2) with a mixture of \(CH_4\) (5.93 ml·min\(^{-1}\))-Argon (52.61 ml·min\(^{-1}\)) fed on the shell side and air (23.56 ml·min\(^{-1}\)) into the lumen side.
5.3.4 Effects of M2 reactor designs on the OCM performance

Due to the outstanding microchannels inside M2, BYS can be dispersed uniformly, which turns M2 into a M2-CHFMMR. The uniform dispersion of BYS catalyst inside the microchannels could help to improve reaction efficiency by delivering dissociated and ionized oxygen directly from membrane towards the reaction sites, which is favourable to the C$_2^+$ formation. The deposition of BYS was repeated for four (4) times and the amount of BYS that can be placed inside the 5 cm conical-shaped microchannels was about 30 mg.

Fig. 5. 15 shows the SEM images of the CHFMMR in secondary scattered electron (SE) and back scattered electron (BSE). BSE is commonly used to differentiate contrast between different elements compositions. The combined use of both imaging modes provides clearer information on the dispersion of BYS inside the M2 microchannels. From the SEM images below, it can be seen that BYS was deposited inside the microchannels without blocking the channels entrance. However, some of the narrow parts of the microchannels did not receive BYS, which means that further improvements on the catalyst deposition are needed.

Fig. 5. 16 compares the pore size distribution of M2 before and after BYS deposition. In addition to a slight decrease in the volume of conical-shaped microchannels, the entrance was found to move towards smaller side due to the deposition of BYS particles. This result was also consistent with the SEM analysis (Fig. 5.15), where no blockage of the entrance to conical-shaped microchannels was observable after the BYS deposition.
Fig. 5. 15 Secondary electron (SE) images of the deposition of BYS in M2. The same specimen is shown in back scatter mode (BSI). The BYS deposition can be differentiated based on contrast in which it appears brighter than LSCF.

Fig. 5. 16 Pore size distribution of M2 before (●) and after (▲) BYS deposition.
Fig. 5. 17 shows the effect of reactor design on OCM performance, with additional performance of M2-blank reactor for the purpose of comparison. From Fig. 5. 17(a), it can be seen that M2-CHFMMR shows lower methane conversion compared to M2-PBHFMRR and FBR, which might be attributed to the higher gas hour space velocity (GHSV) or short contacting time, since the gas flow rate entering each reactor design was kept the same. In comparison with the blank M2-HFMMR, all reactors with BYS catalyst showed better methane conversion, especially at temperatures above 800 °C. This indicates that use of catalyst is necessary in order to accelerate the activation of methane into methyl radicals (\(\cdot\text{CH}_3\)), which is considered as the limiting step in heterogeneous-homogeneous OCM reaction.

From Fig. 5. 17(b), it can be seen that the \(\text{C}_2\) selectivity increases with temperatures, including the blank reactor. However, the \(\text{C}_2\) selectivity of blank reactor increases slowly from 25% to 35% throughout the reaction. This suggests that the use of BYS catalyst is still necessary for greater \(\text{C}_2\) selectivity, although LSCF has been reported with certain catalytic activity towards OCM reaction [38, 39]. In addition, M2-CHFMMR with the highest GHSV shows better \(\text{C}_2\) selectivity over M2-PBHFMRR and M2-FBR, which may be related with less re-oxidation of \(\text{C}_2\) products into CO\(_x\) due to the short contact time of \(\text{C}_2\) products with oxygen inside the reactor.

The \(\text{C}_2\) yield in Fig. 5. 17 (c) indicates that the yield increase with temperature, similar to methane conversion and \(\text{C}_2\) selectivity, with the maximum \(\text{C}_2\) yield of 15% was achieved at 900 °C by M2-CHFMMR. M2-PBHFMRR was initially anticipated to give better \(\text{C}_2\) yield than FBR due to the use of membrane to dose oxygen, which can help to increase the \(\text{C}_2\) selectivity. Interestingly, our study shows that the \(\text{C}_2\) yield for both reactors was almost similar.
throughout the reaction. One of the possible explanations for this low performance of M2-PBHFM is because of the bypass of oxygen from catalyst bed [35], making it to behave like FBR. This was further confirmed with the similarity of CO\textsubscript{x} selectivity obtained in M2-PBHFM and FBR especially at high temperature, where the oxygen permeation was much higher (Fig. 5. 17(d)). The bypass of oxygen is possibly due to the use of long ceramic hollow fibre membrane (30 cm) for reactor preparation, in which 18 cm of the fibre was located inside the reactor. Thus, there is possibility of oxygen to permeate outside the 5 cm reaction zone (catalyst bed) at higher temperature.

Fig. 5. 17 (e) shows C\textsubscript{2}H\textsubscript{4}/C\textsubscript{2}H\textsubscript{6} during OCM reaction. The ratio was observed to be less than 0.5 at temperatures below 800 °C. Thereafter, the C\textsubscript{2}H\textsubscript{4}/C\textsubscript{2}H\textsubscript{6} ratio starts to increase rapidly. Only M2-CHFM managed to obtain a ratio higher at 1.0 at temperature above 850 °C. The increase in the C\textsubscript{2}H\textsubscript{4}/C\textsubscript{2}H\textsubscript{6} with reaction temperatures suggests that the dehydrogenation of C\textsubscript{2}H\textsubscript{6} (which is formed by ∙CH3 coupling in the gas phase) to C\textsubscript{2}H\textsubscript{4} is favoured at high temperatures, and this formation is at the expense of C\textsubscript{2}H\textsubscript{6}. In addition, it is believed that this dehydrogenation occurs not only on the catalyst surface but also partly from homogenous gas phase reaction as the appearance of ethylene was always accompanied by the formation of hydrogen. Interestingly, only a small amount of CO was observed at a high temperature (>850 °C), which may indicate that the gas phase oxidation of C\textsubscript{2}H\textsubscript{4} results in the formation of CO.
Chapter 5  
Fabrication of Micro-Structured \( \text{La}_{0.6} \text{Sr}_{0.4} \text{Co}_{0.2} \text{Fe}_{0.8} \text{O}_{3-\delta} \) Hollow Fibre Membrane Reactor for Oxidative Coupling of Methane

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![Graphs showing the effects of temperature on methane conversion, \( \text{C}_2^+ \) selectivity, \( \text{C}_2^+ \) yield, and \( \text{CO}_x \) selectivity.]

(a) Methane conversion (%)
(b) \( \text{C}_2^+ \) selectivity (%)
(c) \( \text{C}_2^+ \) yield (%)
(d) \( \text{CO}_x \) selectivity (%)

Temperature (°C)

Methane conversion (%)
\( 0 \) to \( 40 \%
\( 650 \) to \( 950 \) °C

\( \text{C}_2^+ \) selectivity (%)
\( 0 \) to \( 100 \%
\( 650 \) to \( 950 \) °C

\( \text{C}_2^+ \) yield (%)
\( 0 \) to \( 16 \%
\( 650 \) to \( 950 \) °C

\( \text{CO}_x \) selectivity (%)
\( 0 \) to \( 100 \%
\( 650 \) to \( 950 \) °C
Fig. 5. 17 Comparison of (a) methane conversion, (b) C$_2$+, selectivity, (c) C$_2$+, yield, (d) CO$_x$ selectivity, (e) C$_2$H$_4$/C$_2$H$_6$ ratio of BYS fixed bed reactor (■ - BYS-FBR), M2-packed bed hollow fibre membrane reactor (◆ - M2-PBHFM), M2-catalytic hollow fibre membrane micro reactor (○ - M2-CHFM), M2-catalytic hollow fibre membrane micro reactor (▲ - M2-Blank HFMR) with a mixture of CH$_4$ (5.93 ml·min$^{-1}$)-Argon (52.61 ml·min$^{-1}$) fed on the lumen side and air (23.56 ml·min$^{-1}$) into the shell side.

As the amount of BYS used in each reactor design was slightly different (0.2, 0.5 and 0.03g for FBR, M2-PBHFM and M2-CHFM, respectively), the performance of the three reactor designs was then compared in terms of productivity rate (Fig. 5. 18(a) and (b)). The C$_2$+ productivity rate of M2-CHFM was observed to be the highest followed by FBR and M2-PBHFM. It is interesting to note that although the amount of catalyst in M2-CHFM (30 mg) was significantly lower than FBR (200 mg) and M2-PBHFM (500 mg), it yield better C$_2$+ productivity rate especially at higher temperatures. The similarity in CO$_x$ productivity rate of
FBR and M2-CHFMMR was related to the amount of catalyst used, as well as other factors such as the amount of oxygen taking part into the reactions. However, from earlier discussion on Fig. 5.17, it has been proved that better overall OCM performance can be achieved using M2-CHFMMR. This is associated to the reactor design of M2-CHFMMR, in which uniform contact between the reactants and catalyst can be achieved. Consequently, allowing easier access of reactants towards the lattice/active site of BYS catalyst, reducing gas phase homogeneous reaction that tends to form COx. Such a unique catalytic micro-structured reactor design (MMR), in which BYS catalyst was attached on LSCF surface, could also facilitate the delivery of dissociated and ionized oxygen directly towards the reaction sites that favours methane and ethane activation.

Although it appears that BYS catalyst “works harder” in CHFMMR compared to other reactor designs, the C2+ yield achieved in this study was still below the industrial expectations. Nevertheless, the final OCM performance can be potentially promoted by optimizing the reactor operation conditions. One of the important parameters that need to be controlled especially when using a membrane reactor is the balance between oxygen permeation and methane concentration. This is because greater oxygen permeation does not always give better C2+ productivity. If the amount of oxygen permeated across the membrane is too high, the oxygen will tend to recombine to gaseous oxygen to from COx. Nevertheless, if it is too low, the conversion and selectivity will decrease.
5.3.5 Membrane stability

Membrane stability is very critical for practical application of CHFMMR in OCM. Fig. 5. 19 shows the XRD patterns of the membrane material (LSCF), catalyst (BYS), fresh and spent CHFMMR. The fresh and spent CHFMMR were ground into powders prior to the XRD analysis. Because of the significantly high peak intensity of the LSCF hollow fibre and a relatively low amount of BYS deposited inside the membranes microchannels, clear representational of BYS in the XRD patterns was inhibited. Only one of the characteristic peak
BYS (2θ =27.5°) was observed in fresh and spent CHFMMR. Besides that, it can be seen that the perovskite structure of LSCF CHFMMR remained unchanged before and after OCM testing and those structure are similar to the fresh LSCF powders. This suggests that the LSCF is very stable and suitable to be used as a membrane material for the fabrication of CHFMMR. Fig. 5. 20 shows the pore size distribution of the fresh and spent CHFMMR. It can be seen that after the OCM reaction, the pore size distribution of the spent CHFMMR shifted to the smaller side indicating that no major changes on the CHFMMR. The shifting shows that pores of the membrane decreased after the reaction, which might be due to the high operation temperature of OCM reaction.

