HIGH PERFORMANCE MICRO-TUBULAR
SOLID OXIDE FUEL CELL

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

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 Information derived from the published and unpublished work of others has been acknowledged in the text and the relevant references are included in this thesis.

Mohd Hafiz Dzarfan Bin Othman

Imperial College London, June 2011
ABSTRACT

The development of micro-tubular solid oxide fuel cells (SOFCs) has received more and more attention recently due to a number of advantages of this configuration, such as high volumetric power output and rapid start-up/shut-down. Previously, the fabrication of micro-tubular SOFC was achieved through multiple-step processes, which involves at least one sintering in each step, making the cell fabrication time-consuming and costly.

For a more economical fabrication of micro-tubular SOFC with more reliability and flexibility in quality control, an advanced dry-jet wet extrusion technique, i.e. a phase inversion-based co-extrusion process, followed by co-sintering and reduction processes has been developed and systematically investigated in this thesis. At the beginning of the study, a dual-layer hollow fibre which consists of a cerium-gadolinium oxide (CGO) electrolyte outer layer of approximately 80 µm supported by an asymmetric nickel (Ni)-CGO anode inner layer, is successfully fabricated using this technique. The resultant cell of the corresponding dual-layer hollow fibre produces the maximum power density of 0.34-0.68 W cm\(^{-2}\) at 550-600 °C.

Improvement on the structure of the dual-layer hollow fibres is performed by reducing the electrolyte layer thickness to as thin as 10 µm and the maximum power density of the corresponding cell increases to about 1.11 W cm\(^{-2}\) at 600 °C. However, the value of power density is still slightly lower than what have been previously reported in the literature. One of the major reasons for such lower power output is the less effective porosity in the anode layer of hollow fibres. Therefore, the optimisation on anode porosity of the dual-layer HF is carried out and resulting in the outstanding
power output of about 2.32 \text{ W cm}^{-2} \text{ at 600 }^\circ\text{C}. This result indeed highlights the advantage of co-extrusion/co-sintering as a fabrication technique in developing high quality micro-tubular SOFC.
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<td>$\eta_\Omega$</td>
<td>ohmic polarisation or loss</td>
<td>V</td>
</tr>
<tr>
<td>OCV</td>
<td>open-circuit voltage</td>
<td>V</td>
</tr>
<tr>
<td>$P$</td>
<td>gas permeability</td>
<td>mol m$^{2}$ s$^{-1}$ Pa$^{-1}$</td>
</tr>
<tr>
<td>$P_{\text{elec}}$</td>
<td>electric power</td>
<td>W</td>
</tr>
<tr>
<td>$P_{\text{d,elec}}$</td>
<td>power density or power normalized by the effective area</td>
<td>W cm$^{-2}$</td>
</tr>
<tr>
<td>$p_{H_2}$</td>
<td>partial hydrogen pressure</td>
<td>Pa or atm</td>
</tr>
<tr>
<td>$p_{H_2O}$</td>
<td>partial water pressure</td>
<td>Pa or atm</td>
</tr>
<tr>
<td>$p_{O_2}$</td>
<td>partial oxygen pressure</td>
<td>Pa or atm</td>
</tr>
<tr>
<td>$p_a$</td>
<td>atmospheric pressure</td>
<td>Pa</td>
</tr>
<tr>
<td>$p_o$</td>
<td>initial pressure measured in the test cylinder</td>
<td>Pa</td>
</tr>
<tr>
<td>$P_f$</td>
<td>final pressure measured in the test cylinder</td>
<td>Pa</td>
</tr>
<tr>
<td>$Q$</td>
<td>gas permeation rate</td>
<td>mol s$^{-1}$</td>
</tr>
<tr>
<td>$R$</td>
<td>gas constant</td>
<td>J mol$^{-1}$ K$^{-1}$</td>
</tr>
<tr>
<td>$\rho_a$</td>
<td>anode resistance</td>
<td>$\Omega$</td>
</tr>
<tr>
<td>$\rho_e$</td>
<td>electrolyte resistivity</td>
<td>$\Omega$ cm</td>
</tr>
<tr>
<td>$V$</td>
<td>operating cell voltage</td>
<td>V</td>
</tr>
<tr>
<td>$V_C$</td>
<td>volume of the test cylinder</td>
<td>m$^3$</td>
</tr>
<tr>
<td>$V_N$</td>
<td>Nernst voltage</td>
<td>V</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
<td>Unit</td>
</tr>
<tr>
<td>--------</td>
<td>------------------------------</td>
<td>--------------------</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature</td>
<td>K</td>
</tr>
<tr>
<td>$t$</td>
<td>time</td>
<td>s</td>
</tr>
<tr>
<td>$\Delta P$</td>
<td>pressure difference</td>
<td>Pa</td>
</tr>
<tr>
<td>$\Delta G_T$</td>
<td>Free or Gibbs energy</td>
<td>J mol$^{-1}$</td>
</tr>
<tr>
<td>$\Delta H_T$</td>
<td>Reaction enthalpy</td>
<td>J mol$^{-1}$</td>
</tr>
<tr>
<td>$\Delta S_T$</td>
<td>Reaction entropy</td>
<td>J mol$^{-1}$ K$^{-1}$</td>
</tr>
</tbody>
</table>
CHAPTER 1

Introduction

1.1 Background
One of the most challenging issues facing our world today is the soaring energy demand due to the fast growth of the global population. In order to satisfy this need, huge giga-watt thermal power plants have been built up to convert fossil energy resources into electricity. In the meantime, the world community has started to realise the importance of alternative energy sources due to two main reasons; firstly, global fossil energy resources are limited and we are heading to the end of these resources and secondly, discharge of gasses associated with the use of fossil fuel may threaten the environment and health of people.

Although the use of cleaner and more environmentally friendly energy sources such as solar energy, wind energy, geothermal energy and hydroelectric energy reduces the dependency on fossil fuels, it will take a long time before being able to meet the need of global energy consumption, in addition to the financial and technical challenges. As a result, the efficiently use of fossil fuel with less impact on environment is the main concern for today. Due to the same reason, the fuel cell has received a lot of attention as a promising energy converting device. A fuel cell in general is a battery-like energy generator that produces electricity through an electrochemical process without involving combustion. As fuel cells convert the chemical energy directly into electricity, they have the potential to operate at higher efficiency than an internal combustion engine, extracting more electricity from the same amount of fuel. They
are also more environmental friendly because they produce less emission than combustion system. Furthermore, fuel cells are able to continuously generate electricity as long as the fuel and the oxidant are provided to the cell. The fuel of fuel cells is stored externally and therefore, it will not become internally depleted. Fuel cells are mechanically ideal because these devices have no moving parts, making them quiet and reliable sources of power.

A general schematic diagram of a fuel cell is provided in Figure 1.1. The heart of a fuel cell system is an electrolyte, which is sandwiched between the two conducting electrodes (anode and cathode). Fuel cells operate on a combined oxidation-reduction reaction. Fuel is oxidised in the anode compartment and oxidant is reduced in the cathode compartment. The ions (whether positive or negative ions, depend on type of fuel cells) migrate through the electrolyte from one electrode to the other, while the electrons travel through an external circuit which results in the generation of an electric current.
Fuel cells are not a new technology. Their origin can be dated back to the 19th century, when Sir William Grove invented a “gas voltaic battery” cell [1], which drew a current between two platinum strips (one in hydrogen and another in oxygen) positioned in two separated test tubes filled with dilute sulphuric acid, as illustrated in Figure 1.2.

![Figure 1.2: Schematic of gas voltaic battery cell [2].](image)

However, due to the corrosion of the electrodes and instability of the materials, Grove’s fuel cell was not practically useful, that is why there were not many efforts carried out in the following years. Yet, Ludwig Mond and Charles Langer were among the first researchers using the term of “fuel cell” when they constructed a fuel cell device in 1889 using industrial coal gas as the fuel and air as the oxidant [3].

Significant work on fuel cells resumed again in the 1930s by a British inventor, Francis Thomas Bacon, when he experimented with Grove’s use of activated platinum gauze with a sulphuric acid electrolyte [4]. In the 1940s, Bacon successfully produced the first practical fuel cell which was an alkaline version. He used an alkaline electrolyte instead of dilute sulphuric acid and the electrodes were constructed from
porous sintered nickel powder so that the gases could diffuse through the electrodes to be in contact with the aqueous electrolyte. This effort greatly increased the contact area between the electrodes, the gases and the electrolyte, resulting in the increased power density of the fuel cell. In addition, the use of nickel was much less expensive than platinum. In late 1950s, National Aeronautics and Space Administration (NASA) began developing a compact electricity generator for the use on space missions and fuel cells have been providing electricity and water on spacecraft since the 1960s. More recently, many companies and governmental agencies have supported research of fuel cell technology for the possible uses in stationary power plants, homes, vehicles, watercraft and portable electronic devices including cell phones.

Fuel cells can be classified according to their operation temperatures, cell operating fuels and/or design features; nevertheless the most common classification is based on the type of electrolyte as different kinds of ions can be conducted by different types of electrolytes. Table 1.1 summarises the characteristics of different types of fuel cells. Proton exchange membrane fuel cells (PEMFC), alkaline fuel cells (AFC), and phosphoric acid fuel cells (PAFC) are operated under a low temperature range. Molten carbonate fuel cells (MCFC) and solid oxide fuel cells (SOFC) are high temperature fuel cells. For SOFCs, temperatures below 700 °C are considered as the intermediate operation temperatures.
Table 1.1: Characteristics of different types of fuel cells.

<table>
<thead>
<tr>
<th></th>
<th>PEMFC</th>
<th>AFC</th>
<th>PAFC</th>
<th>MCFC</th>
<th>SOFC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrolyte</td>
<td>Ion-exchange membrane</td>
<td>Mobilized or immobilized KOH</td>
<td>Immobilized liquid H₃PO₄</td>
<td>Immobilized liquid molten carbonate</td>
<td>Ceramic</td>
</tr>
<tr>
<td>Operating temperatures (°C)</td>
<td>80</td>
<td>120-250</td>
<td>200</td>
<td>650</td>
<td>500-1000</td>
</tr>
<tr>
<td>Charge carrier</td>
<td>H⁺</td>
<td>OH⁻</td>
<td>H⁺</td>
<td>CO₃²⁻</td>
<td>O²⁻</td>
</tr>
<tr>
<td>Prime cell components</td>
<td>Carbon-based</td>
<td>Carbon-based</td>
<td>Graphite-based</td>
<td>Stainless steel-based Nickel</td>
<td>Ceramic</td>
</tr>
<tr>
<td>Catalyst (Electrodes)</td>
<td>Platinum</td>
<td>Platinum</td>
<td>Platinum</td>
<td>Nickel</td>
<td>Oxide perovskites or metal ceramic composites</td>
</tr>
<tr>
<td>Product water management</td>
<td>Evaporative</td>
<td>Evaporative</td>
<td>Evaporative</td>
<td>Gaseous product</td>
<td>Gaseous product</td>
</tr>
</tbody>
</table>
SOFCs exhibit various advantages over other types of fuel cells. The use of a solid electrolyte, instead of liquid, makes SOFC easier to maintain as it reduces corrosion and catalyst wetting problems. A major advantage of SOFC is that hydrocarbons can be used directly as fuels without the need for further transformation. The high operating temperature ensures that fuels will internally reform and then being oxidised rapidly without the need for any specialised and expensive catalysts. The lack of high-activity catalysts that can be easily poisoned also gives SOFC a high tolerance to impurities. SOFC can achieve the highest total energy efficiency among all types of fuel cells. Besides, generated heat can be easily utilised in a simple and economical way.

There are several designs of SOFCs and currently the micro-tubular SOFC with sub-millimeter inner diameters is being extensively investigated [5-16]. This configuration shows the advantages in terms of volumetric power densities and thermal shock resistance. Previously, the fabrication of micro-tubular solid oxide fuel cells (SOFCs) can only be achieved through multiple-step processes, where each step involves a high temperature heat treatment, making the cell fabrication extremely expensive and time-consuming [5-15]. Clearly, combining the multiple steps into a single step is desirable in cutting the production time and costs, and simultaneously reduces the fuel cell price.

In this work, a novel single-step phase-inversion based co-extrusion/co-sintering technique has been employed to fabricate electrolyte/anode dual-layer hollow fibre for intermediate temperature micro-tubular SOFCs. Prior to the co-extrusion process, the electrolyte and anode materials are separately mixed with solvent, polymer binder and additives to form the outer and inner layer suspensions respectively. Both suspensions
are then simultaneously co-extruded through a triple-orifice spinneret, passing through an air gap and finally into an external coagulation bath. In the meantime, a stream of internal coagulant is supplied through the central bore of the spinneret. The layer thicknesses are controlled by adjusting the extrusion rate and sizes of the spinneret orifices, while the macrostructures can be varied by adjusting suspension viscosity, air gap and flow rate of internal coagulant. The hollow fibre precursor is finally co-sintered at high temperatures as a procedure to remove polymer binder and densify the ceramic materials.

1.2 PhD Objectives

The main objective of this thesis is to develop high quality electrolyte/anode dual-layer hollow fibres for intermediate temperature micro-tubular solid oxide fuel cells (SOFCs) via a single-step phase inversion-based co-extrusion/co-sintering technique. This objective has been achieved by accomplishing the following specific objectives:

i) To fabricate defect-free dual-layer hollow fibre precursors in a single step co-extrusion process

Cerium-gadolinium oxide (CGO) electrolyte/CGO-nickel oxide (NiO) anode dual-layer hollow fibre precursors for micro-tubular SOFC is prepared by the phase inversion-based co-extrusion process using a triple-orifice spinneret. The main concern of this task is to produce a hollow fibre which consists of a uniform and delamination-free electrolyte outer layer supported by a thick asymmetric anode inner layer.
ii) To determine the optimum co-sintering profile of the dual-layer hollow fibres

The dual-layer hollow fibre precursor is subjected to the co-sintering process as a procedure to transform the precursor into a strong ceramic body. Since the use of right sintering profile is essential to prevent the formation of crack, therefore the sintering behaviour analysis was carried out in this work. The effects of co-sintering temperature on the properties of the dual-layer hollow fibre, such as shrinkage behaviour, morphology, mechanical strength, gas-tightness of the electrolyte layer, gas diffusion and conductivity of the anode layer, are also investigated by varying the co-sintering temperatures from 1450 to 1550 °C.

iii) To develop a micro-tubular SOFC and measure its electrochemical performance

A micro-tubular SOFC is built up by depositing a multi-layer cathode onto the dual-layer hollow fibre followed by the connection of current collectors to both anode and cathode layers. The electrochemical performance of the cell is measured by a potentiostat/galvanostat at temperatures of 550 to 600 °C, using humidified hydrogen as the fuel and air as the oxidant.

iv) To improve cell performance by reducing electrolyte layer thickness

The effects of the electrolyte thickness of dual-layer hollow fibre on the electrochemical performances of the cell are studied. In the meantime, the minimum thickness that can guarantee the gas-tightness of the electrolyte layer is also investigated together with a series of characterisation on other hollow fibre properties such as the macrostructure and mechanical strength.
Chapter 1  Introduction

v)  *To fabricate anode hollow fibre with different asymmetric structures and investigate the effect of the macrostructure on the anode properties*

Anode single-layer hollow fibres with various asymmetric structures, which are characterised by the length of finger-like voids, are fabricated by varying the non-solvent content in the spinning suspension. The macrostructure of these anode hollow fibres is observed using scanning electron microscopy and mercury porosimetry analysis and the properties of the hollow fibres are studied using gas permeation test, three-point bending test and electrical conductivity measurements.

vi)  *To optimise the anode porosity of the dual-layer hollow fibre SOFC*

A further development on the structural design of the electrolyte/anode dual-layer hollow fibres has been carried out, aiming to produce high performance micro-tubular SOFC. Various asymmetric structures of the anode inner layer of dual-layer hollow fibre are achieved by applying the knowledge that is gained through controlling the asymmetric structure in anode single-layer hollow fibre. The three-point bending test, gas permeation test and electrochemical measurements have been used to investigate the effect of finger-like voids thickness on the bending strength, gas-tightness property and fuel cell performance of the dual-layer hollow fibres, respectively.

1.3  Thesis Structure and Presentation

This thesis is comprised of 7 chapters addressing different aspects of the fabrication of the dual-layer hollow fibres, the use of these fibres as micro-tubular SOFC and how to enhance cell performance by adjusting fibre thickness and macrostructures. Figure 1.3 shows the overall structure of the thesis.
Chapter 1 briefly introduces the concept and history of fuel cells, the objective of the study and overview of the thesis. Chapter 2 describes the operation, thermodynamic and materials of the SOFCs in more detail and systematically reviews the research.
background and up-to-date development of micro-tubular SOFCs. The concepts of phase inversion-based co-extrusion/co-sintering technique are also explained in this chapter. Chapter 3 reports the success of the fabrication of electrolyte/anode dual-layer hollow fibre precursors using the co-extrusion technique. This chapter also reports the effect of co-sintering temperature on the properties of dual-layer hollow fibres and the development of a complete fuel cell from the corresponding dual-layer hollow fibre.

Chapter 4 describes the improvement on the structure of the dual-layer hollow fibres by studying the effects of the electrolyte thickness on the properties and electrochemical performance of the dual-layer hollow fibre. Meanwhile, Chapter 5 explains the fabrication of the anode single-layer hollow fibres with different asymmetric structures and their characterisations, with respect to the pore size distributions, porosity of fibres, mechanical strength, gas permeation and electrical conductivity. Chapter 6 reports the development of high performance micro-tubular SOFC using an improved anode structure of the dual-layer hollow fibre, in which the procedure to fabricate such structures are described in detail in the Chapter 5. Finally, Chapter 7 concludes the progress achieved in micro-tubular SOFCs and some suggestions for future study are given.

References


CHAPTER 2

Literature Review

2.1 The Operation Principles and Thermodynamics of SOFC

The operation of a SOFC involves two primary electrode reactions, i.e. the oxidation of fuel at the anode and the reduction of oxidant at the cathode. In theory, any gases capable of being electrochemically oxidised or reduced at the SOFC operating temperature can be used as fuel or oxidant. However, hydrogen is presently the most commonly used fuel in SOFCs because it has high electrochemical reactivity and can be derived from common fuels such as hydrocarbons, alcohol and coal. Oxygen is the most common oxidant for SOFCs since oxygen is readily and economically available from air.

The operating principles of a hydrogen-oxygen SOFC is shown in Figure 2.1. The electrolyte is usually made of an oxygen ion conducting material with oxygen vacancies in the crystal structure allowing the diffusion of oxygen ions at high temperatures. At the cathode, oxygen gas “captures” electrons and is reduced to oxygen ions. The oxygen ions move through the electrolyte and then react with hydrogen gas at the anode to release electrons and form water as the product. The electrons flow from the anode to the cathode through an external circuit where the current is generated.
The operation principle of the SOFC is based on well understood thermodynamics and electrochemistry. The efficiency ($\varepsilon$) of a fuel cell is the ratio of the electrical energy produced by the cell to the chemical energy of the reaction [1]. The energy output is expressed by the free or Gibbs energy ($\Delta G_T$) of the combustion reaction of the fuel at the operational temperature ($T$). The chemical energy of the reaction is expressed in terms of enthalpy ($\Delta H_T$) or heat of combustion of the fuel at the operational temperature. Thermodynamically

$$\varepsilon = \frac{\Delta G_T}{\Delta H_T} = \frac{\Delta H_T - T\Delta S_T}{\Delta H_T} = 1 - \frac{T\Delta S_T}{\Delta H_T} \quad (2.1)$$

where $\Delta S_T$ is the entropy of the reaction at the operational temperature $T$.

The Nernst voltage ($V_N$) is the maximum voltage that can be achieved by a SOFC under specified temperature and gas compositions. $V_N$ can be calculated from the Nernst equation, which is

$$V_N = \frac{-\Delta G_T}{2F} + \frac{RT}{2F} \ln \left(\frac{p_{H_2}}{p_{H_2O}} \sqrt{\frac{p_{O_2}}{p_{O_2}}}ight) \quad (2.2)$$
where $\Delta G_T$ is the Gibbs energy at the operational temperature, $F$ is the Faraday constant, $R$ is the gas constant, $T$ is the cell temperature and $p_{H_2}$, $p_{O_2}$ and $p_{H_2O}$ are the partial pressures of hydrogen, oxygen and water, respectively.

The voltage of an operating cell ($V$) is normally lower than $V_N$. As current density ($j$) is drawn from the fuel cell, the cell voltage falls due to the increase of the cell polarisation. The three main polarisations in SOFC are (i) activation polarisation, $\eta_a$, (ii) ohmic polarisation or loss, $\eta_\Omega$, and (iii) concentration polarisation, $\eta_c$ [2].

Activation polarisation, $\eta_a$, is related to the reaction rate at the electrodes. Chemical reactions involve an energy barrier that must be overcome by the reacting species and this energy barrier, called the activation energy, results in activation polarisation. Activation polarisation is related to current density, $j$, by the following equation:

$$j = j_o \exp \left[ \frac{\alpha \eta_s F}{RT} \right] - j_o \exp \left[ \frac{(1-\alpha) \eta_s F}{RT} \right]$$

(2.3)

where $\alpha$ is the charge transfer coefficient and $j_o$ is the exchange current density. The transfer coefficient is considered as the fraction of the change in the polarisation which leads to a change in the reaction rate constant. The exchange current density is the forward and reverse electrode reaction rate at the equilibrium potential. Activation polarisation is generally due to one or more slow rate-determining steps in the electrode reactions. The slow step could be the adsorption of reactant onto the electrodes surface, electron transfer, desorption of product or any other steps in the reactions. The electrode reaction rate is a function of temperature, pressure and electrode material. At high temperature operation, reaction rate is usually very fast and as a result, activation polarisation in SOFC is usually small.
The ohmic polarisation, $\eta_\Omega$, is usually caused by ionic resistance at the electrolyte, mixed ionic and electronic resistances at the electrodes and contact resistance at the interfaces. In a SOFC, the resistivity of the electrodes is relatively much smaller than that of the solid electrolyte, $\rho_e$. Assuming that the contact resistance is negligible, the ohmic polarisation is a direct function of the electrolyte thickness, $l_e$:

$$\eta_\Omega = j \rho_e l_e$$  \hspace{1cm} (2.4)

The resistances of SOFC components are commonly expressed by the area specific resistance (ASR). $\text{ASR}_e$ is the electrolyte resistance per unit area. In this way, $\eta_\Omega$ is simply expressed as

$$\eta_\Omega = j \text{ASR}_e$$  \hspace{1cm} (2.5)

Concentration polarisation, $\eta_c$, or also known as diffusion polarisation can be significant when the electrode reaction is hindered by mass transport effects for example, when the feeding of the reactant and/or removing of the reaction product from the electrode is slower than the discharge of current density, $j$. When the electrode process is governed completely by the gas diffusion (because of low concentration of reactant in the feed gases or because the reactant conversion is approaching 100 %), the limiting current density ($j_L$) is reached (characterised by a rapid drop in cell voltage). For an electrode process free of activation polarisation, the concentration or diffusion polarisation is expressed as

$$\eta_c = \frac{RT}{nF} \ln \left(1 - \frac{j}{j_L}\right)$$  \hspace{1cm} (2.6)

The operating voltage ($V$) of the SOFC at any current density ($j$) can be estimated by subtracting all the voltage losses discussed above from the Nernst voltage ($V_N$) or the open-circuit voltage (OCV) [2]. Therefore, the voltage of an operating cell is given by
Figure 2.2 shows the operating cell voltage as a function of the operating current density. It also illustrates the region in which various types of voltage losses predominate. From this figure, it can be seen that at low current density, the major contribution to the cell voltage losses is from the activation polarisation as indicated by the sharp drop in cell voltage with the increasing current density. As the current increases, the internal resistance polarisation or ohmic loss dominates, as exhibited by the slight voltage decrease in Figure 2.2. At high current density, the cell resistance is mainly from the mass transport limitations, resulting in a rapid decrease in cell voltage. Under ideal conditions (i.e. all the polarisation losses are zero), a constant voltage is expected and characterised by a straight line parallel to the current density axis, as indicated by the dotted line in Figure 2.2.

\[
V = V_N - \eta_a - \eta_\Omega - \eta_c
\]  

(2.7)

Figure 2.2: Schematic of typical SOFC current-voltage curve showing the operating cell voltage and voltage losses as a function of the operating current density.
The electrical power produced by the SOFC can be calculated from the operating cell voltage and current produced by the SOFC, $I$:

$$P_{\text{elec}} = V \times I \quad (2.8)$$

The power density or power produced normalised by the effective area is a commonly used metric in the fuel cell domain. The active area used to compute the current density at any current is usually the area of the fuel (or working) electrode [3]. In the case of the micro-tubular SOFC, in which the anode (fuel electrode) is commonly in the inside of the micro-cell, the SOFC area ($A$) is given by:

$$A = \pi D_i L \quad (2.9)$$

where $D_i$ is the inner diameter of the micro-tubular SOFC and $L$ is the active length of the micro-tubular SOFC. The current density ($j$) and power density ($P_{d,\text{elec}}$) are then computed from the measured current $I$ by:

$$j = \frac{I}{A} \quad (2.10)$$

$$P_{d,\text{elec}} = \frac{P_{\text{elec}}}{A} = V \times j \quad (2.11)$$

### 2.2 SOFC Components

Selection of materials for SOFC components is very difficult due to their high operating temperatures of typically around 500-1000 °C. The component materials must be chemically stable and compatible and should be similar in thermal expansion coefficients (TECs) in order to minimise the thermal induced stresses between the cell components and avoid crack formation during fabrication and operation processes. The materials must also be stable in the oxidising and/or reducing operating environments and exhibit high strength and toughness. Furthermore, the cost of the
component materials and manufacturing processes are important factors in the choice of materials. The four major components in a fuel cell are the electrolyte, the anode, the cathode and the interconnect and each of these is briefly discussed in the following section.

2.2.1 Electrolyte

The electrolyte of a SOFC is a solid oxide material which is capable of conducting oxygen ions at elevated temperatures. It should be solid and impermeable to gasses to avoid direct contact between fuel and oxidant. The electronic conductivity of the electrolyte should be negligible to minimise power losses due to short circuiting. Other properties that an electrolyte should possess include great thermal and chemical stability at elevated temperatures under both oxidising and reducing environments. Furthermore, its TEC should compatible with other cell components [2].

The most commonly used electrolyte in SOFC is stabilised zirconia (ZrO$_2$) with fluorite structure because of the high oxygen-ion conductivity and desirable stability in both oxidising and reducing atmospheres. ZrO$_2$ in its pure form exhibits three well-defined polymorphs. At room temperature, ZrO$_2$ has a monoclinic crystal structure. The monoclinic structure changes to a tetragonal form above 1170 °C and to a cubic fluorite structure above 2370 °C. The cubic phase exists up to the melting point of 2680 °C. However, the addition of certain aliovalent oxides can stabilise the cubic fluorite structure of ZrO$_2$ from room temperature to its melting point. The common stabilising dopants for ZrO$_2$ include calcium oxide (CaO), yttria (Y$_2$O$_3$), magnesia (MgO), scandia (Sc$_2$O$_3$) and certain rare-earth oxides. The stabilisation of ZrO$_2$ using these kinds of dopants has also resulted to the improvement in the mechanical and thermal properties of the ZrO$_2$. Furthermore, the addition of substitutional cations
(e.g. Ca$^{2+}$, Y$^{3+}$, Mg$^{2+}$, Sc$^{3+}$) which have lower valence than zirconium ion (Zr$^{4+}$) induces the generation of oxygen vacancies for charge compensation. As an example, the substitution of Zr$^{4+}$ with Y$^{3+}$ causes negative net charge in the lattice; for every mole of Y$_2$O$_3$ incorporated into the ZrO$_2$ lattice, the charge neutrality condition is kept by forming an oxygen vacancy.