Fig. 5. 19 XRD patterns of LSCF, BYS, fresh LSCF CHFMMR and spent LSCF CHFMMR
Fig. 5.20 Pore size distribution of LSCF CHFMMR before (●) and after (○) OCM reaction

5.4 Conclusions

Asymmetric micro-structured LSCF hollow fibre membranes with different microchannel characteristics were fabricated in this study using solvent-based bore fluids. From PBHFMR analysis, it is evident that M2 has high oxygen permeability due to its thinner separation layer and more open conical-shaped microchannels. The outstanding microchannels inside the M2 also allow it to be used as a substrate where BYS catalyst can be deposited uniformly, forming a catalytic hollow fibre membrane microreactor (CHFMMR). The performance of M2-CHFMMR was found to be substantially better than its PBHFMR counterpart, as the same catalyst can "work harder. Our proof of principle study further proves that, uniformly dispersing catalyst inside micro-structured ceramic hollow fibre membranes is an efficient route
promoting performance and efficiency of catalytic membrane reactors and can be transferred potentially to other catalytic reactions of great importance.

5.5 References


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CHAPTER 6

An Oxygen Permeable Membrane Microreactor with an In-Situ Deposited Bi$_{1.5}$Y$_{0.3}$Sm$_{0.2}$O$_{3-δ}$ Catalyst for Oxidative Coupling of Methane

Abstract

In this study, a novel catalytic hollow fibre membrane microreactor (CHFMMR) was developed using a micro-structured La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3-δ}$ (LSCF) hollow fibre as an oxygen separation membrane as well as a functional substrate for in-situ deposition of a Bi$_{1.5}$Y$_{0.3}$Sm$_{0.2}$O$_{3-δ}$ (BYS) catalyst using a sol-gel method for oxidative coupling of methane (OCM) reaction. A nano-thickness BYS catalytic layer (300-500 nm) was successfully deposited onto the microchannel walls throughout the whole hollow fibre. The differences in the OCM performances between the in-situ sol-gel prepared CHFMMR and a washcoat CHFMMR are highlighted. The performance of such CHFMMR is found to be strongly dependent on the properties of BYS and the reaction conditions. When the particle size of BYS was reduced to nano-sizes and was uniformly dispersed, the performance of such CHFMMRs changes drastically, in which higher oxygen permeation rate and methane conversion were obtained. A decrease in residence time was observed to give a better C$_{2+}$ selectivity and C$_{2+}$ yield, achieving a maximum value of 79% and 39%, respectively at 900 °C. To the best of our knowledge, the C$_{2+}$ yield obtained in this study is the highest value reported so far. The C$_{2+}$ productivity rate
of the in-situ design CHFMMR was observed to be nearly four times higher than that of the washcoat CHFMMR due to the better accessibility of reactants towards lattice/active site of the uniform BYS catalytic layer.

6.1 Introduction

Oxidative coupling of methane (OCM) is a heterogeneous catalytic process where methane is converted directly into ethane and ethylene (C₂, products), one of the largest commodities and a vital building block for a vast range of chemicals. In addition, this process avoids thermodynamic constraints by kinetically coupling C-H bond activation with removal of hydrogen via oxidation [1-3]. Despite of these advantages, the formation of the target products (C₂⁺) is always accompanied by further oxidations to carbon oxides, which limits the overall process efficiency [1]. Since the pioneering work by Keller and Bhasin [4], extensive studies have been carried out on various aspects of the OCM reaction, such as catalyst composition and design [5-8], reaction mechanism [1, 9] and reactor design [10-12]. Nevertheless, after over 40 years, this process is not yet commercialized. Most of the OCM studies have revealed that one of the major barriers to the commercialization of OCM processes is the decrease of C₂⁺ selectivity with the increasing methane conversion. This is due to the thermodynamically favoured oxidation reaction of C₂⁺ products into COₓ [13]. Many studies show that the use of membrane reactor has a major benefit in offering higher C₂⁺ selectivity over conventional co-feed reactor, particularly when an oxygen permeable membrane takes the role of supplying, controlling and distributing oxygen [14-17]. This is because the oxygen is added uniformly into
the catalyst bed along the length of the reactor. As a result, a high ratio between local hydrocarbon and oxygen in the reaction zone can be maintained. Besides, direct contact between gaseous oxygen (O\(_2\)) and methane can be avoided, as methane and oxygen are fed from two different reactor compartments, thus limiting the non-selective oxidation of C\(_{2+}\) products and therefore improving the C\(_{2+}\) yield.

In our recent work [18], LSCF hollow fibre membranes with designed micro-structures facilitating oxygen permeations and catalyst deposition were developed and used as catalytic hollow fibre membrane microreactor (CHFMMR) for OCM. Other than significantly reduced mass transfer resistance across the membrane, the conical-shaped microchannels inside the LSCF hollow fibre membranes could act as a substrate where catalyst can be deposited for the catalytic reaction to take place. Thus, the contact between reactants and catalyst is substantially improved.

In addition to having a highly oxygen permeable membrane, enhancements in catalytic activity of the catalyst is also crucial. This is because a decrease in C\(_{2+}\) selectivity could occur if the oxygen supply rate by the membrane is too high when compared to the catalyst activity [19]. Similarly, a decrease in methane conversion can also happen if a low oxygen permeable membrane is used together with a highly active catalyst. Therefore, the selection of catalyst should be matched with the oxygen supplied by the membrane in order to ensure a high performance membrane reactor.
Among the metal oxide catalysts investigated for OCM, Bi$_{1.5}$Y$_{0.3}$Sm$_{0.2}$O$_{3-\delta}$ (BYS), which is of a fluorite structure and developed by Zeng et al. [20] and Akin et al. [14], was found to give great C$_2$+ yield. This material appears to be not only highly ionic conductive for migration of oxygen ions, but also catalytic active for OCM, a reaction with both heterogeneous and homogeneous reaction mechanisms [14, 21, 22]. In addition, BYS is also mechanically and chemically stable for OCM reaction, making it suitable to be used as an OCM catalyst [14].

In this study, an in-situ sol-gel based process was employed to deposit BYS inside the microchannels. Apart from investigating the effects of this catalyst deposition route on microstructures and catalytic activity of the catalytic layer inside microchannels, comparisons of the reactor performances between the newly developed reactor and the previously washcoat reactor was also outlined.

6.2 Experimental

6.2.1 Chemicals and materials

Bismuth (III) nitrate pentahydrate (Bi(NO$_3$)$_3$·5H$_2$O), yttrium (III) nitrate tetrahydrate (Y(NO$_3$)$_3$·4H$_2$O) and samarium (III) nitrate hexahydrate (Sm(NO$_3$)$_3$·6H$_2$O) were purchased from Sigma-Aldrich and used as metal precursors for the preparation of BYS catalyst. Citric acid (C$_6$H$_8$O$_7$; Fisher Scientific) and ethylene glycol (C$_2$H$_6$O$_2$; VWR) were used as the complexing agents. La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3-\delta}$ (LSCF; Fuel Cell Materials, USA) were used as the
membrane material. N-methylpyrrolidone (NMP; VWR), polyvinylpyrrolidone (PVP-K30) and polyethersulfone (PESf Radal A300, Ameco Performance) were used as a solvent, additive and polymer binder for spinning suspensions, respectively. In order to obtain the micro-structured hollow fibre membranes, a mixture of 10% ethanol (VWR) in NMP was used as the bore fluid and tap water was used as the external coagulant.

### 6.2.2 Preparation of BYS catalyst via sol-gel technique

\( \text{Bi}_{1.5}\text{Y}_{0.3}\text{Sm}_{0.2}\text{O}_{3-\delta} \) (BYS) was synthesized by a citrate sol-gel route [23, 24] using corresponding metal nitrates: \( \text{Bi(NO}_3\text{)}_3\cdot5\text{H}_2\text{O} \), \( \text{Y(NO}_3\text{)}_3\cdot4\text{H}_2\text{O} \) and \( \text{Sm(NO}_3\text{)}_3\cdot6\text{H}_2\text{O} \) as shown in Fig. 6. 1. The appropriate quantities of the metal nitrates were fully dissolved in nitric acid solution under magnetic stirring followed by addition of citric acid solution and ethylene glycol in a ratio of (1:2:3). Ethylene glycol was added to the solution to inhibit cation segregation, leading to a homogeneous precursor solution. The resulting solution was continuously stirred at 75-85°C for 3-5 hours to accelerate polyesterification reaction of citric acid and ethylene glycol, and continuous polymerization until a transparent BYS catalytic sol was formed. After that, the catalytic sol was dried overnight in an oven at 40 °C to continue the polymerization process and to remove excess water until it becomes a highly viscous sol/gel. In order to transform the as-prepared BYS viscous sol/gel into powder, it was calcined in a furnace over a temperature range of 700-900 °C for 5 hours, at a heating and cooling rate of 2 °C/min and 3 °C/min, respectively. For the in-situ preparation and deposition of BYS catalyst using the sol-gel technique, the viscous BYS sol was used, instead of the BYS powder [1].
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**Fig. 6.1 Flowchart diagram for the preparation of BYS using citrate sol-gel technique**

- Bi(NO$_3$)$_3$·5H$_2$O,
- Y(NO$_3$)$_3$·4H$_2$O
- Sm(NO$_3$)$_3$·6H$_2$O

**Steps:**
1. **Nitric acid/H$_2$O**
   - Dissolved and stirred at 75-80 °C in oil bath
2. **Metal nitrate solution**
3. **Citric acid/H$_2$O**
4. **Ethylene glycol**
5. **BYS pre-cursor solution**
   - Continuously stirred at 75-80 °C
6. **BYS sol**
   - Overnight in oven at 40 °C
7. **Highly viscous BYS sol/gel**
   - High temperature calcination in furnace
8. **BYS powder**
6.2.3 Fabrication of LSCF catalytic hollow fibre membrane microreactor (CHFMMR) using washcoat and in-situ sol-gel approaches

The LSCF hollow fibre membranes were fabricated using a viscous fingering induced phase inversion process, which have been described elsewhere [18]. Fig. 6. 2 shows the steps involve in the preparation of CHFMMR. Prior to the deposition of BYS, the hollow fibres membranes were wrapped with PTFE tape (Fig. 6. 2(1)) to minimize any contamination on the outer surface of the hollow fibre. The hollow fibres were then inserted into a transparent tube and connected to the experimental setup as shown in Fig. 6. 2(2). The BYS catalyst was deposited inside the membrane microchannels using a vacuum technique to form the CHFMMR. The vacuum pump was used to aid the removal of air inside the fibre in order to obtain a uniform catalyst deposition inside the microchannels. After the air inside the hollow fibre was removed, the catalyst solution was introduced slowly into the tube. The in-situ sol-gel coating was carried out using the BYS sol that was prepared earlier in section 6.2. For comparison purpose, a washcoat of commercial BYS powder was carried out by using a catalyst suspension that consists of 5 wt.% BYS powder in a mixture of co-polymer and ethanol [18]. After the coating process, excess catalyst slurry was blown out from the lumen of hollow fibre membrane to avoid microchannels plugging. The fibres were then left to dry vertically overnight at 40 °C, before being calcined at 900 °C (sol-gel) and 600 °C (washcoat) to remove the organic binder. The amount of BYS deposited inside the microchannels was determined by weighing the membranes before and after the coating and calcination steps. The catalytic hollow fibre membranes was then assembled into a ceramic tube and sealed using epoxy resins to form the CHFMMR as shown in Fig. 6. 2(3).
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1. The membranes were wrapped using PTFE tape prior catalyst coating.

2. Catalyst coating using vacuum technique; (i) direct wash-coating of BYS powder and (ii) sol-gel coating of BYS.

3. The membranes were sealed inside a ceramic tube and sealed both end using epoxy resins.

Fig. 6.2 Photograph of BYS catalyst coating and membrane reactor preparation.
6.2.4 Characterizations

A JEOL JSM-5610LV scanning electron microscope with secondary electron (SE) was used to observe the membrane microstructure and the deposition of BYS catalyst. A high-resolution field emission gun scanning electron microscope (FEGSEM-Gemini 1525) was then used to observe the deposition of BYS inside the membrane microchannels. The samples were coated with gold under vacuum before the observation. In addition, a digital microscope (Dino Lite-AM211) was also used as a preliminary tool in observing the catalyst deposition. The X-ray diffraction patterns were obtained with an X’celerator detector (X’Pert PRO model) using Cu-Kα as the radiation source. The XRD scans were carried out in 2θ range from 10° to 80° using a step width of 0.05°. The equipment voltage and current were set at 40 kV and 40 mA, respectively. Mercury intrusion porosimetry (Autopore IV 9500, Micromeritics) was used to investigate pore structure of a membrane, before and after BYS deposition. Mercury intrusion data were collected under absolute the pressure ranging from 1.98-136.29 Psi.

6.2.5 Catalytic hollow fibre membrane micro reactor (CHFMMR) for OCM reaction

The experimental setup for OCM reaction is shown in Fig. 6.3. A hollow fibre membrane of 30 cm in length was housed in a dense ceramic tube in the preparation of CHFMMR. The CHFMMR was then positioned horizontally in a tubular furnace (uniform heating length of 5 cm) and heated to the desired reaction temperature in argon. Similarly, a fixed bed reactor (FBR) was prepared by mixing 0.01 g of BYS powder with 2 g of silica carbide and packed at
the centre of dense ceramic tube (internal diameter = 6 mm), giving 5 cm of catalyst zone. The setting temperature of the furnace was referred as the operating temperature. Air and a mixture of methane and argon were fed into the shell and lumen sides of the hollow fibre, respectively. The flow rates of the reactants were controlled using mass flow controllers (Brooks Instrument, model 0154). All gas flows were at standard temperature and pressure.

Once the furnace temperature reached 600 °C, argon was replaced with a mixture of methane in argon. Then the furnace was further heated up to desired reaction temperatures (700-900 °C). The analysis of the reactor effluents was performed on-line by gas chromatography (GC), once the reaction temperature was stabilized for 1 hour. Two types of GC (Varian 3900) detectors were used in the analysis; thermal conductivity detector (TCD) for permanent gasses (H₂, O₂, N₂, CO and CO₂) and flame ionisation detector (FID) for light hydrocarbons (CH₄, C₂H₄, C₂H₆). The OCM performance was evaluated based on the CH₄ conversion ($X_{CH_4}$) as well as selectivities ($S_j$) of C₂⁺ and COₓ using the equations shown below:

$$X_{CH_4} = \frac{F_{CH_4\text{ inlet}} - F_{CH_4\text{ outlet}}}{F_{CH_4\text{ inlet}}} \times 100\% \quad (6.1)$$

$$S_j = \frac{\sum n_j F_j}{F_{CH_4\text{ inlet}} - F_{CH_4\text{ outlet}}} \times 100\% \quad (6.1)$$

where $n_j$ is the number of carbon atom in the carbon-containing product $j$, $F_{CH_4}$ and $F_j$ are the flow rates of methane and product $j$ in mol/min. The productivity rate of C₂⁺ ($Y_{C_2^+}$) is then calculated using equation below:

$$Y_j = \frac{\sum n_j F_j}{M_{cat}} \quad (6.2)$$
Fig. 6.3 Schematic diagram of OCM experimental setup for in-situ sol-gel prepared CHFMMR and FBR of BYS powder

6.3 Results and Discussion

6.3.1 Characterizations and OCM performance of the synthesized BYS

As the structure of BYS is known to have a crucial impact on the OCM activity [20, 25], XRD was first used to characterize the phase structure of the prepared BYS. Fig. 6.4 compares the XRD pattern of BYS powders prepared by citrate sol-gel route at different calcination temperatures, using the commercial BYS powder as a reference. The commercial BYS powder was observed to have a typical single-phase fluorite structure ($\delta$, fcc), which is known to lead to better OCM activity. The BYS prepared using the sol-gel route requires a high
calcination temperature (900 °C) because the transformation of α-Bi₂O₃ into the fluorite δ-
Bi₂O₃ (fluorite) usually occurs at high temperature. In addition, significant impurity phases
such as carbon residual cannot be completely removed especially at lower calcination
temperatures (700 and 800 °C). As the calcination temperature increases, the impurity phases
were eliminated and more intense XRD patterns were observed. The calcination temperature
strongly affect the crystallite size due to different energy input, in which higher temperature
will consequently produce larger BYS grains. This also proved that BYS with a fluorite
structure could be prepared using the citrate sol-gel route as long as appropriate calcination
temperature was used [26].

**Fig. 6.4** XRD patterns of commercial and as obtained BYS prepared by sol-gel route at
different calcination temperatures
Fig. 6. 5 compares the morphologies of the commercial and sol-gel prepared BYS powders. It can be seen that, in contrast to the commercial BYS powder used in the washcoat solution, the powder prepared by sol-gel is considerably sintered, with comparable grain sizes. This was likely due to the high calcination temperature used (900 °C), which increases the grain boundary diffusion and therefore, the particles become denser by forming necks between each particle as they coalesce into larger ones.

**Fig. 6. 5** SEM images of (a) commercial and (b) sol-gel BYS calcined at 900 °C with magnification of (i) 10 000 X and (ii) 50 000 X
Fig. 6. 6 compares the OCM performance (methane conversion, C$_2$+ selectivity and C$_2$+ yield) of commercial and sol-gel prepared BYS powders (0.01 g) in FBR configurations, under the identical operating conditions with our previous study [18]. From Fig. 6. 6(a), it can be seen that the methane conversion increases slowly from approximately 10 % to 14 %, as the temperature was increased from 700 to 800 °C. As the operating temperature was further increased to 850 °C, the conversion increases rapidly and continues to rise with temperatures, which is due to the increase in reaction rate. The C$_2$+ selectivity was also observed to be strongly dependent on the operating temperatures. Further increasing the operating temperature to 900 °C, the C$_2$+ selectivity decreases due to deep oxidation of the C$_2$+ products into CO$_X$. The C$_2$+ yield (Fig. 6. 6(c)) of both FBRs were observed to increase with temperature, similar to methane conversion and C$_2$+ selectivity. All these results suggest that OCM reaction is favoured at high temperatures, which is in agreement with literatures [27]. Apparently, the overall performances of both powders were very close, although the sol-gel prepared powder appeared to be considerably sintered (Fig. 6. 5). This indicates that the performances of BYS catalyst with grain size of around 1 µm are less likely to be affected by the catalytic surface area, which is in agreement with our previous findings [18].
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Fig. 6.6 Comparison of (a) methane conversion, (b) $C_2^+$ selectivity and (c) $C_2^+$ yield of the FBR prepared using commercial BYS (■) and sol-gel prepared BYS (●).
6.3.2 LSCF catalytic hollow fibre membrane microreactor (CHFMMR) prepared using washcoat and in-situ sol-gel approaches

Fig. 6. 7 shows the SEM images of the micro-structured LSCF hollow fibre membrane, which is prepared using a fingering induced phase inversion process, without the catalyst deposition. It can be seen that an asymmetric membrane structure consisting of conical-shaped microchannels (Fig. 6. 7(a)) open at the inner surface (Fig. 6. 7(b)) and a dense structure in the outer region (Fig. 6. 7(c)) was obtained via the wet spinning process, by using a solvent-based bore fluid (N-methylpyrrolidone (NMP)–ethanol). The finger-like region was observed to have hundreds of conical shaped microchannels, in which the microchannels length varied from 50-200 µm and the opening radius decreases from inner to outer surface (Fig. 6. 7(a)). Since the microchannels opening was significant; in a range of 20-50 µm, it can be used as a substrate for the BYS catalyst deposition in order to enhance the surface exchange kinetics and catalytic reaction. In addition, the outer surface of the membranes was free from defects and fully densified, making it suitable for oxygen separation (Fig. 6. 7(c)). By distributing the oxygen ions into the reaction zone, the reaction can be selectively controlled and hence, an increase in the product selectivity can be expected. Therefore, the micro-structured LSCF hollow fibre membrane prepared in this study could be considered as surpass candidates for further development of CHFMMR for OCM reaction.

In this study, two approaches were used for the deposition of BYS catalyst inside the membrane microchannels to form CHFMMR: (1) an in-situ sol-gel BYS and (2) a washcoat of commercial BYS powder. After the BYS deposition, the membranes were calcined at 900°C.
for the sol-gel and at 600°C for the washcoat approaches. The amount of BYS deposited inside the CHFMMRs for 5 cm of reaction zone is shown in Table 6. The quantity of BYS in in-situ CHMMR was observed to be three times lower than the washcoat CHFMMR.

![SEM images of micro-structured LSCF membrane](image)

**Fig. 6.7** SEM images of micro-structured LSCF membrane: (a) cross section; (b) inner surface and (c) outer surface

<table>
<thead>
<tr>
<th>Deposition technique</th>
<th>Amount of BYS deposited in CHFMMR (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Washcoat</td>
<td>31.4</td>
</tr>
<tr>
<td>Sol-gel</td>
<td>10.1</td>
</tr>
</tbody>
</table>

**Table 6.1** Amount of catalyst deposited in CHFMMR
The XRD analysis was first used to identify the presence of BYS inside the CHFMMR as shown in Fig. 6.8. However, due to the significantly high peak intensity of the LSCF hollow fibre and a relatively low amount of BYS deposited inside the membranes microchannels, only the characteristic peak of BYS at $2\theta = 27.5^\circ$ can be clearly identified in both CHFMMRs.

*Fig. 6.8* XRD patterns of CHFMMR prepared using washcoat and in-situ sol-gel approaches

(● LSCF; ▲ BYS)
Fig. 6. 9 shows the microscope images of the washcoat commercial BYS inside the membrane microchannels. The deposition of BYS inside the microchannels can be easily identified using the digital microscope due to the colour of BYS (light orange) in compared with the LSCF hollow fibre (black). The BYS particles were observed to be scatteredly dispersed along the hollow fibre membrane. In addition, some of the narrow parts of the microchannels did not received BYS. A clear observation using the digital microscope, however, could not be obtained for the sol-gel prepared CHFMMR. This is because the quantity of BYS catalyst and the thickness of the catalyst layer were really small and thin.