In order to understand the formation of oxygen vacancy in an oxide, a short explanation of defect chemistry is given. In an ideal crystal structure, ionic conduction is hindered because the atoms are tightly bonded and no migration is possible. However, in real crystals, defects occur. Such defects can be point defects, line defects or planar defects. Point defects can lead to ionic conductivity in the crystal, as point defects are missing atoms (vacancies) or substitutional atoms on sites that would normally be occupied by another type of atom. By taking Y$_2$O$_3$ as the example of the stabilising dopant, the point defect chemistry of zirconia occurs through the creation of oxygen vacancies according to the reaction below.

$$ Y_2O_3 \leftrightarrow_{ZrO_2} 2Y'_Zr + V''_O + 3O^x_O \quad (2.12) $$

The standard Kroger-Vink notation that is used in this thesis is explained in Figure 2.3, for example, Y$'_Zr$ means Y in the Zr site with the apparent negative charge and V$''_O$ is the vacancy in the oxygen site with two positive charges. O$^x_O$ is the lattice oxygen, i.e. oxygen in the oxygen site with net charge of zero.
The existence of vacancies on the oxygen site gives rise to the high ionic conductivity of stabilised ZrO$_2$. Oxygen is transported by hopping through its vacancy sites (vacancy diffusion mechanism). The maximum conductivity of stabilised ZrO$_2$ is obtained at or near the minimum quantity of dopant required to fully stabilise the cubic fluorite phase [4-6]. The conductivity then decreases with further increases in dopant concentration which believed to be due to defect ordering, vacancy clustering, or electrostatic interaction at high dopant concentrations [7]. Although Y$_2$O$_3$-stabilised ZrO$_2$ (YSZ) does not have the highest conductivities, YSZ is most frequently used as SOFC electrolyte because of its availability and low cost [2]. For YSZ system, the Y$_2$O$_3$ composition at which the maximum conductivity occurs appears to fall between 8 and 10 mol% [8].

### 2.2.2 Anode

The main function of the anode is to provide reaction sites for the electrochemical oxidation of the fuel. For this purpose, the anode needs to be porous and permeable to gasses [9]. Other important properties that the anode should have are good electrical (electronic) conductivity, high catalytic activity for the fuel oxidisation reaction and thermally and chemically stable at high temperatures and reducing atmospheres.
addition, the TEC of anode have to be matched with that of the other fuel cell components [2].

Many metals and ceramic materials have the required properties for a SOFC anode. Due to its low cost, high electronic conductivity and good catalytic activity for the oxidation of hydrogen, metal like nickel (Ni) is most suitable. As a standard practice, Ni is always mixed with the electrolyte material (e.g. YSZ). The functions of the YSZ in the anode are to support the nickel-metal particles, inhibit coarsening of the metallic particles at the fuel cell operating temperature, provide anode’s TEC acceptably close to that of electrolyte (TEC of Ni and YSZ are \( \sim 17 \times 10^{-6} \text{ K}^{-1} \) [10] and \( \sim 11 \times 10^{-6} \text{ K}^{-1} \) [2], respectively) and also enlarge the triple-phase boundary (TPB) region. TPB is the area in the electrodes (anode and cathode) where three important components, i.e. oxygen ion, gas and electron, could reach. Therefore, in the anode, TPB is always referred to the region where it contains porous cermet of Ni-electrolyte material (e.g. YSZ) as the oxygen ions transport through the YSZ phase, fuel diffuse through the porous structure and the electrons produced travel through the Ni phase. The concentration limit of Ni, at which there is enough Ni to form a continuous electronically conducting path and to absorb a sufficient quantity of hydrogen during the oxidation at anode, is generally accepted to be around 40-60 wt.% [11].

One of the key factors in the preparation of Ni-YSZ anodes is to tailor and control their morphology because the characteristics and stability of the anode microstructure significantly affect electrochemical performance of electrode [12]. In most cases, the SOFC anode is first made with NiO and YSZ. The NiO is then reduced in-situ to Ni metal when exposed to the fuel in the fuel cell. The reduction of NiO to Ni increases the porosity of the anode due to the volume change as a result of oxygen loss. In terms
of the conductivity, although the anode usually reaches its maximum conductivity very quickly, it may fall-off slowly until a steady state is achieved [13,14]. The maximum conductivity is achieved when enough NiO is reduced to form a continuous Ni-metal matrix and the fall-off corresponds to loss of Ni particle contact as the particles shrink due to further NiO reduction.

It is generally accepted that Ni metal plays a catalytic role in the fuel oxidation reaction. Although the definite mechanism for the hydrogen oxidation at Ni-YSZ anodes has not been well established, it is believed that the reaction proceeds through at least two steps [2]:

1. Dissociative adsorption of hydrogen on Ni:

\[ \text{H}_2 \leftrightarrow 2\text{H}_{\text{ad},\text{Ni}} \]  \hspace{1cm} (2.13)

2. Charge transfer reaction:

\[ 2\text{H}_{\text{ad},\text{Ni}} \leftrightarrow 2\text{H}^+_{\text{ad},\text{Ni}} + 2\text{e}^- \]  \hspace{1cm} (2.14)

\[ \text{O}^x_{\text{O}} \leftrightarrow \text{O}^{2-}_{\text{ad},\text{YSZ}} + \text{V}^{**}_{\text{O}} \]  \hspace{1cm} (2.15)

\[ 2\text{H}^+_{\text{ad},\text{Ni}} + 2\text{O}^{2-}_{\text{YSZ}} \leftrightarrow 2\text{OH}^-_{\text{YSZ}} \]  \hspace{1cm} (2.16)

\[ 2\text{OH}^-_{\text{YSZ}} \leftrightarrow \text{H}_2\text{O} + \text{O}^{2-}_{\text{YSZ}} \]  \hspace{1cm} (2.17)

There is evidence that suggesting the YSZ plays an important catalytic role in the hydrogen oxidation reaction if H$_2$O or oxygen-containing molecules are present in the fuel [2]. Water may provide adsorbed oxygen species on the Ni, and the kinetics of the hydrogen oxidation is probably related to the oxygen activity on the metal surface [15]. In this case, the proposed mechanism is as follows, in which both the Ni and YSZ surface contribute to the anode process [2]:

1. Dissociative decomposition of H$_2$O:


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2. Dissociative adsorption of hydrogen:

\[ H_2 \leftrightarrow 2H_{ad,YSZ} \text{ (on YSZ surface)} \] (2.19)

\[ H_2 \leftrightarrow 2H_{ad,Ni-O} \text{ (on O}_{ad}^\text{-covered Ni surface)} \] (2.20)

3. Charge transfer reaction:

\[ O^x_{ad,YSZ} \leftrightarrow O^{2-}_{ad,YSZ} + V^\bullet_{O} \] (2.21)

\[ O^{2-}_{ad,YSZ} + O_{ad,Ni} \leftrightarrow O_{ad,YSZ} + O^{2-}_{ad,Ni} \] (2.22)

\[ O^{2-}_{ad,Ni} \leftrightarrow O_{ad,Ni} + 2e^- \] (2.23)

\[ 2H_{ad,YSZ} + O_{ad,YSZ} \leftrightarrow H_2O \] (2.24)

\[ 2H_{ad,Ni-O} + O_{ad,Ni} \leftrightarrow H_2O \] (2.25)

Apart from that, it was also found that the presence of H$_2$O strongly influences the polarisation of the electrochemical oxidation of hydrogen in the anode [2]. The oxidation of dry hydrogen occurs with significant polarisation or interfacial resistance, whereas the polarisation is much smaller for hydrogen/H$_2$O mixtures [16-18]. A few mole percent of H$_2$O in hydrogen can dramatically reduce the anode interfacial resistance [16] but the resistance would increase at high H$_2$O concentrations [17]. The role of H$_2$O in the hydrogen oxidation is yet not clearly understood although H$_2$O is believed to adsorb on the surface of the YSZ and broaden reactive sites around the TPB, as shown in the above reaction mechanism (2.18-2.25), resulting in the increase of reaction rate [19].

2.2.3 Cathode

The function of the cathode is to provide reaction sites for the electrochemical reduction of the oxidant. For this purpose, cathode should be porous and permeable to
gasses. Other important properties of a cathode are high electrical (electronic) conductivity, catalytically active for the reduction reaction and thermally and chemically stable at high temperatures and oxidising condition. In addition to these, TEC of the cathode should match with other fuel cell components [2].

Noble metals and conducting (electronic or mixed) oxides are suitable for SOFC cathodes due to their stability at high temperatures. Noble metals like platinum are very expensive and hence, not practical. A variety of doped oxides meet the conductivity and stability requirements but, very few have TECs compatible with electrolyte which usually is YSZ. The TEC of lanthanum manganite (LaMnO$_3$) is almost similar to YSZ and as a result, it has been widely used as the cathode of high temperature SOFC. LaMnO$_3$ belongs to the class of perovskite oxides of the general formula ABO$_3$. LaMnO$_3$ shows intrinsic p-type conductivity due to the formation of cation vacancies and its electrical conductivity is about $10^{-4} \text{ S cm}^{-1}$ and $0.1 \text{ S cm}^{-1}$ at room temperature and 700 °C respectively [2]. The electrical conductivity of LaMnO$_3$ can be enhanced by substituting a lower valence cation on either the A or the B sites. LaMnO$_3$ has been substituted with various cations such as barium (Ba$^{2+}$), calcium (Ca$^{2+}$), cobalt (Co$^{2+}$), magnesium (Mg$^{2+}$), nickel (Ni$^{2+}$), pottasium (K$^+$), sodium (Na$^+$), strontium (Sr$^{2+}$), and yttrium (Y$^{3+}$).

Up to now, Sr$^{2+}$ dopant is most commonly used in SOFCs because LaMnO$_3$ doped with this cation or commonly known as lanthanum strontium manganite (LSM) shows high electronic conductivity in oxidising atmospheres and its thermal expansion matches with the other cell components [20-29]. Strontium doping enhances the electronic conductivity of LaMnO$_3$ by increasing the Mn$^{4+}$ content by the substitution
of \( \text{La}^{3+} \) by \( \text{Sr}^{2+} \) as shown below and the electronic conductivity of LSM takes place via the small polaron conduction mechanism [2].

\[
\text{LaMnO}_3 \xrightarrow{\Delta \text{SrO}} \text{La}_{1-x}^{3+}\text{Sr}_x^{2+}\text{Mn}_{1-x}^{3+}\text{Mn}_x^{4+}\text{O}_3
\]  \hfill (2.13)

Similar to the anode, LSM is usually mixed with YSZ in order to minimise the TEC difference between cathode (TEC of LSM = \( \sim12\times10^{-6}\ \text{K}^{-1} \) [2]) and electrolyte (TEC of YSZ = \( \sim11\times10^{-6}\ \text{K}^{-1} \) [2]) and also to improve the ionic conductivity property and subsequently broaden the TPB region in the cathode.

### 2.2.4 Interconnect

Under typical operating conditions (with the fuel of hydrogen and the oxidant of oxygen), the voltage of a single cell is usually less than 1 V. Thus, practical SOFCs are not operated as a single unit, but are connected in electrical series to build voltage. A component known as interconnect connects the anode of one cell to the cathode of the next cell in a stack. It also separates the oxidant channel of a cell from the fuel channel of the next cell. The gas channels are formed on the faces of the interconnect to distribute the gasses along the surface of electrodes. The interconnect should be solid and impermeable to gasses and have good electrical conductivity. It should also be thermally and chemically stable at high temperatures and in both oxidising and reducing environments. Its thermal expansion has to be comparable with the other cell components [2].

Lanthanum chromite (LaCrO\(_3\)) has been widely used as the interconnect material of high temperature SOFC. The particularly attractive features of the material include high electronic conductivity under fuel and oxidant atmospheres, adequate stability in the fuel cell environment and reasonable compatibility with other cell components.
Moreover, LaCrO$_3$ is often doped with other elements to tailor and control its properties for SOFC application [30-33].

2.3 Intermediate Temperature SOFC

High temperature SOFCs (HT-SOFCs) operated at 800-1000 °C normally show less voltage losses due to the higher electrolyte conductivity and faster electrode reaction rates. Direct use of hydrocarbons as the fuels is another advantage of HT-SOFCs because of possible internal reforming at elevated temperatures. In addition, carbon monoxide is a fuel, instead of an electrocatalyst poison for HT-SOFC, in contrast to some low temperature fuel cells (e.g. alkaline fuel cell). However, materials used at high temperatures have to meet strict requirements and thus limited materials can be used for high temperature operation and they are generally expensive and hard to fabricate. Furthermore, inter diffusion of elements is quite fast at high temperatures, leading to the change in composition and material structure of the components. As an example, LSM cathodes and YSZ electrolyte might react at the interfaces and form lanthanum zirconate (La$_2$Zr$_2$O$_7$) with high resistivity, leading to the gradual degradation of the cell performance [34].

By lowering the operating temperature of SOFCs to around 500-700 °C, a much wider range of materials can be used allowing more economical fabrications particularly for the stacking components. The other advantages of operating at lower temperatures are that it accelerates start-up/shut-down times, reduces corrosion rate of metallic components, improves durability (as the material degradation and elemental inter-diffusion between component are significantly slowed down) and enhances the construction robustness through the use of less-sophisticated sealants and metallic
interconnects. This makes intermediate-temperature SOFCs (IT-SOFCs) preferable to HT-SOFCs.

There are mainly two routes by which SOFCs can be operated at lower temperatures with comparable cell performance to the higher temperature counterparts. Firstly, the dimensional thickness of the electrolyte can be reduced to a very low level to reduce the area specific resistance of the cell. Secondly, use of materials with high ionic conductivity at lower temperatures for the electrolyte [35]. When the temperature is lowered than 700 °C, the thickness of YSZ electrolyte has to be reduced to 15 µm or less for sufficient ionic conductivity, which implies that the electrolyte can no longer be self-supported. In this case, the thin YSZ electrolyte layer is usually supported on an electrode support. However, if the temperature is further dropped to 500-600 °C, the conductivity of YSZ turns out to be too low even if a very thin layer is used [36]. Thus, an alternative electrolyte material which exhibits a higher ionic conductivity at those temperatures has to be used.

2.3.1 Electrolyte of IT-SOFC

As a primary component of the SOFC, an electrolyte of high ionic conduction and good compatibility with electrodes is essential to maintain high cell performance at lower operating temperatures. The development of electrolyte materials for IT-SOFCs has been systematically reviewed recently [37-40] and a number of electrolyte materials with high ionic conductivity have been disclosed and studied for IT-SOFC such as calcium oxide-stabilised zirconia (CaSZ), gadolinia-doped ceria or commonly known as cerium-gadolinium oxide (CGO), yttria-doped ceria (YDC), calcium oxide-doped ceria (CDC), strontia, magnesia and cobalt oxide-doped lanthanum gallate (LSGMC) and yttria-stabilised bismuth oxide (YSB). Figure 2.4 compares the
The transport of oxygen ions in electrolyte of SOFCs is thermally activated and as the result, the electrolyte conductivity is strongly dependent on temperatures. As can be seen in Figure 2.4, most of these electrolyte materials except CaSZ show higher ionic conductivity at intermediate temperatures when compared with YSZ.

**Figure 2.4**: Conductivity of selected SOFC electrolytes as a function of reciprocal temperature. YSB $[(\text{Bi}_2\text{O}_3)_{0.75}(\text{Y}_2\text{O}_3)_{0.25}]$; LSGMC ($\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.115}\text{Co}_{0.085}\text{O}_3$); CGO ($\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{0.19}$); YDC ($\text{Ce}_{0.8}\text{Y}_{0.2}\text{O}_{1.96}$); CDC ($\text{Ce}_{0.9}\text{Ca}_{0.1}\text{O}_{1.8}$); YSZ $[(\text{ZrO}_2)_{0.92}(\text{Y}_2\text{O}_3)_{0.08}]$; CaSZ $(\text{Zr}_{0.85}\text{Ca}_{0.15}\text{O}_{1.85})$. 
Doped ceria (CeO\(_2\)) is considered as one of the most promising electrolyte materials for IT-SOFC and will be discussed in detail in this section. Ceria has a stable fluorite-type structure from room temperature to its melting point [42] and therefore, CeO\(_2\) does not need any stabilisation. The Ce\(^{4+}\) cation adopts cubic close packing and all the tetrahedral sites are occupied by O\(^{2-}\) anions leaving an 8-fold Ce coordination with oxygen, as shown in Figure 2.5.

![Cubic fluorite structure of CeO\(_2\).](image)

**Figure 2.5:** Cubic fluorite structure of CeO\(_2\).

Pure CeO\(_2\) shows n-type electrical conducting behaviour, which takes place through a small polaron hopping mechanism. The absolute electrical conductivity of CeO\(_2\) is a function of temperature and oxygen partial pressure. Pure CeO\(_2\) has negligible ionic conductivity. Doping CeO\(_2\) with low-valence metal oxide results in the formation of oxygen vacancies which subsequently increases the ionic conductivity of the doped CeO\(_2\). Various dopants have been studied such as lanthana (La\(_2\)O\(_3\)), yttria (Y\(_2\)O\(_3\)), samaria (Sm\(_2\)O\(_3\)), gadolinia (Gd\(_2\)O\(_3\)), and other rare-earth oxides. It has been generally agreed that the closer the ionic radius of aliovalent doping cation to the host cation, the higher the ionic conductivity is observed and it is Sm\(^{3+}\) or Gd\(^{3+}\) in the case of Ce\(^{4+}\) [41]. Gd-doped CeO\(_2\) or commonly known as CGO is the most extensively studied for CeO\(_2\)-based electrolyte. Similar to YSZ, ionic conductivity of CGO also occurs due to
the diffusion of oxygen vacancies ($V_{\circ}^{\bullet\bullet}$) through the lattices. For the Gd$_2$O$_3$ as the dopant, the oxygen vacancy reaction is as follows:

$$\text{Gd}_2\text{O}_3 \xrightarrow{\text{Ce}^{4+}} 2\text{Gd}^{++} + V_{\circ}^{\bullet\bullet} + 3\text{O}_x^{+}$$  \hspace{1cm} (2.8)

A higher concentration of these vacancies results in a better ionic conductivity of the material due to a large number of the charged diffusion species. As can be seen in Figure 2.4, the ionic conductivity of CGO is much higher than that of YSZ at temperature range of 500 to 700 °C. However, at high temperature (>650 °C) and/or low oxygen partial pressure ($\sim 1x10^{-19}$ atm), Ce$^{4+}$ of CGO tends to partially reduce to Ce$^{3+}$ and the consequences of this reduction are; (i) there is a volume expansion of the lattice which can result in mechanical failure of the electrolyte; and (ii) electronic (n-type) conductivity takes place and reduces cell’s OCV due to the electronic current leakage between the anode and cathode. Although both ionic and electronic conductivities increase with temperatures, the increase of electronic conductivity is faster. This is why ceria based fuel cells should be operated at 500-600 °C instead of higher temperatures. As an alternative, the use of a bilayer electrolyte has been investigated to overcome this electronic current leakage issue. Scandia-stabilised zirconia (ScSZ) [43] and ((Bi$_2$O$_3$)$_{1-x}$(Er$_2$O$_3$)$_x$)Ag (ESB) [44] have been used as a second electrolyte layer on top of the CGO layer. Both gave a significant improvement in the OCV of the cells as compared to a single-layer CGO electrolyte cell.

The optimal Gd doping concentration to attain maximum ionic conductivity varies slightly in the literature, i.e. between 10 mol% (Ce$_{0.9}$Gd$_{0.1}$O$_{1.95}$) and 20 mol% (Ce$_{0.8}$Gd$_{0.2}$O$_{1.9}$) [35,45-48]. However, Ce$_{0.9}$Gd$_{0.1}$O$_{1.95}$ has been shown to have better stability than Ce$_{0.8}$Gd$_{0.2}$O$_{1.9}$ at low oxygen partial pressures [35].
2.3.2 Anode, cathode and interconnect materials for IT-SOFC

Similar to HT-SOFC, Ni is the most proficient anode material in IT-SOFC. In order to provide the anode’s TEC close to that of CGO electrolyte, a Ni-CGO cermet is commonly used. Furthermore, it has been recognized that the replacement of YSZ in the anode by CGO offers further advantages. In reducing environments such as in the anode, CGO conducts oxygen ions as well as electrons (i.e. it is a mixed ionic electron conductor, MIEC) whereas in the Ni-YSZ cermet, Ni conducts electrons and YSZ conducts oxygen ions. Thus, the mixed-conductivity of CGO can increase the number of reaction sites by facilitating electron and oxygen ion transport in the anode as illustrated in Figure 2.6.

Due to the high electrical conductivity and the low cost, anode is the most prominent supporting layer of planar fuel cells. Furthermore, in comparison with the electrolyte-supported configuration, the design of anode-supported SOFC is more suitable to be operated at lower temperatures [9,50] because smaller ohmic loss and better interface contact can be realised, especially when composite electrodes are used to increase the density of TPB [51,52].

Figure 2.6: Triple-phase boundary (TPB) with (a) a Ni-YSZ; (b) a Ni-CGO (reproduced from [49]).
However, the use of Ni in the anode at intermediate temperature operation of SOFC can still be problematic due to the reoxidation of Ni to NiO when fuel conversion rates approach 85% at operation below 700 °C [35,53]. The Ni reoxidation of this type is detrimental to the catalytic activity and electric conductivity of anode. The expanded volume of NiO may even cause crack formation in the supported electrolyte. Furthermore, the carbon deposition is another major issue in Ni-based anodes when hydrocarbons are used as fuels [54-56]. The Ni surfaces, pores and voids may be fouled by carbon due to the cracking/condensation reactions of hydrocarbons fuels. It has been found out that the quantity of deposited carbon during hydrocarbon reforming is strongly affected by the operating temperatures and the hydrocarbon/steam ratio. Operating at high temperatures or at steam to hydrocarbon ratios below a critical value can cause the formation of carbon deposits that plug the electrode pores and voids, and can also pulverize the anode surface [54].

Therefore, the search for alternative anode materials has drawn lots of attention. Many research groups have been developing non-metallic anodes and the most attractive one is doped LaCrO$_3$ with the perovskite structure. LaCrO$_3$ that generally used as an interconnect material is stable in reducing condition. Pure LaCrO$_3$ is normally doped with divalent dopings on the La and/or the Cr sites in order to enhance its electronic conductivity. The La site can generally be doped with strontium [57,58] and calcium [59,60] while the Cr site is usually doped with transition metals such as manganese, iron, copper and nickel [58,60,61].

For the cathode of IT-SOFC, LSM is not a good choice due to the slow oxygen ion transport, while MIECs materials with better conducting properties turn out to be a better alternative for the operations at intermediate temperatures. (La,Sr)CoO$_3$ has
been identified as possessing perhaps the best transport properties in terms of both ionic and electronic conductivities. However, the TEC of this material is much higher than the CGO electrolyte and can be hardly used directly as cathode material. Substituting iron for cobalt results in compound of La$_{1-x}$Sr$_x$Co$_{1-y}$Fe$_y$O$_{3-d}$ (LSCF) with fast ion transport, good electronic conduction and excellent oxygen reduction kinetics. Similar to the use of LSM in the cathode of HT-SOFC, it is more advantageous to develop composite cathodes, consisting of LSCF and electrolyte material, in an effort to produce suitably active cathode of IT-SOFC [41,62] and to reduce the thermal expansion difference between cathode and electrolyte layers (TEC of LSCF is $\sim 15 \times 10^{-6}$ K$^{-1}$ [63] and TEC of CGO is $\sim 12-13 \times 10^{-6}$ K$^{-1}$ [64].

As has been mention above, ceramic materials such as LaCrO$_3$ are usually used as the interconnect materials in HT-SOFC. These ceramic materials are expensive and the corresponding single cells are difficult to be assembled together because of the brittleness. The reduction in the operating temperatures of SOFC makes it possible to consider oxidation/corrosion-resistant metallic alloys as interconnect materials. Metallic alloys have gained more and more attention in recent years as the replacement of the LaCrO$_3$-based ceramics due to a number of intrinsic advantages such as low cost, high toughness and excellent manufacturability. So far, the metallic material systems such as Cr-based, Fe-based and Ni-based alloys are being explored for interconnect applications [65-67].

2.4 SOFC Geometries
SOFCs may be classified in a number of ways such as cell component that provides the major mechanical strength to the cell (i.e. anode-, cathode-, electrolyte-, or
interconnect-supported) and the geometrical shape (planar or tubular). Figure 2.7 shows schematic diagrams of electrolyte-supported, cathode-supported and anode-supported cells.

**Figure 2.7:** Different geometries of SOFC.

In general, the support layer of a planar cell is fabricated by either die-pressing or tape-casting, giving a thickness of ~0.1 to 2 mm. The other component layers are then applied by screen-printing, spray pyrolysis, chemical vapour deposition or other wet deposition techniques. In the case of electrolyte-supported cells, the relatively low ionic conductivity of the electrolyte layer leads to a high ohmic resistance in the SOFC. Therefore, most research studies are currently focused on anode or cathode-supported cells with a thin electrolyte layer of less than 40 µm. Previous studies have proved that anode-supported planar SOFCs show outstanding power density of 0.8-3.3 Wcm\(^{-2}\) at temperatures of 700 °C or under [68-70]. While planar SOFCs are beneficial due to their relatively high power density and low cost of fabrication, the main limitations are that they require sophisticated gas seals and interconnect materials for the high operating temperatures of the SOFC. Also, thermal gradients may be present in the cell, causing mechanical stress during thermal cycling. Consequently, these cells must be heated and cooled at a very slow rate to prevent failure of the cell. This leads to undesirably long start-up times, of the order of hours.
In comparison to planar cells, tubular SOFCs show advantages such as ease of sealing because the sealing part is normally positioned outside the hot zone. Therefore, low temperature sealing materials may be utilised. Two cell geometries of tubular SOFCs are the cathode-supported and anode-supported tubular cells. The cathode-supported tubular cell developed by Siemens-Westinghouse (SW) is formed by extrusion of the cathode support (~1.4 mm thick) [71]. Figure 2.8 shows a schematic of the cathode-supported tubular cell.

![Cathode-Supported Tubular SOFC Schematic](image)

**Figure 2.8:** Schematic diagram of the Siemens-Westinghouse cathode-supported tubular SOFC [71].

The dense electrolyte (about 40 µm in thickness) of the SW cell is electrochemically vapour deposited, followed by the application of the Ni-YSZ anode by slurry dip-coating and sintering at 1350 °C. The final tubes are ~2.2 cm in outer diameter and 150 cm in length with air flowing inside the tube and the fuel gas on the outer surface. The fabrication process of this type is costly and time-consuming with the resultant cell giving lower power densities than the corresponding planar geometry. A single cell of this design could only generate up to 210 W (DC) at atmospheric pressure and
1000°C [72], and the maximum power density of the single cell is calculated to be 0.20 W cm$^{-2}$ (i.e. 210 W/(150 cm × 2.2 cm × 3.14)) [73]. Other studies using the similar tubular design of different dimensions showed that the maximum power densities achieved were 0.15-0.31 W cm$^{-2}$ at temperatures of 800 °C or under [74,75]. Furthermore, this cell design still requires a heat up time of 4-6 hours [76].