![Microscope images of washcoat BYS powder inside the membrane microchannels](image)

**Fig. 6. 9 Microscope images of washcoat BYS powder inside the membrane microchannels**
Fig. 6. 10 compares the deposition of BYS inside conical-microchannels using the in-situ sol-gel and washcoat approaches. In general, both approaches allow the deposition of BYS catalyst without blocking the microchannel entrances. For the washcoat CHFMMR, grainy BYS particles can be observed scatteredly on the microchannels wall. While for the BYS deposited via in-situ sol-gel, cracks were observed in the catalyst layer close to microchannel entrances. In addition, this catalyst layer was observed to be slightly thicker than the part inside the microchannels. This might be linked to the potential migration of sol towards the microchannels entrance during the course from sol to gel and possible faster evaporation of solvent in BYS sol. While for the part inside the microchannels, LSCF grains beneath the sol-gel coating can be observed, indicating a really thin catalyst layer.
A closer observation on the sol-gel prepared CHFMMR using the high-resolution SEM images (Fig. 6. 11) revealed the presence of a very thin and uniform BYS layer of less than 400 nm. Interestingly, the particle size of the BYS deposited using the in-situ sol-gel CHFMMR is approximately three times smaller and significantly different from the one shown in Fig. 6. 5. This may be due to the fact if the BYS growth is space constricted or is free during the calcination process. It is likely that the growth of BYS particles in the hollow fibre was dominated by two-dimensional island formation due to the confined space of the hollow fibre.
However, when the calcination of BYS was carried out in free surrounding (Fig. 6.5), bigger particle size was formed due to the three dimensional island formation [28].

Fig. 6. 11 Hi-RES SEM images of in-situ sol-gel coated BYS inside the membrane microchannels: (a) thin catalytic coating inside the membrane microchannels and (b) thickness of the nano-layer BYS coating

Fig. 6. 12 shows the pore size distributions of the micro-structured LSCF hollow fibre membranes before and after BYS catalyst deposition. In the fresh fibres, two main pore size distributions that corresponding to dead-pores throughout the sponge-like structure ($D_p = 1$-$5 \mu m$) and the entrance of the conical-shaped microchannels ($D_p = 5$-$100 \mu m$) were observed.
After the deposition of BYS inside the conical-shaped microchannels, the pore size distribution was seen to move to a smaller side and there is an addition of smaller pore size distribution between \( D_p = 0.2-1 \, \mu m \). These results indicate that there is a decrease in the volume of CHFMMR microchannels after the BYS deposition.

**Fig. 6.12** Pore size distribution of fresh LSCF hollow fibre and BYS-coated CHFMMR
6.3.3 OCM Performance of LSCF CHFMMR using different catalyst deposition techniques

Fig. 6. 13 (a) compares the calculated oxygen permeation across the CHFMMR during the OCM reaction. A mixture of CH₄ (75%) in argon of 42 ml.min⁻¹ was fed in the lumen side while 100 ml.min⁻¹ of air was maintained at the shell side of the CHFMMR. From Fig. 6. 13 (a and b), it can be seen that the oxygen permeation flux and methane conversion of both types of CHFMMRs were observed to enhance with temperatures. The in-situ sol-gel CHFMMR with less amount of catalyst shows higher oxygen permeation and methane conversion than those of the washcoat CHFMMR. At 900 °C, the sol-gel prepared CHFMMR showed oxygen flux up to 1.6 times higher than that of the washcoat CHFMMR. For OCM reaction over Bi₂O₃-based oxides with fluorite-type fcc phase structure, mobile lattice oxygen ions (O²⁻) is known to be the active sites for methane activation [7]. Therefore, smaller BYS particles allow more ionic oxygen taking part into the reaction, promoting oxygen permeation and as a result, higher methane conversion can be obtained. This phenomenon was not observed in the earlier FBR study (Fig. 6. 6) and in our previous work [18], when the BYS grain size is about 1 micron (Fig. 6. 5) and are considerably sintered. In addition, the thin and uniform BYS deposition in the in-situ CHFMMR improves the surface exchange kinetic rate and provides better oxygen mobility, thus further promotes the methane activation rate/surface methyl radical formation. This high reactivity of methane with oxygen could also leads to more oxygen consumption and consequently lowering the oxygen partial pressure in the reaction side [12]. Therefore, the driving force (oxygen concentration difference) across the membrane is improved, giving higher oxygen permeation. Such enhancement in oxygen permeation rate due to reaction and catalyst applications were also observed by many other researchers [15, 29-31]. In addition,
the high reaction activity in the membrane downstream can also cause a shift of the electronic
transport in BYS from p-type to n-type, leading to a significantly higher oxygen permeation flux
[22]. As methane conversion efficiency was found to be mainly controlled by the oxygen
permeation rate [32], the increase in oxygen permeation rate of the sol-gel prepared CHFMMR
instinctively led to an increase in its methane conversion. At 900 °C, a methane conversion of
57% was achieved by the sol-gel prepared CHFMMR in comparison to 39%, achieved using
the washcoat CHFMMR.

Fig. 6. 13(c) show the C\textsubscript{2+} selectivity of the in-situ prepared and washcoat CHFMMR, as a
function of temperature. The C\textsubscript{2+} selectivity increases with temperature. However, the C\textsubscript{2+}
selectivity of the in-situ sol-gel CHFMMR was much lowered than the washcoat CHFMMR.
This is related to the excess supply of oxygen inside the sol-gel CHFMMR. As the oxygen
permeation rate across the membrane increases, the deep oxidation reaction could take place
leading to lower C\textsubscript{2+} selectivity. Almost zero gaseous oxygen was observed in the product
streams of the sol-gel prepared CHFMMR in comparison to the washcoat CHFMMR. This
indicates that the permeated oxygen was fully consumed for both selective and non-selective
oxidations of methane and C\textsubscript{2+} products in the in-situ CHFMMR. Due to the same amount of
methane provided to both CHFMMRs, higher oxygen from the in-situ design indicated a higher
ratio between oxygen and methane than the washcoat design. As a result, from the point of
improving the C\textsubscript{2+} selectivity, more methane or less catalyst are suggested.

Due to the lower selectivity and higher conversion than those in the washcoat design,
comparable C\textsubscript{2+} yield is obtained for both CHFMMRs (Fig. 6. 13(d)). The C\textsubscript{2+} yield observed
for both reactors was almost similar at lower temperatures, but at temperature above 750 °C, the C\textsubscript{2+} yield obtained by the sol-gel prepared CHFMMR was slightly higher. Both reactors can achieve C\textsubscript{2+} yield between 25- 35% when the operating temperature was above 850 °C. From the reaction kinetics, it is possible to further increase the C\textsubscript{2+} yield, by matching the oxygen permeation rate across the membrane with surface catalytic activation of methane on the membrane surface, since the overall C\textsubscript{2+} yield is determined by the combined effects of both important factors [19, 30]. Therefore, it is essential to improve the surface catalytic activation of methane in parallel with the increase in the oxygen permeation rate.

Residence times can significantly affect the OCM performances due to the consecutive oxidations of hydrocarbon products into CO\textsubscript{x}. In order to increase the C\textsubscript{2+} selectivity of in-situ sol-gel prepared CHFMMR, higher flow rate of reactant (a mixture of methane and argon) at fix methane concentration was used and the results are shown in Fig. 6. 14. In general, it can be seen that the C\textsubscript{2+} selectivity (Fig. 6. 14(a)) and methane conversion (Fig. 6. 14(b)) were greatly affected by the residence times in comparison with the C\textsubscript{2+} yield. A significant increase in the C\textsubscript{2+} selectivity from 61.5% to 79.5 % at 900°C was observed when the residence time was decreased. The increase in the C\textsubscript{2+} selectivity was due to shorter contact time between the intermediate products with the oxygen, thus preventing the non-selective oxidation reactions toward CO\textsubscript{x}. On the other hand, shorter residence times can lead to a decrease in methane conversion (Fig. 6. 14(b)), due to the decrease in reaction probability on the catalyst surface. Besides that, there is a high possibility where the reactant gasses could not achieved the optimum temperature inside the heated CHFMMR, when higher reactant flow rates were used [16]. Although methane conversion was observed to be slightly reduced when shorter
residence time is used, it is still higher than washcoat design with more BYS (Fig. 6. 13(b)). The significantly improved selectivity of the in-situ sol-gel CHFMMR compared with the washcoat CHFMMR proves our earlier discussion (Fig. 6. 13). The residence time was observed to have greater effect on the C$_{2+}$ selectivity than the methane conversion. From the C$_{2+}$ yield plot (Fig. 6. 14(c)), it can be observed that both CHFMMRs have similar C$_{2+}$ yield and at higher temperatures, a slight increase in yield was observed, achieving 39 % at 900 °C. Fig. 6. 14 (d) shows the oxygen permeation rate across the CHFMMRs at different residence times. The oxygen permeation rate was observed to increase slightly when a shorter residence time was used. This is because the increasing of reactant flow rate can leads to the increase of the driving force and thus, higher oxygen permeation rate was obtained. The in-situ design CHFMMR was found to give higher oxygen permeation and therefore, it is important to match this oxygen permeation rate with the OCM reaction rate in order to circumvent the deep oxidation reaction that could diminish the final C$_{2+}$ yield [19, 30].

As the amount of BYS deposited using the sol-gel technique was different from the washcoat technique, the C$_{2+}$ productivity rate was then used to compare the performance between both CHMMRs. From Fig. 6. 15, it is obvious that C$_{2+}$ productivity rate of the in-situ sol-gel prepared CHFMMR was extremely high especially at temperature above 750 °C, although the amount of BYS catalyst deposited inside the microchannels was 3 times lowered than that of the washcoat CHFMMR. This further indicates that smaller BYS particle size (< 100 nm) would contribute to higher efficiency of OCM due to the high accessibility of reactants towards lattice/active site of the uniform BYS catalytic layer, which favours methane and ethane activation.
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Fig. 6. 13 Comparison of (a) oxygen permeation, (b) methane conversion, (c) C$_{2+}$ selectivity and (d) C$_{2+}$ yield of in-situ sol-gel (•) and washcoat (■) CHFMMRs
Fig. 6. 14 Effects of reactant flow rates on (a) C₂⁺ selectivity, (b) methane conversion, (c) C₂⁺ yield and (d) oxygen permeation of in-situ CHFMMR: (● - \( F_{\text{lumen}} = 42 \text{ ml.min}^{-1} \) and ○ - \( F_{\text{lumen}} = 63 \text{ ml.min}^{-1} \))
Chapter 6
An Oxygen Permeable Membrane Microreactor with an In-situ Deposited Bi$_{1.5}$Y$_{0.3}$Sm$_{0.2}$O$_{3-δ}$ Catalyst for Oxidative Coupling of Methane

Fig. 6. 15 $C_2^+$ productivity rate of washcoat (■) and in-situ sol-gel CHFMMRs at different reactant flow rates: (● - $F_{lumen} = 42$ ml·min$^{-1}$ and ■ - $F_{lumen} = 63$ ml·min$^{-1}$)

6.4 Conclusions

The micro-structured functional LSCF hollow fibre prepared using a fingering induced phase inversion process was successfully used as a membrane for oxygen separation and simultaneously as a substrate for the deposition of BYS catalyst in the development of CHFMMR for OCM. The in-situ sol-gel prepared CHFMMR was observed to have a uniform nano-thickness coating of BYS catalyst inside the membrane microchannels unlike the washcoat CHFMMR where the washcoat catalyst was scatteredly dispersed. The oxygen permeation across the membranes and the final OCM performances were found to be significantly affected by the deposition of BYS catalyst. A maximum $C_2^+$ yield of 39% was obtained at 900 °C using the in-situ CHFMMR, which is the highest value reported so far to the best of our knowledge. A decrease in residence times was observed to give better $C_2^+$
selectivity achieving a maximum value of 79%. The C$_2^+$ productivity rate of the in-situ design CHFMMR was observed to be nearly four times higher than that observed in the washcoat CHFMMR due to the better accessibility of reactants towards lattice/active site of the uniform BYS catalytic layer, which favours the OCM activity.