For tubular cells, power density depends upon the inverse of cell diameter, which indicates that smaller cell diameter is always preferred for better cell performance [72]. Efforts to improve the performance of tubular SOFCs by downsizing the cell have led to the fabrication of micro-tubular SOFC initiated by K. Kendall in the early 1990s [77]. Apart from high power density (resulting from the increase in the electrode surface area per unit volume), the micro-tubular design exhibits high thermal shock resistance and thus, possesses short start-up/shut-down times of a few seconds for a single cell [76].

### 2.5 Progress in the Micro-Tubular SOFC Research

The micro-tubular SOFC developed in early 1990s by K. Kendall was based on ram-extruded YSZ electrolyte tubes up to 5 mm in diameter with the wall thicknesses of 100-200 µm, which the anode and cathode layers were then added to this supporting tube [77]. A few years later, Kilbride [78] reported another similar cell design using silver as the cathode current collectors. The work on current collectors in micro-tubular cells was further carried out by Hatchwell et al. [79]. In 2000, Sammes et al. [80] reported the electrical characteristics of a micro-tubular SOFC system running on internally reformed butane fuel. However, this electrolyte-supported design was “abandoned” probably due to the high ohmic losses of the thick electrolyte layer. Wei and Li [81] in the late 2000s developed an improved electrolyte-supported design by
using asymmetric YSZ hollow fibres fabricated by a dry-jet wet extrusion (involving phase inversion process) technique. An asymmetric YSZ electrolyte hollow fibre, which consists of a finger-like void structure growing from the inner surface and an outer thin gas-tight layer, is potentially an ideal structure to support the electrode layers in a micro-tubular SOFC because of its lower electrolyte resistance. Moreover, the finger-like void structure allows easier impregnation of anode materials with higher electrode surface area (using electroless plating technique). However, a small entrance size of the finger-like voids on the inner surface of the hollow fibre has hindered the deposition of a high quality Ni anode layer onto inner surface of the hollow fibres and was consequently one of the main reasons for the poor cell performance. More studies of using the dry-jet wet extrusion technique to fabricate ceramic hollow fibres have been reported recently, aiming at improving the quality of the anode layer inside the YSZ electrolyte hollow fibre [82,83].

Other designs of micro-tubular SOFC have also been developed with anode-supported cells and this design has emerged as strong competitors to the electrolyte-supported model [76]. Most of the recent micro-tubular SOFC research have focused on anode-supported cells [84-92], probably due to the lower material cost (Ni or NiO is relatively cheaper than other fuel cell components) and easier of fabrication. Furthermore, the use of anode support tube allows for a thinner electrolyte (as thin as 5 µm) and therefore lower ohmic resistance. Any sophisticated techniques of depositing the electrode inside the micro-tubes are also not necessary for this design. Suzuki and co-workers [84,85] from National Institute of Advanced Industrial Science and Technology (AIST), Japan were among first several groups developing anode-supported SOFC based on CGO using traditional plastic mass ram extrusion and coating technique. The same group [86,87] employed pore former for a more porous
anode tube prepared using the same fabrication technique. Dikwal et al. [88] then investigated the redox tolerance (where the fuel flow is interrupted and restarted at a constant temperature) of Ni-YSZ anode-supported micro-cells in partial oxidation and reduction conditions. Lee et al. [89] employed methane as the fuel in their study, while Akhtar et al. [90] studied four anode-supported cells with various cathode location/size, i.e. inlet, centre, outlet and full size. Yang et al. [91] reported the fabrication of a hollow-fiber SOFC of 1.7 mm in diameter, using the dry-jet wet extrusion and vacuum assisted coating techniques. By employing the similar support fabrication techniques, Yang et al. [92] significantly improved the cell’s power output by impregnating the electrode catalyst into the porous electrode matrix.

Cathode-supported micro-tubular SOFC is also another attractive design due to the good stability under a redox environment. This is an advantage over the anode-supported counterpart in which there is a volume contraction and expansion during redox cycles. However, not much attention has been paid to the cathode-supported SOFCs [93-95] although SW successfully achieved tubular cathode-supported SOFCs [71]. Two of the most challenging issues affecting cell performance of the cathode-supported SOFCs are: 1) the chemical reaction between cathode and electrolyte at high sintering temperatures and 2) the high polarisation resistance of the cathode tube [96,97].

Table 2.1 summarises the recent development on single micro-tubular SOFC. Only the support fabrication technique and main materials for the major cell components are listed in this table. The further information on how the complete cells were produced as well as detail of binders and pore-formers used can be found in the referenced papers.
Table 2.1: Recent developments of single micro-tubular SOFCs.

<table>
<thead>
<tr>
<th>Ref.</th>
<th>Year</th>
<th>Support design</th>
<th>Support fabrication technique</th>
<th>Anode</th>
<th>Electrolyte</th>
<th>Cathode</th>
<th>Cell diameter (mm)</th>
<th>Fuel stream</th>
<th>Temp. (°C)</th>
<th>OCV (V)</th>
<th>Max. power density (W cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[84]</td>
<td>2006</td>
<td>Anode-supported</td>
<td>Plastic mass ram extrusion</td>
<td>Ni-CGO</td>
<td>CGO</td>
<td>LSCF-CGO</td>
<td>1.60</td>
<td>Humidified H₂-N₂</td>
<td>570</td>
<td>0.84</td>
<td>0.35</td>
</tr>
<tr>
<td>[85]</td>
<td>2006</td>
<td>Anode-supported</td>
<td>Plastic mass ram extrusion</td>
<td>Ni-CGO</td>
<td>CGO</td>
<td>LSCF-CGO</td>
<td>0.80</td>
<td>Humidified H₂-N₂</td>
<td>550</td>
<td>0.85</td>
<td>0.35</td>
</tr>
<tr>
<td>[98]</td>
<td>2007</td>
<td>Anode-supported</td>
<td>Plastic mass ram extrusion</td>
<td>Ni-CGO</td>
<td>CGO</td>
<td>LSCF-CGO</td>
<td>1.48</td>
<td>Humidified H₂-N₂</td>
<td>550</td>
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<td>0.40</td>
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<tr>
<td>[99]</td>
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<td>ScSZ</td>
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<td>1.06</td>
<td>1.06</td>
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<td>[93]</td>
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<td>CGO</td>
<td>LSCF-CGO</td>
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<td>0.60 (at 0.5 V)</td>
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<td>[95]</td>
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<td>LSCF-CGO</td>
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<td>[86,87]</td>
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<td>LSCF-CGO</td>
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<td>LSM</td>
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<td>H₂-Argon</td>
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<td>LSM-YSZ</td>
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<td>Humidified H₂</td>
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<td>LSM-YSZ</td>
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<td>CGO</td>
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<td>YSZ</td>
<td>LSM-YSZ</td>
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<td>Humidified H2</td>
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<td>1.03</td>
<td>0.78</td>
</tr>
<tr>
<td>[106]</td>
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<td>Anode-supported</td>
<td>Dry-jet wet extrusion</td>
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<td>YSZ</td>
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<td>YSZ</td>
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<tr>
<td>[109]</td>
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<td>BZCYYb</td>
<td>LSCF-BZCYYb</td>
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<td>Humidified H2</td>
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<td>[110]</td>
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<td>CGO</td>
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<td>3.0</td>
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<td>CGO</td>
<td>LSCF-CGO</td>
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<td>Humidified CO-H2</td>
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<td>[113]</td>
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<td>YSZ</td>
<td>LSCF-CGO</td>
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<td>CGO</td>
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<td>1.8</td>
<td>Humidified H2</td>
<td>550</td>
<td>0.93</td>
<td>0.34</td>
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</table>

*ScSZ = (ZrO$_2$)$_{0.89}$(Sc$_2$O$_3$)$_{0.1}$CeO$_2$)$_{0.01}$, BZCYYb = BaZr$_{0.1}$Ce$_{0.7}$Y$_{0.1}$Yb$_{0.1}$O$_{3.8}$, LSCM = (La$_{0.75}$Sr$_{0.25}$)$_{0.95}$Cr$_{0.3}$Mn$_{0.2}$O$_{3.8}$, SDC = Sm$_{0.2}$Ce$_{0.8}$(NO$_3$)$_3$, SSC = Sm$_{0.5}$Sr$_{0.5}$CoO$_3$
As can be seen in this table, the anode-supported design with Ni cerments as the anode materials has been widely employed in the recent studies of micro-tubular SOFCs. It should be noted here that, the highest power densities of the micro-tubular SOFCs reported in the literature up to now are 1.29 $\text{W cm}^{-2}$ at 600 °C and 1.31 $\text{W cm}^{-2}$ at 550 °C, which were achieved by Suzuki et al. [86,87] and Sammes et al. [13,105] respectively.

In terms of fabricating micro-tubular supports, there are two common techniques: (1) plastic mass ram extrusion and (2) dry-jet wet extrusion. For the ram extrusion technique, the support materials are mixed with binder and solvent to form a viscous paste. The paste is then extruded through a custom-made die using a ram extruder to obtain the support tubes. The support tubes are dried and cut to the desired length prior being subjected to the sintering process. The fabricated support tubes are usually of a symmetrical structure with large wall thicknesses, which results in a large resistance for the diffusion of fuel into the anode (in the case of anode-supported design). In contrast, the dry-jet wet extrusion technique offers greater control over the morphology of hollow fibre (common terminology for the tubes prepared using this technique). The dry-jet wet extrusion is similar to the ram extrusion process. The main difference is that the spinning suspension or dope for the dry-jet wet extrusion is in liquid form and the ram extrusion is in paste or plastic mass form. Another major difference is the solidification process of the tube (or hollow fibre). In dry-jet wet extrusion, the solidification of the hollow fibre occurs via phase inversion process initiated by the solvent/non-solvent exchange. While in ram extrusion process, the tube is dried straight away after the extrusion prior to being subjected to the sintering process. The detailed explanation about the dry-jet wet extrusion technique combined with the sintering process is further described in the following section.
2.6 Combined Dry-Jet Wet Extrusion/Sintering Technique for the Preparation of Ceramic Hollow Fibre

Early development of ceramic hollow fibre using dry-jet wet extrusion/sintering technique was applied in gas separation and ultra-filtration by Okubo et al. [115]. This technique was further established by Tan et al. [116] and Liu et al. [117]. Since then, the dry-jet wet extrusion/sintering technique has been widely used to prepare ceramic hollow fibres for different applications. There are basically three main steps in preparing ceramic hollow fibres using dry-jet wet extrusion/sintering technique: preparation of a spinning suspension, extrusion of ceramic hollow fibre precursors, and finally sintering [118]. Each step plays a specific and crucial part in the production of desired ceramic hollow fibres, as listed in Table 2.2.
Table 2.2: Step of dry-jet wet extrusion/sintering, their factors and influences to resultant hollow fibre properties.

<table>
<thead>
<tr>
<th>Steps</th>
<th>Factors</th>
<th>Influences</th>
</tr>
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<tr>
<td>Preparation of spinning</td>
<td>Concentration of compounds</td>
<td>Homogeneous</td>
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<td>suspension</td>
<td>Particle size/distribution</td>
<td>Viscosity</td>
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<td>Particle/binder ratio</td>
<td>Particle packing density</td>
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<td></td>
<td>Solvent types</td>
<td>Rheology</td>
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<tr>
<td></td>
<td>Dispersant</td>
<td>Particle dispersion</td>
</tr>
<tr>
<td></td>
<td>Additives</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mixing speed (shear stress)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mixing temperature</td>
<td></td>
</tr>
<tr>
<td>Extrusion of ceramic hollow</td>
<td>Suspension viscosity/homogeneous</td>
<td>Uniformity (bore shape)</td>
</tr>
<tr>
<td>fibre precursors</td>
<td>Particle size/distribution</td>
<td>Particle packing density</td>
</tr>
<tr>
<td></td>
<td>Extrusion speed</td>
<td>Surface morphology (smooth/rough)</td>
</tr>
<tr>
<td></td>
<td>Air gap</td>
<td>Precursor morphology (dense/porous)</td>
</tr>
<tr>
<td></td>
<td>Environment conditions (humidity/temperature)</td>
<td>Precursor structure (symmetric/asymmetric)</td>
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<td>Spinneret dimension/ configuration</td>
<td>Precursor thickness</td>
</tr>
<tr>
<td></td>
<td>Internal/external coagulant (solvent %, flow rate, temp.)</td>
<td>Precursor dimension</td>
</tr>
<tr>
<td></td>
<td>Suspension temperature</td>
<td>Precursor length</td>
</tr>
<tr>
<td>Sintering process</td>
<td>Particle characteristics (thermal expansion)</td>
<td>Membrane dimension</td>
</tr>
<tr>
<td></td>
<td>Particle size/distribution</td>
<td>Membrane morphology (dense/porous)</td>
</tr>
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<td>Sintering profile</td>
<td>Cracking/defect</td>
</tr>
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<td>Sintering placement (vertical/horizontal)</td>
<td>Grain size</td>
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<td>Environmental gas</td>
<td>Porosity</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pore size</td>
</tr>
</tbody>
</table>

2.6.1 Preparation of a spinning suspension

The spinning suspension is a viscous mixture composed of ceramic particles, solvent, binder and additives, in each of which has different influence on the suspension. The particle size, distribution and shape are important factors to consider when selecting the ceramic powders as they could affect the dispersion of ceramic particles in the suspension and properties of the produced fibre. For the binders, most of them are long-chain polymers that dissolve in the solvent. It should be noted that the binder must be fully burned away without leaving ash or tar during the sintering process. The
interaction between the binder and the solvent is very important as it determines the rheology of the suspension and affects the solidification process of a hollow fibre. Solvents used in the dry-jet wet extrusion technique must exhibit a high exchange rate with non-solvents (the term that is used to refer to coagulant). The exchange rate between solvent and non-solvent has an effect on cross-sectional structure of the hollow fibre. Other additives such as dispersants or lubricants are often added to improve the particle dispersion in the suspension. The dispersion depends on the ability of the dispersant to break the surface interaction between particles to allow them to remain separate. The amount of additive used should be as small as possible to increase the volume fraction of ceramic particles in spinning dope.

The typical process to prepare a homogeneous spinning suspension involves several steps as given here: (1) mixing a dispersant with a selected solvent in a container; (2) adding ceramic particles which must be well dispersed by a sieve; (3) adding milling balls to homogenize the particle suspension; (4) adding polymer binders and additive and (5) degassing the suspension dope before the extrusion process. A typical spinning suspension may contain approximately 50-70 wt% of ceramic material, 20-40 wt% of solvent, 5-7 wt% of binder and very small amount of dispersant (~0.1-1.5 wt.%). Ceramic material by far is the main constituent of the suspension and it is important that the spinning suspension is mixed sufficiently so that ceramic particles are completely surrounded by the binder. The suspension should also have a considerable viscosity for ease of fibre forming, at the same time playing an important role in varying the hollow fibre structure [119].
2.6.2 Extrusion of ceramic hollow fibre precursor

The second step in the dry-jet wet extrusion/sintering method is the extrusion of hollow fibre precursors. The hollow fibre precursor is the terminology used to refer to the extruded hollow fibre before sintering, which consists of ceramic material, polymer binder and dispersant. Prior to the extrusion process, it is essential to degas the prepared spinning suspension to prevent the incorporation of gas bubbles into the hollow fibre structure that reduces its integrity and uniformity. The spinning suspension is then extruded through the opening of a tube-in-orifice spinneret to form a fibre precursor. At the same time, the non-solvent internal coagulant is pumped through the centre of the spinneret, causing the precursor to be in the form of a hollow and longitudinal fibre. The fibre will then travel into the non-solvent external coagulation bath where it forms a coil.

The formation of the hollow fibre precursor results from the exchange between the solvent and the non-solvent (coagulant) which induces the precipitation of polymer in the suspension and hence consolidates the ceramic material [120]. This process is known as phase inversion [121] and the basic concept of this process can be explained by using the ternary phase diagram of polymeric system, which involves polymer, solvent and non-solvent, as shown in Figure 2.9. The entire phase inversion process of a polymeric solution is represented by the path from A to D. The original polymeric solution is at point A where no precipitation agent (non-solvent) is present in the solution. After immersion of the polymeric solution into a non-solvent coagulation bath, the solvent diffuses out of the polymer solution, while non-solvent diffuses into the solution. In the case that the solvent flux is higher than the non-solvent flux, the polymer concentration at the interface would increase, and at some point, the polymer starts to precipitate (is represented by point B). The continuous replacement of solvent...
by non-solvent would result in solidification of the polymer-rich phase (point C). Further solvent/non-solvent exchange would cause shrinkage of the polymer-rich phase and finally reach point D, where two phases (solid and liquid) are in equilibrium. A solid (polymer-rich) phase which forms the membrane structure represented by point S and a liquid (polymer-poor) phase which constitutes the membrane pores filled with non-solvent represented by point L.

![Ternary Phase Diagram](image.png)

**Figure 2.9:** Schematic ternary phase diagram of polymer/solvent/non-solvent during polymeric membrane formation [122].

It should be noted that the types of solvent, polymer binder or non-solvent could affect the precipitation mechanism in the phase inversion process. As an example, the N-Methyl-2-pyrrolidone (NMP) and dimethyl sulfoxide (DMSO) systems possess dissimilar precipitation line (Figure 2.10), where the precipitation point for the polyethersulfone (PESf)/DMSO/water system is much closer to the original casting solution (0 % water) line than that of the PESf/NMP/water system. Since the rates of solvent/non-solvent exchange for both systems are not very much different, therefore, the time to reach the precipitation point for PESf/DMSO/water system is much shorter
than that for the PESf/NMP/water system. As the macrostructure of the membrane is largely determined at the precipitation point, PESf/DMSO/water and PESf/NMP/water systems would yield different macrostructures.

![Phase diagrams for (a) PESf/DMSO/Water and (b) PESf/NMP/Water systems.](image)

**Figure 2.10:** Phase diagrams for (a) PESf/DMSO/Water and (b) PESf/NMP/Water systems. Thick line, binodal line; thin line, spinodal line; dashed lines, tie-lines; dot, solidification point (Reproduced from [123] and [124]).

Great effort has been made to both control and understand the formation mechanisms for the wide range of structures observed in polymeric membrane formation [125-126]. However, due to the large differences between polymeric and ceramic systems, in particular the low polymer concentration, this information is of limited use during ceramic membrane preparation. In fact, only two morphologies have so far been observed in ceramic systems, i.e. (1) finger-like voids and (2) a sponge-like structure, which the example of these two structures is given in Figure 2.11.
Hydrodynamically unstable viscous fingering is a well known phenomenon that occurs at the interface between fluids with different viscosities in the first moments of mixing and has been applied here to explain the formation of finger-like voids in ceramic membrane precursors [119]. When the suspension is in contact with non-solvent, a steep concentration gradient results in solvent/non-solvent exchange, a rapid increase in local viscosity and finally precipitation of the polymer phase. However, due to instabilities at the interface between the suspension and the precipitant there is a tendency for viscous fingering to occur, initiating the formation of finger-like voids. Under normal circumstances a stable interface would be established between the two phases of differing viscosities, however, due to the presence of invertible polymer binder a rapid viscosity increase followed by polymer precipitation retains the viscous fingering structure. The relative thickness of finger-like and sponge-like regions greatly affects the properties of the membrane or membrane support such as mechanical strength and permeation flux and, due to the

**Figure 2.11:** Example of the macrostructure of ceramic hollow fibre precursor [127].
versatility of ceramic hollow fibres, it is essential that fibre morphology can be controlled so that it may be tailored to specific applications [118, 119].

The first attempt to fabricate Ni-based anode hollow fibre support for micro-tubular SOFC via dry-jet wet extrusion was done by Yang et al. [128]. The morphology of the obtained anode hollow fibre was asymmetric which consisted of finger-like voids originating from the inner lumen of the hollow fibre and a sponge-like region on the outer side of the hollow fibre. Another design of morphology for anode support so-called sandwich-like structure which is represented by a structure of the finger-like voids originating from both inner and outer sides and sponge-like structure exists in the middle of the hollow fibre, was proposed by Droushiotis et al. [129]. Both finger-like voids and sponge-like regions are important to the anode support. Finger-like voids may provide a route with less resistance for transportation of the fuel gas and the products, while the sponge-like structure provides a large number of TPB for the electrochemical reactions [130] and also gives mechanical strength to the hollow fibres. However, it is believed that only finger-like voids from inner surface are useful, while the presence of the voids from outer side would only reduce the conductivity and mechanical strength of the hollow fibre and affect the gas-tightness of the electrolyte outer layer. Therefore, the asymmetric structure hollow fibre is preferable as the support for micro-tubular SOFC.

2.6.3 Sintering process

The hollow fibre precursors which normally comprise ceramic particles, binder and dispersant are heat treated in a furnace to develop the desired microstructure and properties. Ideally, this treatment or commonly known as sintering is the process by which a powder compact is transformed into a strong and dense ceramic body without
melting them. As the sintering process is required for the ceramic hollow fibre precursor prepared from dry-jet wet extrusion and therefore, this method is often called the “combined dry-jet wet extrusion and sintering technique”.

The sintering of the hollow fibre precursors can be divided into three major stages, pre-sintering, thermolysis and final sintering. Pre-sintering is a means of removing residual liquid that may remain after formation of the fibre precursor and any moisture adsorbed from the atmosphere during transporting and setting. The adsorbed moisture may persist in the precursor up to 200 °C [118]. It is important to increase the temperature slowly as expanding vapour within the lattice may cause cracks and fractures. Thermolysis is a process which burns out the organic components such as binder and dispersant and occurs as the temperature is increased to approximately 800 °C. It is an important step as incomplete binder removal and uncontrolled thermolysis may introduce defects in the hollow fibre which then may impair the performance of the hollow fibre.

Final sintering is defined as a transforming process of ceramic particles into a strong and dense ceramic body and it does not start to densify until the temperature reaches approximately 60-80 % of the melting point of the fibre material. For CGO with the melting point of approximate 2300 °C [130], the sintering temperature is roughly between 1400 to 1700 °C. The final sintering process usually involves three stages; initial stage, intermediate stage and final stage, which are shown in the Figure 2.12. The initial stage consists of the rearrangements of ceramic particle and neck growth at contacting points between particles. The initial stage lasts until the radius of the grown neck reach 40 to 50 % of the particle radius. In the intermediate stage, the grain boundaries start to develop. Ceramic particles are bounded together and pore channels
are formed along the grain edges. This stage normally covers the major part of the sintering process and leads to a major shrinkage of the ceramic membrane. When pores continue shrinking and some of them pinch off and become isolated at the grain corners, it is considered that the final stage has started. The growth of grains mainly occurs in this stage and the pores are gradually eliminated until the membrane turns into a fully dense structure. However, in most of the cases, the macrostructure of the fibre precursor formed during the phase inversion process is retained during sintering. Finger-like voids above a certain size cannot be eliminated, although at elevated sintering temperature sponge-like regions will be densified and eventually become gas tight for some ceramic materials [118,119].

![Figure 2.12: Development of ceramic microstructure during sintering process.](image)
2.7 Dual-Layer Hollow Fibre via Novel Co-extrusion/Co-sintering Technique

A more advanced dry-jet wet extrusion, i.e. phase inversion-based co-extrusion technique, has been developed to fabricate ceramic dual-layer hollow fibre. In this co-extrusion technique, one of the layers has to be thick in order to provide mechanical strength to the fibre. The use of co-extrusion has many advantages over conventional dry-jet wet extrusion methods such as simplified fabrication process and better control over the membrane structure. Furthermore, the risk of defects formation could be reduced and at the same time realising great adhesion between the layers. A fibre is basically prepared in the same way of the single-layer counterpart, except that the outer layer suspension is extruded through the outer annulus of the triple-orifice spinneret to form a dual-layer hollow fibre. The principals regarding the formation of finger-like and sponge-like structures as a result of viscous fingering during the phase inversion process are also very similar to the single-layer hollow fibres.

Studies on the fabrication and use of polymeric dual-layer hollow fibre membranes via phase inversion-based co-extrusion began in the late 1970s for haemodialysis [132]. Later, in the late 1980s, Yanagimoto invented dual-layer asymmetric flat sheet and hollow fibre membranes to improve the antifouling properties of polymeric membranes used for water purification [133,134]. The patent disclosures about the procedures of fabricating polymeric multi-layer hollow fibres for gas separation were made by Du Pont de Nemours [135]. Although there have been extensive investigations on the polymeric dual-layer hollow fibres in the recent 10 years [136-140], very limited research have been involved in the fabrication using ceramic materials [141-143] due to a number of challenges in the fabrication processes, such as adhesion problem and different sintering behaviour between the layers.
Realising the huge potential that is offered by the co-extrusion technique, a dual-layer hollow fibre support for intermediate temperature micro-tubular SOFCs has been developed in this study. Two spinning suspensions are separately prepared and then simultaneously co-extruded through a custom-made triple-orifice spinneret. The hollow fibre precursor is then subjected to a co-sintering process, followed by a simple reduction process. As a result, a dual-layer hollow fibre consisting of a CGO electrolyte outer layer (thickness in a range of 10-80 µm) supported by a 200-220 µm thick Ni-CGO anode inner layer has been successfully achieved, as shown schematically in Figure 2.13.

![Figure 2.13: Schematic drawing of electrolyte/anode dual-layer hollow fibre.](image)

### 2.8 Conclusions

For decades, many studies on SOFCs have been focused on compact design and cell performance enhancement. Micro-tubular SOFCs have recently attracted much attention for their greater tolerance to thermal cycling, quicker start-up capability, higher volumetric output density and portable characteristics when compared with the conventional planar and tubular SOFCs. Recently, the dry-jet wet extrusion technique has been used to fabricate ceramic hollow fibre supports of the micro-tubular SOFC. Compared with the conventional plastic mass ram extrusion technique, this dry-jet
wet extrusion shows better control over the internal macrostructure of the hollow fibre. The versatility of dry-jet wet extrusion is further demonstrated by the preparation of dual-layer hollow fibre supports in a single step by using co-extrusion/co-sintering. The use of this technique significantly simplified the fabrication process when compared with the single layer extrusion methods, while still allowing full control over the hollow fibre structures.

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CHAPTER 3

Single-Step Fabrication of Electrolyte/Anode Dual-Layer Hollow Fibres for Micro-Tubular Solid Oxide Fuel Cells

Abstract

This chapter reports the fabrication of defect-free cerium-gadolinium oxide (CGO)/nickel oxide (NiO)-CGO dual-layer hollow fibre precursor using novel co-extrusion process. In the early stage of this work, four hollow fibre precursors with variation in the anode structures were prepared. However, only hollow fibre precursor with anode asymmetric structure was chosen to be characterised. In order to find the optimum co-sintering temperature, the hollow fibre precursor was co-sintered at three different temperatures (1450 °C, 1500 °C and 1550 °C) which then followed by a simple reduction process. The produced CGO/nickel (Ni)-CGO hollow fibres can be distinguished by their electrolyte outer layer of approximately 80 µm supported by an asymmetric anode inner layer of approximately 220 µm. Advantageously, this fabrication technique results in great adhesion between the anode layer and the electrolyte layer. Moreover, no elemental inter-diffusion between layers, such as Ni, is observed even at 1550 °C. By increasing the co-sintering temperature, the mechanical strength of the developed dual-layer hollow fibre, gas-tightness of the electrolyte layer and electrical conductivity of the anode layer are increased. However, gas permeability through the anode layer decreases dramatically with the increase of the co-sintering temperature, which may greatly reduce the gas diffusion in the anode during the fuel cell operation and consequently affects the performance of the
corresponding micro-tubular SOFC. Based on the investigation of the effects of co-sintering temperature on the mechanical, structural and electrical conducting properties of the dual-layer hollow fibres, the hollow fibre that co-sintered at 1500 °C shows the most favourable properties and therefore, it was chosen for the construction of micro-tubular solid oxide fuel cells (SOFC). Micro-tubular SOFC fed with humidified hydrogen at the anode and air at the cathode produces acceptable maximum power densities, i.e. 0.34-0.68 W cm\(^{-2}\) at 550-600 °C.