6.5 References


Chapter 6
An Oxygen Permeable Membrane Microreactor with an In-situ Deposited Bi1.5Y0.3Sm0.2O3-δ Catalyst for Oxidative Coupling of Methane


[18] N.H. Othman, Z. Wu, K. Li, A micro-structured La0.6Sr0.4Co0.2Fe0.8O3-δ hollow fibre membrane reactor for oxidative coupling of methane, Journal of Membrane Science, 468 (2014) 31-41.


Chapter 6  An Oxygen Permeable Membrane Microreactor with an In-situ Deposited Bi$_{1.5}$Y$_{0.3}$Sm$_{0.2}$O$_{3-δ}$ Catalyst for Oxidative Coupling of Methane


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CHAPTER 7

Overall Research Conclusions and Recommendations for Future Work

7.1 General conclusions

This thesis focuses on the fabrication of micro-structured functional ceramic hollow fibre membrane that can be used as a catalytic hollow fibre membrane reactor (CHFMR) for methane conversion processes particularly partial oxidation of methane (POM) and oxidative coupling of methane (OCM). With an aim to improve the oxygen permeation rate and better contact between oxygen and methane, a dense oxygen permeable membrane reactor with two different microstructure designs was developed. The first design involves the development of ceramic hollow fibre membranes with dual functional layers, i.e. an outer oxygen separation layer and an inner catalytic substrate layer (DL-CHFMR) using a novel single step membrane fabrication process, i.e. a co-extrusion and co-sintering process. The second design involves the development of functional ceramic hollow fibre membranes with an outer dense oxygen separation layer integrated with a porous layer, consisting of a plurality of conical-shaped microchannels open at the inner surface using a fingering induced phase inversion process to form a catalytic hollow fibre membrane microreactor (CHFMMR). In this work, the possibility
of achieving higher products yields using such membrane reactor designs have been demonstrated.

7.2 Major findings

7.2.1 Fabrication of BYS based dual layer catalytic hollow fibre membrane reactor (DL-CHFMR)

In chapter 3, a micro-structured catalytic hollow fibre membrane reactor with two functional layers, i.e. an outer oxygen separation layer and an inner catalytic substrate layer was developed as a dual-layer catalytic hollow fibre membrane reactor (DL-CHFMR) and used for oxidative methane conversion processes such as POM and OCM. As an objective to promote oxygen permeation, Bi$_{1.5}$Y$_{0.3}$Sm$_{0.2}$O$_{3-δ}$ (BYS) was used both in the outer oxygen separation layer and in the inner catalytic substrate layer. However, the insufficient chemical stability of BYS in the strong reducing atmosphere of POM resulted in changes of BYS structure and consequently catalytic activity of the inner layer. This leads to a decrease in the POM performance of the DL-CHFMR. The advantages of such reactor design, however, has been proved and can be transferred to other important catalytic reactions, where no strong reducing environment is required. As BYS was observed to have excellent catalytic activity particularly for OCM, it can be used as catalyst and membrane materials in the further membrane reactor development.
7.2.2 Fabrication of micro-structured BYS catalyst

In chapter 4, BYS, a ceramic material showing great activity and selectivity to oxidative coupling of methane (OCM), was fabricated into catalyst rings (i.e. capillary tubes) with a plurality of self-organised radial microchannels. A modified combined phase inversion and sintering process also known as a fingering induced phase inversion, was employed in the fabrication of the micro-structured BYS catalyst rings. The unique microchannels inside such BYS catalyst rings allow easier access of reactants, as well as increased the surface area per reaction volume, which contributes to higher reaction efficiencies due to the improvement in mass transfer. A remarkable improvement in $C_2^+$ yield ($Y_{C_2^+} > 20\%$) was obtained in the monolith-like structured reactor compared to fixed bed reactor configuration, which proves the advantages of using a micro-structured catalyst with an ideal flow in the feed for OCM.

7.2.3 Fabrication of micro-structured LSCF catalytic hollow fibre membrane

In Chapter 5, an enhancement of oxygen permeation flux of the frequently used $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3-\delta$ (LSCF) membrane was achieved by modifying the membrane microstructure. An asymmetric LSCF hollow fibre membrane, which consist of conical-shaped microchannels open at the inner surface and an outer dense oxygen separation layer has been developed via a fingering induced phase inversion technique, using different bore fluids. The use of these solvent-based bore fluids results in different membrane microstructures, such as dimensions of the conical-shaped microchannels and thickness ratios between the inner layer with such microchannels and the outer dense separation layer. Apart from the
substantially reduced resistance across the membrane, the microchannels act as a structured substrate where catalyst can be deposited for the catalytic reaction to take place.

### 7.2.4 OCM performance of the micro-structured LSCF catalytic hollow fibre membrane reactor

In Chapter 5, a catalytic hollow fibre membrane microreactor (CHFMMR), which employs an asymmetric micro-structured LSCF hollow fibre, has been used for oxidative coupling of methane (OCM). The micro-structured functional LSCF hollow fibre was used as a membrane for oxygen separation and as a substrate for the deposition of BYS catalyst to further increase the catalytic properties of the ceramic hollow fibre membrane reactor. Commercial BYS powders were incorporated inside the membrane microchannels via a washcoating technique to form the CHFMMR. In order to address the advantages of such microreactor design, the OCM performance of CHFMMR was then compared with a fixed bed reactor (FBR) and a packed hollow fibre membrane reactor (PBHFMR), where the same BYS catalyst was packed outside the hollow fibre membrane. The performance of CHFMMR was found to be substantially improved due to the thin oxygen separation layer, great mass transfer inside microchannels where BYS catalyst was coated and efficient delivery of both dissociated and ionized oxygen directly from membrane towards the reaction sites, which favourable in forming $\text{C}_2^+$ and therefore improved $\text{C}_2^+$ yield. This study further proves that the efficient route to promote the efficiencies CHFMMR is by uniformly dispersing a small amount catalyst inside the micro-structured ceramic hollow fibre membranes.
7.2.5 Fabrication of catalytic hollow fibre membrane microreactor (CHFMMR) using in-situ sol-gel deposition of BYS

In Chapter 6, an in-situ sol-gel approach was used to deposit BYS inside the micro-structured functional LSCF hollow fibre membrane forming a CHFMMR. A nano-thickness BYS catalytic layer (300-500 nm) was successfully deposited onto the microchannels wall throughout the whole hollow fibre. The difference in the OCM performances between the in-situ sol-gel prepared CHFMMR and the washcoated CHFMMR are outlined. It was found that the performance of such CHFMMR was strongly dependent on the properties of the BYS and the OCM reaction conditions. Higher oxygen permeation rate and methane conversion were observed when the particle size of BYS was reduced drastically from micron-sized (commercial powder) to nano-sized (in-situ sol-gel) and uniformly dispersed onto the microchannels. A decrease in residence time was observed to give a better \( \text{C}_2^+ \) selectivity of 79% and \( \text{C}_2^+ \) yield achieving a maximum value of 39% at 900 °C. To the best of our knowledge, the \( \text{C}_2^+ \) yield obtained in this study is the highest value reported so far. The \( \text{C}_2^+ \) productivity rate of the in-situ design CHFMMR was observed to be nearly four orders of magnitude higher than that obtained in washcoated CHFMMR due to the better accessibility of reactants towards lattice/active site of the uniform BYS catalytic layer. In order to achieve great \( \text{C}_2^+ \) yield for such a reactor design, the oxygen permeation flux and OCM reaction rate need to be well matched.
7.3 Recommendations for Future Work

Oxidative coupling of methane into C₂⁺ has been widely investigated by researcher around the world, including several renowned companies such as Union Carbide and Arco since 1980s, but none has been commercialized due to the low C₂⁺ yield. A minimum C₂⁺ yield of 30% is required to attain commercial competitiveness OCM [1, 2]. However, a recent progress on OCM catalyst by Siluria Technologies has reported encouraging results at the pilot scale and they are currently developing a demonstration plant for OCM in Texas [3]. In this study, the developed La₀.₆Sr₀.₄Co₀.₂Fe₀.₈O₃₋δ (LSCF) CHFMRR using Bi₁.₅Y₀.₃Sm₀.₂O₃₋δ (BYS) catalyst has showed promising performance achieving C₂⁺ yield of 39% by fine-tuning the operating conditions. In order for such reactor to be viable for scale up, several further steps suggested as below can be taken in order to improve the overall performance of CHFMRR:

7.3.1 Development of micro-structured LSCF hollow fibre membrane

In this study, a highly micro-structured LSCF with an open microchannels and a thin dense oxygen separation layer was successfully produced using a combined phase inversion and sintering process by employing solvent as bore fluid. The microchannels properties and the thickness of dense separation layer were determined by the bore fluid types and compositions. Therefore, by varying these parameters, the dimensions of the conical shaped microchannels and the thickness ratio between the microchannels and dense separation layer can be varied independently depending on the catalyst properties, thus eliminating the ‘over/under designed’ catalyst substrate. Due to generic advantages of such membrane fabrication technique, new
ceramic materials that possess higher oxygen permeation and better stability in methane conversion processes, with a possibility to operate at lower temperatures can be used in the future development of micro-structured hollow fibre membrane.

7.3.2 Development of catalytic hollow fibre membrane microreactor (CHFMMR)

In this work, BYS was observed not only to provide the OCM catalytic activity towards the membrane but would also lead to significant improvement in the oxygen permeability due to the enhancement of surface exchange kinetics that is normally limiting the oxygen transport in the hollow fibre membrane. However, if the amount of oxygen permeate across the membrane is too high, it could lead to a decrease in OCM performance due to the deep oxidation of products. Therefore, further research in investigating the effect of BYS catalytic layer thickness inside the microchannels towards the oxygen permeation and OCM activity should be carried out. A more detail study on the sol-gel approach used for the in-situ deposition of BYS catalyst onto the CHFMMR microchannels should be carried out in order to gain full control on the thickness and properties of the catalytic layer. Besides that, stability studies on the BYS catalyst deposited inside the membrane microchannels are very important to estimate the CHFMMR lifetime. Due to generic advantages of such CHFMMR design, incorporation of other selective catalyst for OCM such as Li/MgO [4] and Na-W-Mn/SiO₂ [5] can be considered in the future development of CHFMMR.
7.3.3 Catalytic hollow fibre membrane microreactor (CHFMMR) stability and durability studies

In order to integrate the CHFMMMR technology into practice, long-term stability test (>1000 hours) under actual reaction conditions and other reducing gases such as H₂ should be carried out. Besides that, the stability tolerance of the CHFMMR should also be observed in the presence of poisoning trace compounds such as CO₂ and H₂O to ensure it complies with the industrial operating conditions. The CHFMMR should also be robust when operated over a wide range of operating conditions without performance loss. Further examination on thermo-mechanical properties of CHFMMR such as creep, stiffness and thermal expansion coefficients is needed. This step is crucial especially to ensure its applicability for operating conditions involving severe heating and cooling cycles. Other engineering issues such as the sealing of the membrane especially at high temperature need to be further improved to ensure nitrogen free environment in the CHFMMR.

7.3.4 Reactor modelling

OCM is known to be strongly dependent on reaction conditions. Therefore, a series of experiment needs to be carefully designed in order to investigate the effects of reaction conditions such as temperature, gas hour space velocity (GHSV), methane concentration, pressure. Further improvement on reaction setup is required in order to increase the sensitivity analysis of the OCM reaction. The reaction setup should include equipment such as multipoint thermocouple to measure both axial and radial heat rise during the reaction, backpressure
regulator and etc.. In this work, the reaction was carried out at atmospheric pressure. However, for commercial applications, it necessary to perform the OCM reaction at elevated pressure in order to reduce the size of reactor and economically favours the product separation and further energy saving. Besides that, most of the ethylene-related processes are operated at elevated pressure \[6\]. Reaction modelling can be used to evaluate the behaviour and performance of CHFMMR and by the theoretical simulations, the advantages and possible problems during the real reaction can be avoided. A detailed study in understanding the reactant flow distribution, particularly in the conical shaped microchannels should be carried out using mathematical modelling in order to understanding its influence in enhancing the reaction performance. Other than membrane reactor design, the efficiency of CHFMMR depends on the activity of the catalyst and its reaction kinetics. Therefore, more detailed study on the kinetics and reaction mechanism (hetero-homogeneous) of OCM when LSCF CHFMMR and BYS catalyst are used, should be carried out. Several established techniques that can be used are dynamic x-ray diffraction, isotopic transient kinetics and temporal analysis of products (TAP) can be used. The heat transfer across the membrane is considered negligible in this study due to the small reactor volume. However, in order to put this process into practice, it is important to investigate the effects of heat transfer especially during the reactor scale up. One \[7\] or two-dimensional \[8, 9\] models can be adopted in order to predict the effects of temperature gradient and radial transportation method, which could be not negligible in a large-scale membrane reactor.
7.4 References


APPENDIX A

List of notations and symbols

F-T   Fisher-Tropsch
POM   Partial oxidation of methane
OCM   Oxidative coupling of methane
SMR   Steam methane reforming
ESR   Ethanol steam reforming
LNG   Liquefied natural gas
SOFC  Solid oxide fuel cells
OSD   Oxygen sorption and desorption
MR    Membrane reactor
FBR   Fixed bed reactor
DL-CHFMR Dual-layer catalytic hollow fibre membrane reactor
PBHFMR Packed bed hollow fibre membrane reactor
CHFMMR Catalytic hollow fibre membrane microreactor
CMR   Catalytic membrane reactor
HFMR  Hollow fibre membrane reactor
MMR   Membrane microreactor
MIEC  Mixed ionic electronic conducting
CH₄   Methane
CO    Carbon monoxide
CO₂   Carbon dioxide
H₂    Hydrogen
O₂    Gaseous Oxygen
C₂H₆  Ethane
C₂H₄  Ethylene
Appendix A

List of notations and symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>A mixture of carbon monoxide and carbon dioxide</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>A mixture of ethane and ethylene</td>
</tr>
<tr>
<td>N₂</td>
<td>Nitrogen</td>
</tr>
<tr>
<td>Ar</td>
<td>Argon</td>
</tr>
<tr>
<td>MIEC</td>
<td>Mixed ionic and electronic conductive materials</td>
</tr>
<tr>
<td>ABO₃</td>
<td>Perovskite</td>
</tr>
<tr>
<td>A₂B₂O₅</td>
<td>Brownmillerite</td>
</tr>
<tr>
<td>Aₙ₊₁BₙO₃n+₁</td>
<td>Ruddlesden-Popper</td>
</tr>
<tr>
<td>Bi₁.₅Y₂.₃Sm₀.₂O₃-δ (BYS)</td>
<td>Bismuth yttrium samarium oxide</td>
</tr>
<tr>
<td>La₀.₆Sr₀.₄Co₀.₂Fe₀.₈O₃-δ (LSCF)</td>
<td>Lanthanum strontium cobalt iron oxide</td>
</tr>
<tr>
<td>ScSZ</td>
<td>Scandia stabilized zirconia</td>
</tr>
<tr>
<td>YSZ</td>
<td>Yttria stabilized zirconia</td>
</tr>
<tr>
<td>NiO</td>
<td>Nickel oxide</td>
</tr>
<tr>
<td>Ni</td>
<td>Nickel</td>
</tr>
<tr>
<td>PESf</td>
<td>Polyethersulfone</td>
</tr>
<tr>
<td>PVP</td>
<td>Poly(vinylpyrrolidone)</td>
</tr>
<tr>
<td>DMSO</td>
<td>Dimethyl sulfoxide</td>
</tr>
<tr>
<td>NMP</td>
<td>N-methylpyrrolidone</td>
</tr>
<tr>
<td>EtOH</td>
<td>Ethanol</td>
</tr>
<tr>
<td>DI</td>
<td>Deionised</td>
</tr>
<tr>
<td>Bi(NO₃)₃·5H₂O</td>
<td>Bismuth (III) nitrate pentahydrate</td>
</tr>
<tr>
<td>Y(NO₃)₃·4H₂O</td>
<td>Yttrium (III) nitrate tetrahydrate</td>
</tr>
<tr>
<td>Sm(NO₃)₃·6H₂O</td>
<td>Samarium (III) nitrate hexahydrate</td>
</tr>
<tr>
<td>C₆H₈O₇</td>
<td>Citric acid</td>
</tr>
<tr>
<td>C₂H₆O</td>
<td>Ethylene glycol</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction XRD</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
</tr>
<tr>
<td>SE</td>
<td>Scattered electron</td>
</tr>
<tr>
<td>BSE</td>
<td>Back-scattered electron</td>
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<table>
<thead>
<tr>
<th>Notation</th>
<th>Definition</th>
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</thead>
<tbody>
<tr>
<td>FEGSEM</td>
<td>Field emission gun scanning electron microscope</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller</td>
</tr>
<tr>
<td>TCD</td>
<td>Thermal conductivity detector</td>
</tr>
<tr>
<td>FID</td>
<td>Flame ionisation detector (FID)</td>
</tr>
<tr>
<td>GHSV</td>
<td>Gas hour space velocity</td>
</tr>
<tr>
<td>$\bullet CH_3$</td>
<td>Methyl radical</td>
</tr>
<tr>
<td>$O_2^-$</td>
<td>Lattice oxygen ions</td>
</tr>
<tr>
<td>$h^+$</td>
<td>Positive electron holes</td>
</tr>
<tr>
<td>$k_c$</td>
<td>Reaction constant</td>
</tr>
<tr>
<td>$O_2^{2-}$</td>
<td>Superoxide oxygen ions (adsorbed)</td>
</tr>
<tr>
<td>$V_0^{\bullet}$</td>
<td>Oxygen vacancy</td>
</tr>
<tr>
<td>$3-\delta$</td>
<td>Non-stoichiometry oxygen</td>
</tr>
<tr>
<td>$SA/V$</td>
<td>Surface to volume ratio</td>
</tr>
<tr>
<td>$n_i$</td>
<td>Number of carbon atoms in species $i$</td>
</tr>
<tr>
<td>$J_O2$</td>
<td>(ml·min$^{-1}$·cm$^{-2}$) Oxygen permeation flux</td>
</tr>
<tr>
<td>$V_f$</td>
<td>(ml·min$^{-1}$) Flowrate of the effluent stream</td>
</tr>
<tr>
<td>$X_{O2}$</td>
<td>(%) Oxygen concentration</td>
</tr>
<tr>
<td>$A_m$</td>
<td>(cm$^2$) Effective membrane area</td>
</tr>
<tr>
<td>$X_{CH4}$</td>
<td>(%) Methane conversion</td>
</tr>
<tr>
<td>$S_i$</td>
<td>(%) Selectivity of species $i$</td>
</tr>
<tr>
<td>$F_{CH4}$</td>
<td>(mol·min$^{-1}$) Flow rates of methane</td>
</tr>
<tr>
<td>$F_j$</td>
<td>(mol·min$^{-1}$) Flow rates of product $j$</td>
</tr>
<tr>
<td>$Y_j$</td>
<td>($\mu$mol·min$^{-1}$·gcat$^{-1}$) Productivity rate of $j$</td>
</tr>
<tr>
<td>$M_{cat}$</td>
<td>(g) Mass catalyst</td>
</tr>
<tr>
<td>$P$</td>
<td>(mol·m$^{-2}$·s$^{-1}$·Pa$^{-1}$) Gas permeance</td>
</tr>
<tr>
<td>$V$</td>
<td>(m$^3$) Volume of the test compartment</td>
</tr>
<tr>
<td>$R$</td>
<td>(J·mol$^{-1}$·K$^{-1}$) Gas constant</td>
</tr>
<tr>
<td>$T$</td>
<td>(K) Measured temperature</td>
</tr>
<tr>
<td>$P_0$</td>
<td>(Pa) Initial measured pressures</td>
</tr>
<tr>
<td>Symbol</td>
<td>Unit</td>
</tr>
<tr>
<td>--------</td>
<td>------</td>
</tr>
<tr>
<td>$P_t$</td>
<td>(Pa)</td>
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<tr>
<td>$P_a$</td>
<td>(Pa)</td>
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<td>$L$</td>
<td>(m)</td>
</tr>
<tr>
<td>$t$</td>
<td>(s)</td>
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APPENDIX B

Additional published works by the author relevant to the thesis but not forming part of it.

Effects of Fabrication Processes on Oxygen Permeation of Nb$_2$O$_5$-doped SrCo$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ Micro-Tubular Membranes

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Abstract

In this study, Nb$_2$O$_5$-doped (0.5 wt.%) SrCo$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ (SCFNb0.5), an oxide of perovskite structure that is chemically and structurally stable for oxygen separation between 550 and 900 $^\circ$C [1], has been used to fabricate two types of micro-tubular membranes, i.e. an asymmetric hollow fibre membrane (SCFNb0.5-HF) and a symmetric capillary membrane (SCFNb0.5-C), using a combined phase inversion and sintering process and plastic extrusion method, respectively. The asymmetric SCFNb0.5-HF membrane is designed to consist of a thin and dense oxygen separation layer (approximately 62 µm) supported on a porous finger-like layer...
(around 415 µm) of the same material, with a highly porous inner surface for a significantly reduced mass transfer resistance during oxygen permeation. The separation layer of the symmetric SCFNb0.5-C is approximately 436 µm. Besides characterizations on membrane structures, oxygen permeations of the two membranes were measured and compared, and linked to the effects of fabrication processes on membrane performance. Further suggestions are also outlined for the future fabrication of ceramic hollow fibre membranes using the combined phase inversion and sintering technique, especially when ceramic materials with complex compositions are employed.