### 3.1 Introduction

Solid oxide fuel cells (SOFCs) have been considered as a promising electricity-generation technology because of their high efficiency in converting chemical energy to electrical power [1]. To date, two types of SOFC designs, i.e. planar and tubular SOFCs, have been widely studied. Although planar SOFCs in a highly compact configuration show high power density, the design of this type is challenged by the sophisticated sealing near the edges of the cell since only few sealants can be employed at a high temperature operation [2]. In contrast, the tubular geometry is more reliable and can be operated in the absence of high temperature sealants. However, it is difficult to achieve high power output due to a less efficient cell packing and low surface area. In order to improve the volumetric power output, the diameter of tubular designs needs to be reduced from a few centimeters (e.g. Siemens-Westinghouse cell) to the order of 1 mm, namely micro-tubular SOFCs as they are often referred to in the literature. The design of this type can significantly increase the surface area of electrodes, improve mechanical properties and more importantly, speed up the start-up and the shut-down processes and as a result, the micro-tubular SOFCs have attracted increasing interests in recent years [3-9].
Besides the progress in SOFC designs, development in the fabrication process is critically important to ensure the success of the cell. Previously, the fabrication of micro-tubular SOFC can only be achieved through multiple-step processes [3-9]. A support layer for example anode tube is first prepared and pre-sintered to provide mechanical strength to the fuel cell. The electrolyte layer is then deposited and sintered prior to the final coating of cathode layer. Each step involves at least one high temperature heat treatment, making the cell fabrication time-consuming and costly with unstable control over cell quality.

For a more economical fabrication of micro-tubular SOFC with reliability and flexibility in quality control, an advanced dry-jet wet extrusion technique, i.e. a phase inversion-based co-extrusion process, is developed. Using this technique, an electrolyte/electrode (either anode or cathode) dual-layer hollow fiber can be formed in a single step. In general, the co-extrusion technique was firstly introduced for fabricating polymeric dual-layer membrane about 30 years ago [10-12] and extensive investigations have been carried out in the recent 10 years [13-18]. However, only a few research groups involved in the development of ceramic dual-layer membranes [19-21], as the result of numerous challenges in the fabrication processes.

In the co-extrusion process, two spinning suspensions have to be prepared. One suspension is extruded through the outer orifice of a triple-orifice spinneret whereas another one is extruded simultaneously through the inner orifice. Concurrently, the internal coagulant must be injected through the inner tube. In comparison with conventional extrusion processes, the co-extrusion is more attractive due to the following reasons: (i) saving the production cost and time as it combines two processes into one [22]; (ii) decreasing the risk of inducing defect [23]; (iii) producing
a great adhesion between layers [19]. However, when the two dopes are made of different materials with different concentrations, the fabrication of dual-layer hollow fibres become more complicated [24]. Furthermore, a co-sintering process, which is needed for the preparation of ceramic dual-layer hollow fibres, is another challenge in the preparation process since the sintering behaviours of the two layers must be well matched to avoid the formation of cracks or defects during the high temperature sintering.

This chapter reports the success of the fabrication of defect-free electrolyte/anode dual-layer hollow fibres using a phase inversion-based co-extrusion/co-sintering technique followed by a simple reduction process. The temperature dependent properties of the developed electrolyte/anode dual-layer hollow fibre, such as sintering behaviour, mechanical strength, gas-tightness of the electrolyte layer and porosity and conductivity of the anode layer, were also investigated by varying the co-sintering temperature from 1450 to 1550 °C, aiming at selecting the right co-sintering profile of the hollow fibres. A complete fuel cell was then developed by applying the cathode and current collectors on the dual-layer hollow fibres before an electrochemical measurement test was carried out on the cell at temperature between 550 to 600 °C using humidified hydrogen as the fuel and air as the oxidant.

### 3.2 Materials and Experimental Methods

#### 3.2.1 Materials

Commercially available cerium-gadolinium oxide (Ce$_{0.9}$Gd$_{0.1}$O$_{1.95}$ or CGO, surface area 35 m$^2$g$^{-1}$, $d_{50}$ 0.32 µm) and nickel oxide (NiO, surface area 5 m$^2$g$^{-1}$, $d_{50}$ 0.55 µm) were purchased from NexTech Materials Ltd. (Ohio) and they were used as supplied.
Polyethersulfone (PESf) (Radel A-300, Ameco Performance, USA), N-methyl-2-pyrrolidone (NMP) (HPLC grade, Rathbone) or dimethyl sulfoxide (DMSO) (Sigma-Aldrich), and polyethyleneglycol 30-dipolyhydroxystearate (Arlacel P135, Uniqema) were used as a polymer binder, solvent and dispersant, correspondingly. Tap water and de-ionized water were used as the external and internal coagulants respectively. Lanthanum strontium cobalt ferrite, La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_3$ (LSCF) (NexTech Materials Ltd., Ohio) and ethylene glycol (99+%, Acros Organic) were used as the materials for cathode slurry.

### 3.2.2 Preparation of electrolyte/anode dual-layer hollow fibres

In the preparation of the electrolyte/anode dual-layer hollow fibres, two ceramic suspensions were prepared separately. The suspension of the anode inner layer was composed of 60 wt.% of NiO and 40 wt. % of CGO, while the one for the electrolyte outer layer contained 100 % CGO powder. The suspensions compositions of four different dual-layer hollow fibres are listed in Table 3.1, in which the fibres are named as HF1, HF2, HF3 and HF4. Ceramic powders were first mixed with solvent (either NMP or DMSO) and the dispersant and stirred for 48 hours. After this time, PESf pellets were slowly added into the mixtures under stirring at ~300 rpm (OST 20 Digital YELLOLINE IKA). The mixing was further carried out for an extra 48 hours to obtain homogeneous spinning suspension.
Table 3.1: Compositions of the spinning suspension for dual-layer hollow fibres.

<table>
<thead>
<tr>
<th>Fibre name</th>
<th>Layer</th>
<th>Solvent type</th>
<th>Composition (wt.%)</th>
<th>Viscosity at 50 s⁻¹ (cP)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>NiO</td>
<td>CGO</td>
</tr>
<tr>
<td>HF1</td>
<td>Anode</td>
<td>NMP</td>
<td>39.60</td>
<td>26.40</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Electrolyte</td>
<td>-</td>
<td>64.00</td>
</tr>
<tr>
<td>HF2</td>
<td>Anode</td>
<td>NMP</td>
<td>40.80</td>
<td>27.20</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Electrolyte</td>
<td>-</td>
<td>64.00</td>
</tr>
<tr>
<td>HF3</td>
<td>Anode</td>
<td>NMP</td>
<td>42.60</td>
<td>28.40</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Electrolyte</td>
<td>-</td>
<td>64.00</td>
</tr>
<tr>
<td>HF4</td>
<td>Anode</td>
<td>DMSO</td>
<td>42.00</td>
<td>28.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Electrolyte</td>
<td>-</td>
<td>64.00</td>
</tr>
</tbody>
</table>
The dual-layer hollow fibre precursors were prepared by a phase inversion-based co-extrusion technique. Prior to the co-extrusion, both spinning suspensions were degassed while stirring at room temperature to fully remove the air trapped inside the suspensions. The both spinning suspensions were then loaded into two stainless steel containers and forced simultaneously through a triple-orifice spinneret. The illustration of co-extrusion process is shown schematically in Figure 3.1, while the photographic images and dimension of the spinneret are shown in Figure 3.2 (a-c).

**Figure 3.1**: Schematic diagram of the phase inversion-based co-extrusion process of the dual-layer hollow fibres precursor.
Figure 3.2: Photographic images of (a) triple-orifice spinneret from side, (b) triple-orifice spinneret from bottom, (c) dimension of the triple-orifice spinneret, (d) example of CGO/NiO-CGO dual-layer hollow fibre precursors.
The inner and outer layers spinning suspensions of HF1, HF2 and HF3 were pressurised using nitrogen gas, where the procedure has been described in detail elsewhere [25], while the extrusion rate of inner and outer layers for HF4 were accurately monitored and controlled by syringe pumps (PHD 2000 Programmable, HARVARD APPARATUS). The operating conditions employed for preparing the electrolyte/anode dual-layer hollow fibres are summarised in Table 3.2.

Table 3.2: Co-extrusion conditions of the dual-layer hollow fibres.

<table>
<thead>
<tr>
<th>Fibre name</th>
<th>Layer</th>
<th>Extrusion pressure/rate</th>
<th>Flow rate of internal coagulant ($\text{cm}^3\text{min}^{-1}$)</th>
<th>Air gap (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF1</td>
<td>Anode</td>
<td>15 psig</td>
<td>13</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>Electrolyte</td>
<td>20 psig</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HF2</td>
<td>Anode</td>
<td>15 psig</td>
<td>13</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>Electrolyte</td>
<td>20 psig</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HF3</td>
<td>Anode</td>
<td>15 psig</td>
<td>13</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>Electrolyte</td>
<td>20 psig</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HF4</td>
<td>Anode</td>
<td>7 cm$^3$ min$^{-1}$</td>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>Electrolyte</td>
<td>7 cm$^3$ min$^{-1}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The selected dual-layer hollow fibre precursors were then co-sintered at three different co-sintering temperatures in a tube furnace (TSH17/75/450, ELITE) under static air atmosphere. The temperature was increased from room temperature to 400 °C at a rate of 2 °C min$^{-1}$ and held for 1 hour, then to 800 °C at a rate of 2 °C min$^{-1}$ and held for 2 hours, and finally to target temperatures (i.e. 1450, 1500 and 1550 °C) at a rate of 15 °C min$^{-1}$ and held for 12 hours. The temperature was then reduced to room temperature at a rate of 5 °C min$^{-1}$.
Finally, the co-sintered CGO/NiO-CGO dual-layer hollow fibres were reduced to CGO/Ni-CGO hollow fibres in tube reactor (The Technical Glass Co, UK) using pure hydrogen. The tube was inserted into a horizontal furnace (MTF 12/25/250, CARBOLITE). Argon of 30 cm$^3$ min$^{-1}$ (20 °C, 1 atm) was used to expel the air until the reactor temperature reaches 550 °C, following which the argon flow was replaced by pure hydrogen of 20 cm$^3$ min$^{-1}$ (20 °C, 1 atm). After 2.5 hours of reduction, the flow of hydrogen was switched to argon until the temperature was reduced to room temperature. The heating and cooling rates were kept at 4 °C min$^{-1}$.

3.2.3 Characterisations of dual-layer hollow fibres

3.2.3.1 Viscosity test
Viscosity data was collected (Physica UDS-200 rheometer) using concentric cylinder geometry at shear rates between 0-100 s$^{-1}$ at 20 °C and spinning suspension samples were taken and tested immediately prior to hollow fibre preparation.

3.2.3.2 Scanning electron microscopy
The morphology of the dual-layer hollow fibres was examined using a JEOL JSM-5610 scanning electron microscopy (SEM). The hollow fibres were snapped in order to obtain cross-sectional fracture. These hollow fibre samples were then placed on a metal holder and sputtered by gold under vacuum. High resolution images of the cross-section of the hollow fibres were taken at different magnifications using secondary electron imaging (SEI) mode.
3.2.3.3 Sintering behaviour analysis

The sintering behaviours of the anode and electrolyte ceramic materials were studied using dilatometer (Netzsch, model DIL 402C). After mixing in ethanol and followed by a drying process, the mixtures of ceramic powders were pressed into rectangular bars with the dimensions of 6mm×6mm×20mm for testing. The measurements were carried out under static air atmosphere, using a heating rate of 3 °C min⁻¹ from room temperature to 1500 °C.

3.2.3.4 Energy dispersive X-ray spectroscopy

The elemental distribution at the interface between inner and outer layers of the hollow fibre was analyzed by energy dispersive X-ray spectroscopy (EDS) technique using JEOL 840 SEM. The sample preparation procedure was similar to the one for the SEM.

3.2.3.5 X-ray diffraction analysis

X-ray diffraction (XRD) analyzer was used to identify the crystal phases of inner and outer layers of the developed hollow fibre and to investigate the reduction of NiO and contamination or solid state reaction of the materials. XRD analysis was applied using an x’celerator detector, soller 004 rad (X’Pert PRO model) and a Cu x-ray tube with Kα radiation (λ = 154.2 pm). The sintered samples were analyzed in the range of 10° ≤ 2θ (°) ≤ 80 at a 1° scan rate.

3.2.3.6 Three-point bending test

The mechanical strength of hollow fibres was examined by three-point bending test using an Instron Model 5544 tensile tester provided with a load cell of 1 kN, as
illustrated in Figure 3.3. Dual-layer hollow fibres were fixed on the sample holder with a 30 mm distance. The bending strength \( B_F \) is calculated using the following equation [26]:

\[
B_F = \frac{8 N L D_o}{\pi (D_o^4 - D_i^4)}
\]  

(3.1)

where \( N \) is the measured load at which fracture occurred (N); \( L, D_o, D_i \) are the length, the outer diameter and the inner diameter of the hollow fibres (m), respectively.