**Keywords:** Asymmetric hollow fibre membrane, symmetric capillary membrane, oxygen permeation, perovskite structure, mixed-conducting ceramics

1. **Introduction**

Use of ceramic membranes fabricated from materials with a unique mixed ionic-electronic conducting (MIEC) property for the separation or production of highly purified oxygen has been of great interest [2-5], due to a number of advantages over conventional techniques. In the last several decades, considerable efforts have been carried out to develop new membrane materials with higher oxygen permeation at possibly lower operating temperatures, together with better thermal and chemical stabilities.

In terms of MIEC materials with the perovskite or perovskite-related structures, the trade-off between oxygen permeation and stabilities has been widely investigated. It has also been
acknowledged that, although the presence of Co with variable valencies significantly facilitates the migration of oxygen, resulting in higher oxygen permeation flux, it is the major reason for the reduced membrane stability at low oxygen partial pressures or at the presence of reducing species such as H₂. The development of MIEC ceramics free of Co effectively improves the material stability [6-16], but accompanied with substantial drops in oxygen permeation flux. As a result, improved stability of MIEC ceramics containing Co is still of great interest and importance.

SrCo₀.₈Fe₀.₂O₃₋δ(SCF) is a typical MIEC ceramic with high oxygen permeation but low tolerance to small oxygen partial pressures or reducing gases [17-21], mainly due to the high concentration of Co. The phase transition from perovskite to brownmillerite structure also substantially decreases oxygen permeation at lower temperatures. Partially substituting the B-site elements of SCF, especially Co, by elements with fixed valence such as Al, Zr, Ti and Nb suppresses the change in oxygen stoichiometry [22-25], and as a result, lowers the thermal and chemical expansion of the materials for better membrane stability. But the lowered oxygen mobility and vacancy concentration also decrease ionic conductivity and oxygen permeation as a consequence. Another way to stabilize the perovskite structure of SCF is to use a secondary stable ceramic phase such as Al₂O₃, ZrO₂, TiO₂, as an effort to suppress the occurrence of the order-disorder phase transition of SCF (at low oxygen partial pressures) by the inter-dissolved oxides [17, 26, 27]. However, the solid-state reactions between SCF and the secondary phase with very limited solubility results in the formation of an additional impurity phase, such as CoAl₂O₄, SrZrO₃ and SrTiO₃, respectively, which lowers oxygen permeation. Recently, Zhang et. al. [1] have developed a series of SrCo₀.₈Fe₀.₂O₃₋δ-Nb₂O₅...
composite materials using solid-state reaction method and systematically investigated the
effects of doped Nb$_2$O$_5$ on the crystal structure, thermal and chemical expansion, electrical
conductivity and oxygen desorption behaviour etc. of the material. The doped Nb$_2$O$_5$ of up to
10 wt.% was completely incorporated into SCF and effectively suppressed the formation of
orthorhombic phase in the bulk cubic SCF, and the perovskite-brownmillerite transition at low
oxygen partial pressures. Besides the consistent cubic perovskite structure at various low
oxygen partial pressures and temperatures, the doping of 0.5 wt.% Nb$_2$O$_5$ resulted in the
smallest cell parameters, the lowest thermal expansion, and more importantly the oxygen
permeation higher than SCF [1].

Besides the progress in new MIEC materials, more versatile membrane fabrication techniques
have also been developed to enhance membrane area per unit volume. A combined phase
inversion and sintering process has been used for fabricating various ceramic hollow fibre
membranes (A$_2$O$_3$, YSZ, La$_{0.8}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3-δ}$ etc.) with controllable asymmetric structures
to escalate oxygen permeation flux of MIEC membranes [28]. Another way of fabricating MIEC
membranes of similar dimensions is plastic extrusion method [29]. The capillary membranes
made in this way are normally of a symmetric structure.

In this study, SCF doped with 0.5 wt.% of Nb$_2$O$_5$ (SCFNb0.5) is employed to fabricate two
types of micro-tubular membranes, i.e. asymmetric hollow fibre membrane and symmetric
capillary membrane, for oxygen separation, using a combined phase inversion and sintering
technique [28] and plastic extrusion technique [29], respectively. In addition to the
characterizations of membrane structures and oxygen permeation, more efforts have been
placed to understand the effects of membrane fabrication process on membrane performances.

2. Experimental

2.1 Materials

Sr(NO$_3$)$_2$, Co(NO$_3$)$_2$.6H$_2$O, Fe(NO$_3$)$_3$.9H$_2$O, EDTA, NH$_4$OH and citric acid (C$_6$H$_8$O$_7$.H$_2$O) were used to prepare SrCo$_{0.8}$Fe$_{0.2}$O$_3$-$\delta$ (SCF), prior to being mixed with Nb$_2$O$_5$ for preparing Nb$_2$O$_5$(0.5 wt.%)-doped SrCo$_{0.8}$Fe$_{0.2}$O$_3$-$\delta$ (SCFNb0.5) powder using solid-state reaction method. Polyethersulfone, (PESf, Radel A-300, Ameco Performance, USA), N-methyl-2-pyrrolidone (NMP, HPLC grade, Rathbone) and Arlacel P135 (Uniqema, UK) were used as polymer binder, solvent and additive, respectively, when fabricating hollow fibre membranes. Either DI water/tap water or ethanol (VWR International S.A.S, > 99.7%) were used as the internal and the external coagulants.

2.2 Fabrication of SCFNb0.5 powder

SrCo$_{0.8}$Fe$_{0.2}$O$_3$-$\delta$ (SCF) was first prepared by dissolving determined amounts of Sr(NO$_3$)$_2$, Co(NO$_3$)$_2$.6H$_2$O, Fe(NO$_3$)$_3$.9H$_2$O, EDTA and citric acid (C$_6$H$_8$O$_7$.H$_2$O) into water, followed by adjusting the pH value to 6-7 using NH$_4$OH. The solution was thermally treated at 250 °C for
5 h to form green powder. SCF powder was obtained by calcining the green powder at 900 °C for 5 h, followed by intensive grindings. Nb$_2$O$_5$ (0.5 wt.%)-doped SrCo$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ (SCFNb0.5) was prepared by ball milling SCF and Nb$_2$O$_5$ in ethanol for 24 h, followed by drying at 80 °C prior to another calcination at 900 °C for 5 h.

2.3 Fabrication of SCFNb0.5 micro-tubular membranes

2.3.1 Fabrication of asymmetric SCFNb0.5-HF membrane

The SCFNb0.5 hollow fibre membrane was fabricated using a combined phase inversion and sintering technique, in which the preparation of spinning suspensions has been described elsewhere [30]. Typically, a pre-determined amount of ceramic powder was first mixed with a mixture of solvent and dispersant using a customized jar miller (Gladstone Engineering, UK). After 72 hours, the polymer binder was added, followed by another continuous milling of 48 hours, ensuring the uniformity of the suspension. The uniform spinning suspension was fully degassed (under vacuum with stirring) prior to being transferred to a stainless steel syringe of 200 ml, with the internal coagulant (DI water or ethanol) in another syringe of the same size. The extrusion rate of the spinning suspension as well as the flow rate of the internal coagulant was accurately controlled and monitored by two Harvard PHD 22/2000 Hpsi syringe pumps, ensuring the uniformity of the prepared fibres. The spinning parameters and the composition of the spinning suspension are listed in Table 1. The formed precursor fibres were then cut into the required length, dried and straightened, and finally sintered at 1200 °C for 3 h, with the heating and cooling rates of 5 and 3 °C/min, respectively.
Table 1. Composition of the spinning suspension and spinning parameters

<table>
<thead>
<tr>
<th>Material</th>
<th>Concentration (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ceramic powder</td>
<td>68</td>
</tr>
<tr>
<td>PESf</td>
<td>6.8</td>
</tr>
<tr>
<td>NMP</td>
<td>24.7</td>
</tr>
<tr>
<td>Additive</td>
<td>0.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Spinning parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air gap (cm)</td>
<td>5</td>
</tr>
<tr>
<td>Extrusion rate (ml/min)</td>
<td>7</td>
</tr>
<tr>
<td>Internal coagulant (ethanol, ml/min)</td>
<td>10</td>
</tr>
<tr>
<td>External coagulant (ethanol, ml)</td>
<td>2000</td>
</tr>
</tbody>
</table>

2.3.2 Fabrication of symmetric SCFNb0.5-C membrane

SCFNb0.5 capillary membranes were fabricated using a conventional plastic extrusion process [29]. SCFNb0.5 powder was first mixed with additives such as polyvinyl alcohol (PVA), dextrin and tung oil in a pug mill under vacuum, to form a uniform slip with a proper plasticity. Such slip was then extruded through a die (OD=3.4, ID= 2.2 mm) to fabricate green membranes. The green membranes were dried, cut into a required length and calcined at 600 °C for 2 h with a heating rate of of 2 °C/min to remove the organic additives, before being sintered at 1200 °C for 5 h to obtain SCFNb0.5 capillary membranes.
2.4 Characterizations

X-ray diffraction (XRD) was used to investigate the crystal structure of the membrane material. Morphology and microstructure of the two micro-tubular membranes were visually observed using a scanning electron microscope (SEM, JEOL JSM-5610LV, Tokyo, Japan). EDS (JEOL, JSM6400) analysis was employed to determine the composition of membrane materials.

2.5 Measurement of oxygen permeation

Oxygen permeation was measured by using the set-up shown schematically in Figure 1. SCFNb0.5 micro-tubular membranes of 3 cm in length were sealed into two dense alumina tubes, positioned at the centre of a tubular furnace with a consistent heating zone of around 5 cm. The outer surface of the membrane was exposed to ambient air, while Ar as the sweep gas (approximately 26.9 ml/min) was directed through the lumen of the membrane and checked by a bubble flow meter. The outlet of the membrane was connected to an oxygen analyzer (SERVOMEX, 572) connected to a digital multimeter (DIGITEK, INO2513) and a workstation, in order to record the variation in oxygen concentration. The highest resolution of oxygen concentration is 0.01%. As a result, any gas leaking due to the possible imperfect high temperature sealing or membrane defects can be co-determined by the variation in sweep gas flow rate and abnormal changes in oxygen concentration. The change of oxygen concentration due to the oxygen permeation at different temperatures can thus be recorded, and used for the calculation of oxygen permeation flux. At every operating temperature, oxygen concentration of each membrane structure was continuously monitored for 30 minutes.
Repeated measurements showed consistent trend in oxygen permeation performance. From room temperature to 550 °C, only a tiny amount of oxygen can be detected in the sweep gas (Ar) (< 5.9×10^{-8} mol.cm^{-2}.s^{-1}). Such a low level of leaking is probably from the imperfection in high temperature sealing and the connections of the measuring system. Symmetric SCF Nb0.5-C membranes were test under the same conditions.

**Figure 1** Schematic presentation of the experimental set-up for oxygen permeation measurement
3. Results and discussion

3.1 Fabrication of SCFNb0.5-HF membrane – water as non-solvent

Besides Al₂O₃ hollow fibres [30], the combined phase inversion and sintering process has been employed frequently to fabricate MIEC hollow fibre membranes for oxygen separation [28, 31-33]. Generally, a uniform spinning suspension consisting of ceramic powder, solvent, polymer binder and additives is prepared, before being extruded through a tube-in-orifice spinneret. Meanwhile, another stream of internal coagulant (non-solvent) goes through the lumen of the fibre, forming the hollow fibre configuration. NMP and water are the most commonly used solvent and internal/external coagulants, respectively, in such membrane fabrication process. When the phase inversion processes is completed, the formed precursor fibre is still pliable, due to the presence of polymer binder.

However, when NMP and water were used to fabricate SCFNb0.5-HF membranes, the precursor fibre became extremely brittle within several minutes contacting with water, with a significant amount of white flakes segregated and covering the surface of the external coagulation bath. Further EDS analysis (Figure 2) revealed that there was a serious variation in the material composition. This is in agreement with the unusual formation of white flakes during the spinning process and the brittle precursor fibres.
XRD results also proves that the typical perovskite structure of the as prepared SCFNb0.5 powder (Figure 3 (a)) is almost destroyed after being in water for 24 h (Figure 3 (c), the sample was collected using filtering paper and dried prior to XRD, without any additional rinsing), while the white flakes in the external coagulation bath is SrCO$_3$ (Figure 3 (d)). All these phenomena indicate a strong interaction between SCFNb0.5 and water, which contributes to the substantial removal of Sr, and possible other elements, from the prepared membrane and consequently destroys the perovskite structure. Ceramic materials are considered normally to be chemically and thermally stable. To the best of our knowledge, such a strong change in
ceramic material composition and crystal structure when immersed in water has not been reported, especially in the field of ceramic membrane.

![XRD patterns](image)

**Figure 3** XRD patterns of (a) as prepared SCFNb0.5, (b) SCFNb0.5 powder in ethanol for 24 h, (c) SCFNb0.5 powder in water for 24 h and (d) SrCO3 from SCFNb0.5 hollow fibre using water as internal-/external-coagulants

### 3.2 Fabrication of SCFNb0.5-HF membranes – ethanol as non-solvent

Although water is one of the most popular non-solvents in the phase inversion process, it has to be replaced due to the strong interaction with SCFNb0.5. Ethanol is always used for the preparation of MIEC ceramics by using the solid-state reaction method [1, 34], and XRD
analysis (Figure 3 (b)) shows little changes of the perovskite structure of SCF Nb0.5 after being immersed in ethanol for 24 h. This indicates that ethanol can be used as both the internal and external coagulants, although the phase inversion process would be slower when compared with water. The spinning parameters of using ethanol as the non-solvent are listed in Table 1. As can be seen in Figure 4 (a), the fabricated SCF Nb0.5-HF membrane is of a typical asymmetric structure consisting of a thin sponge-like layer supported on a finger-like layer. The thickness of the outer layer was measured at approximately 62 µm, while the finger-like layer was 415 µm (Figure 4 (b)). After being sintered at 1200 °C for 3 h, the outer surface is fully densified (Figure 4 (c)), while the inner surface is still very porous (Figure 4 (d)). The outer separation layer is of a dense structure (Figure 4 (e)) and the finger-like voids are closely connected to the porous edge next to the inner surface (Figure 4 (f)). Besides the significantly thinner oxygen separation layer, the asymmetric morphology of this type significantly reduces the mass transfer resistance during oxygen permeation. The effective thickness of the oxygen separation layer, in this case, is same as the outer sponge-like layer (62 µm). And for the purpose of comparison, SEM images of symmetric capillary SCF Nb0.5 membrane (OD=2.24 mm, ID=1.57 mm) is shown in Figure 5, in which the effective separation layer is same as the tube wall of approximately 436 µm. The two surfaces are both dense (Figures 5 (c-d)), with much larger grain sizes than the asymmetric counterpart (Figure 4).
Figure 4 SEM images of asymmetric SCFNb0.5 hollow fibre membranes sintered at 1200 °C for 3 h (a) whole view, (b) cross section, (c) outer surface, (d) inner surface, (e) outer surface edge and (f) inner surface edge
Appendix B

Effect of Fabrication Processes on Oxygen Permeation of Nb:O-doped SrCoFe$_2$O$_{4.8}$ Micro-tubular Membranes

3.3 Oxygen permeation measurements

The temperature dependence of oxygen flux of SCFNb0.5 asymmetric hollow fibre membrane and symmetric capillary membrane is shown in Figure 6. As can be seen, oxygen permeation fluxes of the two SCFNb0.5 membranes keep increasing with increase of temperatures. When compared with the disk-type membrane [1] made from the material of the same composition, oxygen permeation of the symmetric SCFNb0.5 capillary membrane is quite low, even if its
thickness is around half of the counterpart. Further XRD confirmed that its material structure agreed well with the fresh powder. As a result, such a difference in oxygen permeation should be due to the different material fabrication processes, i.e. solid-state reaction method for disk type membrane and Pechini plus solid-state reaction method for the micro-tubular membranes in this study, different membrane fabrication processes and possible differences in measuring procedures, for example air is directed towards the feed side surface of disk type membranes while ambient air is used for capillary membranes in this study.

It can also be seen in Figure 6 that oxygen permeation of asymmetric SCFNb0.5-HF membrane is lower than the SCFNb0.5-C membrane, although its effective separation layer is substantially thinner (approximately 62 µm and 436 µm for SCFNb0.5-HF and SCFNb0.5-
C, respectively). Further XRD tests (Figure 7) proved that, although the sintered hollow fibre (ground into powder for the analysis) maintained a perovskite type structure, the peaks shifted towards higher 2-Theta values when compared with the as prepared powder, besides the formation of a small amount of a secondary phase. Such a change in the material structure should be due to the slight change in material compositions, which is in agreement with EDS analysis listed in Table 2. As can be seen, composition of the fresh powder is quite close to theoretical values, but quite different from the sintered hollow fibre membrane. As a result, the change in membrane material composition is considered to be the major reason for the low oxygen permeation flux of asymmetric SCFNb0.5-HF membrane.

![Figure 7 XRD patterns of (a) as prepared SCFNb0.5 and (b) SCFNb0.5 hollow fibre membrane (ground into powder)](image)
Table 2 Comparison of the elemental compositions

<table>
<thead>
<tr>
<th></th>
<th>Theoretical value (mol %)</th>
<th>Fresh powder (mol %)</th>
<th>Sintered membrane (mol %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr</td>
<td>49.82</td>
<td>47.12</td>
<td>38.72</td>
</tr>
<tr>
<td>Co</td>
<td>39.85</td>
<td>41.86</td>
<td>49.71</td>
</tr>
<tr>
<td>Fe</td>
<td>9.96</td>
<td>10.19</td>
<td>10.04</td>
</tr>
<tr>
<td>Nb</td>
<td>0.37</td>
<td>0.83</td>
<td>1.53</td>
</tr>
</tbody>
</table>

3.4 Interactions between SCFNb0.5 and the phase inversion system

For the phase inversion system in this study, NMP is used as the solvent. Further XRD proved that there is a strong interaction between SCFNb0.5 and NMP. As can be seen in Figure 8, the contact with NMP significantly changes the material structure, resulting in substantially lower peak intensities and the shift of peak positions towards higher 2-Theta values, which is in agreement with the results in Figure 7. From this, the interaction between NMP and SCFNb0.5 is very similar to the one between water and SCFNb0.5 (Figure 8). This also indicates that, when the spinning suspension was prepared, the structure of SCFNb0.5 had been destroyed largely, which can hardly been noticed prior to spinning as the prepared spinning suspension was very uniform. X-ray Fluorescence (XRF) analysis further proves that Sr, Co and Fe are leached out when the powder is in contact with water and NMP. For example, the relative concentrations of these elements are 96.5% (Sr), 2.6% (Co) and 0.9 (Fe) in water, and 47.4% (Sr), 35.9% (Co) and 16.7% (Fe) in NMP.
Figure 8 XRD patterns of (a) as prepared SCFNb0.5, (b) SCFNb0.5 powder in water for 24 h (rinsed with ethanol) and (c) SCFNb0.5 powder in NMP for 24 h (rinsed with ethanol)

When such spinning suspension is in contact with water, a large amount of Sr, as well as other elements, is leached out, leading to the brittleness of the precursor fibre and the formation of white flakes mentioned previously. Different from water, ethanol is a less polar liquid and the solvent-non-solvent exchange between NMP and ethanol resulting in slower precipitation of polymer binder (PESf), which may help to keep most of the metallic elements in SCFNb0.5 from being leached out, or its perovskite type structure will be destroyed even after high temperature sintering. In the subsequent high temperature sintering, solid-state reactions occur again and contributes to re-build the perovskite type structure, but without being able to fully restore the structure, resulting in the shift of XRD peaks and the formation of a small amount of impurity phase (Figure 7). As the consequence, oxygen permeation of the
asymmetric SCFNb0.5 hollow fibre membrane is lower than the capillary membrane (Figure 6).

For such reasons, another less polar solvent rather than NMP has to be used, for example the material structure can be well maintained in hexane and dioxane, together with the corresponding polymer binder matching the solvent-non-solvent exchange between the new solvent and ethanol. In another word, a new phase inversion process needs to be re-designed to match the nature of SCFNb0.5, in order to avoid any change in material structure and composition that has been observed in this study. Although the NMP-PESf-water phase inversion system has been used for fabricating many types of ceramic hollow fibre membranes, and no change in material composition has been reported, SCFNb0.5 is a special case in comparison with the other MIEC ceramics. As a result, a pre-test on the compatibility between the ceramic material and the phase inversion system is recommended, especially when a new membrane material with complex compositions is going to be used for hollow fibre fabrication.

4. Conclusions

Nb$_2$O$_5$-doped (0.5 wt.%) SrCo$_{0.8}$Fe$_{0.2}$O$_{3-δ}$ (SCFNb0.5), a material reported with great oxygen permeation and stabilities, was employed in this study for the fabrication of asymmetric hollow fibre membrane and symmetric capillary membrane for oxygen permeation, using a combined phase inversion and sintering process and plastic extrusion process, respectively. The prepared hollow fibre membrane consists of an outer dense oxygen separation layer of
approximately 62 µm supported on a porous finger-like layer of the same material. Such a membrane structure is favourable for low oxygen permeation resistance. However, the unexpected strong interactions between SCFNb0.5 and NMP (solvent in the spinning suspension) significantly changed the structure and composition of the original membrane material, and consequently decreased the oxygen permeation fluxes. Although SCFNb0.5 is a quite special case, a new phase inversion system, such as less polar solvent and non-solvent with corresponding polymer binder, is suggested to be designed based on the nature of the membrane material. Meanwhile, a pre-test on the compatibility between the ceramic material and the phase inversion system is recommended, especially when a new membrane material is going to be used for fabricating hollow fibre membranes.

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Appendix B

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Appendix B

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