**Figure 3.3:** Schematic representation of three-point bending strength testing apparatus.

### 3.2.3.7 Gas permeation tests

In this chapter, two types of gas permeation tests were performed which (i) for measuring the gas permeation across the anode layer and (ii) for measuring the gastightness of the electrolyte. For conducting the test of the first type, Ni-CGO single-layer hollow fibres had been fabricated using the same condition as the dual-layer hollow fibres. The nitrogen gas flow rate across the anode was measured using bubble flow meter. The hollow fibre for the test was glued into a stainless steel sample holder.
with epoxy resin (UKR-135 resin with UKH-136 hardener; UK Epoxy Resins, Lancashire, UK). It was then assembled into a cell/cylinder with a volume capacity of 300 cm$^3$. The feed gas was supplied at the bore side of hollow fibre, while the permeate gas was collected at the shell side of hollow fibre anode, as shown in Figure 3.4. The gas permeability was determined from the following equation [26]:

$$P = \frac{Q \ln(D_o / D_i)}{\pi L (D_o - D_i) \Delta P}$$

(3.2)

where $P$, $Q$, $D_o$, $D_i$, $L$ and $\Delta P$ are the gas permeability of nitrogen (mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$), the total gas permeation rate (mol s$^{-1}$), the inner and outer diameter of the hollow fibres (m), the hollow fibre length (m), and the pressure difference across the membrane (Pa), respectively. The permeability that obtained for these single-layer hollow fibres can be used to indicate the trend of gas flow through the anode of the dual-layer hollow fibres against the co-sintering temperature.

**Figure 3.4:** Schematic diagram of apparatus for measuring gas permeation.
Gas-tightness of the electrolyte layer of the hollow fibres was studied at room temperature using a gas permeation method described elsewhere [27]. The set-up of this test is slightly similar with the anode permeation test apparatus that shown in Figure 3.4. The main difference in the test is only the way how the gas permeation is measured. If the permeability of anode was obtained from the gas flow rate using bubble flow meter, the gas-tightness of the electrolyte was determined by pressure change over time using a pressure transducer that was connected to the permeation system. Nitrogen (N$_2$) was used as a testing gas. The gas permeability is thus obtained based on the cylinder pressure change with time:

$$P = \frac{V_C}{RT \cdot At} \ln \left( \frac{p_o - p_a}{p_i - p_a} \right)$$  \hspace{1cm} (3.3)

where $P$ is the permeability of the test membrane (mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$); $V_C$ is the volume of the test cylinder (m$^3$); $R$ is the gas constant (8.314 J mol$^{-1}$ K$^{-1}$); $T$ is the measured temperature (K); $p_o$ and $p_i$ are the initial and final measured pressures in the test cylinder (Pa); $p_a$ is the atmospheric pressure (Pa); $A$ (m$^2$) is the hollow fibre area that is $A = \pi(D_o - D_i)L/\ln(D_o/D_i)$, where $D_o$ and $D_i$ are respectively the outer and the inner diameter of the hollow fibre (m); $L$ is the length of the hollow fibre (m); and $t$ is the time for measurement (s).

### 3.2.3.8 Electrical conductivity test

The electrical conductivity measurement of anode hollow fibres is similar to the procedure described by Droushiotis et al. [9]. The conductivity of the samples was measured by using the four-point direct-current (DC) technique, which the set-up was developed in our collaborator laboratory (Professor Geoffrey Kelsall from Chemical Engineering Department, Imperial College London) as shown in Figure 3.5.
The hollow fibre samples were directly connected to the set-up without using a base. An accurate current was generated by applying a fixed potential between the working electrode (WE) and reference electrode (RE) of the potentiostat (Autolab® PGSTAT 30, Netherlands) which was applied across the resistor $R_{\text{known}}$ (100 $\Omega$, Metal film resistance) (counter electrode, $CE$, functions as a current-carrying electrode that completes the cell circuit). The currents were changed by varying the applied potential between 5 and 10 V. Potential drops due to the resistance of the measured length of the fibre were measured using a multimeter (Keithley 195 System SMM). The measurement was carried out at room temperature (ca 20 $^\circ$C). The potential differences across the anode hollow fibres of 20 mm length were measured by passing varying controlled currents (50, 75 and 100 mA). Linear fits to the generated $I$-$V$ data were used to determine anode fibre resistance from which the electrical conductivity of the anode ($\sigma$, S cm$^{-1}$) was estimated from the equation below:
\[ \sigma = \frac{L}{\rho_a \times A} \]  \hspace{2cm} (3.4)

where \( \rho_a \) is the anode resistance (\( \Omega \)), \( L \) is the fibre length (cm) and \( A \) is the cross-sectional area of the hollow fibre (cm\(^2\)), where \( A = \pi(D_o^2-D_i^2)/4 \).

### 3.2.3.9 Electrochemical measurements

Similar to the electrical conductivity set-up, the reactor set-up for electrochemical test of a single-cell of micro-tubular SOFC used in this work was also developed in our collaborator laboratory, Professor Geoffrey Kelsall, together with his PhD student (Nicolas Droushiotis). Prior to the electrochemical measurements, multi-layers of cathode were deposited on the electrolyte of the dual-layer hollow fibres. Two cathode material slurries (one was a mixture of 50 wt.% LSCF and 50 wt.% CGO, while another one was 100 wt.% LSCF) were prepared by mixing the powders with ethylene glycol in ratio 1:1 in weight. The co-sintered dual-layer hollow fibres were then cut to 50 mm length and the outer layer surface was then covered with masking tape, leaving 10 mm uncovered surface at the centre of the fibers. The cathode multi-layers, which the first and second layers were the mixture LSCF-CGO and the third layer was 100 wt.% LSCF, were deposited using brush painting technique onto the hollow fibres. Each layer was left to dry in air for 1 hour, before the next layer was applied. After the third layer dried, the hollow fibres were sintered at 1200 °C for 5 hours to form a complete micro-tubular SOFC with 10 mm length cathode.

The resultant cell was then fixed in a gas-tight alumina tube (Multilab Ceramics, UK) using a ceramic sealing paste, Ceramabond (Aremco, USA), after applying current collectors, as shown in Figure 3.6. The current collection was made by wrapping silver wire around the cathode layer and conductive platinum paste was used to reduce...
potential losses between the wire and the cathode surface. Silver wool was packed inside the fibre lumen for the anode current collection, producing excellent electrical contact onto the anode wall. The complete cell reactor was inserted in the centre of a tube furnace (MTF 12/25/250, CARBOLITE). An additional thermocouple (K-type thermocouple, YC-747D-4 Channel data logger) was placed close to the cell in the furnace in order to measure the temperature of the cell surface. The silver wires attached to the anode and the cathode were then connected to a potentiostat/galvanostat (Autolab® PGSTAT 30, Eco Chemie, Netherlands) and a booster (Autolab BSTR10A, Eco Chemie, Netherlands).

![Diagram of a micro-tubular SOFC with current collectors](image)

**Figure 3.6**: Experimental apparatus of the single micro-tubular SOFC reactor.
Prior to the fuel cell test, the anode of the cell was pre-conditioned in 5 cm$^3$ min$^{-1}$ of hydrogen (saturated with water vapour of 0.12 cm$^3$ min$^{-1}$ at 20 °C, 1 atm) at 550 °C for 2.5 hours in order to reduce NiO-CGO to Ni-CGO. Hydrogen of 15 cm$^3$ min$^{-1}$ (saturated with water vapour of 0.35 cm$^3$ min$^{-1}$ using a bubbling cylinder at 20 °C, 1 atm) and air of 40 cm$^3$ min$^{-1}$ (20 °C, 1 atm) were then flowed through the anode and cathode respectively in a counter-flow arrangement. The current-voltage ($I$-$V$) characterisation was recorded using cycling Voltammetry at galvanostatic mode (software Nova 1.5, Autolab, Eco Chemie) at operating temperature of 550 to 600 °C and a current step of approximately 1.1 second. The AC impedance spectra were measured on the same electrochemical workstation (0.01 Hz-100 kHz) with signal amplitude of 10 mV under open-circuit conditions from 550 to 600 °C and was controlled by FRA 4.9 (Frequency Response Analyzer connection, Autolab, Eco Chemie).

3.3 Results and Discussion

3.3.1 Macrostructure

Figure 3.2 (d) shows a photographic image of the dual-layer hollow fibre precursors developed in this study. The light yellow outer layer contains CGO powder, PESf and a small amount of dispersant. Meanwhile, the dark green inner layer is the mixture of NiO-CGO powders, PESf and dispersant. In order to study the structure of the obtained hollow fibre, the SEM images of the precursors HF1, HF2, HF3 and HF4 are shown in Figure 3.7. The anode inner layer cross-section of HF1 exhibits a sandwich-like structure with finger-like voids from both inner and outer sides, leaving a small sponge-like region in the middle of the hollow fibre.
Figure 3.7: SEM images of the (a) overall view and (b) cross-sectional view of the CGO/NiO–CGO dual-layer hollow fibre precursors HF1, HF2, HF3 and HF4. The images were taken using secondary electron imaging (SEI) mode.
It is believed that only finger-like voids originating from inner surface could facilitate
the fuel diffusion in the anode, while the presence of the voids from outer side would
reduce the conductivity and mechanical strength of the hollow fibre and affect the
gas-tightness property of the electrolyte outer layer. Therefore, effort has been done to
eliminate the finger-like voids in the outer surface of the anode by increasing the
initial viscosity of the inner layer suspension. Kingsbury and Li [28] reported that the
finger-like voids are formed when the suspension comes in contact with the non-
solvent (i.e. coagulant) which results in solvent/non-solvent exchange, leading to a
rapid increase in local viscosity and finally precipitation of the polymer binder phase.
However, due to instabilities at the interface between the suspension and the non-
solvent, there is a tendency for viscous fingering to occur which results in creation of
finger-like voids structure. These voids are then stopped by locally rising viscosity at
the front of advancing finger-like void which then leads to the formation of a sponge-
like structure. As fibre formation involving phase inversion is a dynamic process
involving the precipitation of the polymer phase, both the initial suspension viscosity
and the rate at which the viscosity increases during the fibre formation process are
important in determining the final fibre structure. The initial suspension viscosity
prior to phase inversion dictates how close the system is to the viscosity at which
viscous fingering is eliminated (critical viscosity). If the system is close to this point
then the critical value will be exceeded very soon after the phase inversion process is
initiated by contact with non-solvent and viscous fingering will be reduced.

As shown in Table 3.1, the inner layer suspension viscosity is increased by the
increase of particles (mixed NiO and CGO) loading from 66 wt.% to 68 wt.% and is
dramatically enhanced when the particles loading is 71 %. Although the fibre HF2
prepared from 68 wt.% has similar structure with HF1 in which the finger-like voids
are created from both inner and outer sides of the anode, the void length and size from the outer side of anode is slightly reduced. A sponge-like region occupying approximately 20% of the fibre cross-section presents between the inner and outer finger-like voids. The length of the finger-like voids structure is further reduced when the particles loading is increased to 71 wt.%, as shown in SEM images for HF3 (Figure 3.7). Despite of that, the macro-voids structure from the outer surface of the anode is still created due to the insufficient viscosity which causes to the formation of such void structure.

Therefore, DMSO is introduced as the solvent to replace NMP (which were used as a solvent in HF1, HF2 and HF3) in order to further suppress the formation of finger-like voids in outer surface of the inner layer. DMSO was chosen due to its high freezing point (i.e. 18.5 °C) which increases both the initial suspension viscosity and the rate of viscosity increase during phase inversion and thus, results in an incipient increase of the resistance against the formation of finger-like voids (i.e. freezing effect) [29]. As a result, different morphology is formed for HF4, as it presents an asymmetric structure with short finger-like voids structure originating from the inner surface to approximately 35% of the inner layer thickness, whereas the other 65% consists of a sponge-like structure.

As shown in Figure 3.7, the electrolyte outer layer for all the dual-layer hollow fibres is uniformly deposited on the anode inner layer. The electrolyte outer layers thickness of the HF1, HF2 and HF3 are similar due to the use of same suspension composition and co-extrusion conditions, however HF4 which used DMSO as a solvent shows a thicker electrolyte layer. The outer layer of HF4 also shows small finger-like voids near the outer surface and sponge-like structures occupying the rest of the layer. This
figure also highlights the advantage of developing dual-layer ceramic hollow fibre using the co-extrusion technique. For most of the other methods fabricating multi-layer ceramic membranes (disk and tubular membranes), the adhesion between the layers is always a concern. As can be seen in Figure 3.7, great adhesion between the layers has been achieved without any delamination for all batches of the fabricated hollow fibres, which can be attributed to the good material compatibility between the two suspensions. PESf and DMSO (or NMP) were used as the binder and solvent(s) respectively in both the inner and the outer layer suspensions and contribute to form a seamless interface between the layers. A higher ceramic powder concentration in the inner layer suspension can result in a smaller shrinkage during the phase inversion, when compared with the outer layer suspension. This further improves the adhesion between the layers, fully prevents the delamination which is unfavourable to hollow fibre’s integrity and structural stability [30].

For ceramic membranes with a dual-layer structures, especially when the two layers are made of different materials, co-sintering is always challenging due to the different sintering behaviours of the membrane materials. The co-sintering of ceramic hollow fibres would be more difficult because of higher surface area and higher curvity of the fibre when compared with disk or tubular counterparts. Prior to the co-sintering of the dual-layer hollow fibres, the sintering behaviours of the membrane materials were investigated using a heating rate of 3 °C min⁻¹ and the results of which are shown in Figure 3.8. When compared with the anode inner layer, the electrolyte outer layer starts to shrink at lower temperature with a much higher final shrinkage of about 14.7 % (Figure 3.8(a)). Moreover, the highest sintering rate of the electrolyte layer is almost twice of that of the anode layer and turns up at a temperature of about 200 °C lower than the anode layer, as shown in Figure 3.8(b). Due to the significantly
different sintering behaviours between inner and outer layers and as an effort to delay the sintering temperature of electrolyte layer so that it close to that of the anode layer, a heating rate as high as 15 °C min\(^{-1}\) is used during the co-sintering process of the dual-layer hollow fibre, below which heating rate, the fibres might not survive the co-sintering as has been observed experimentally.

![Figure 3.8](image.png)

**Figure 3.8:** (a) Sintering curves and (b) sintering rate curves of the inner and outer layer materials. The ceramic powders of each layer were pressed into rectangular bars and were carried out under static air atmosphere using of heating rate of 3 °C min\(^{-1}\).
As the desire anode structure is achieved in HF4, only HF4 was co-sintered, reduced and characterised. After co-sintering the CGO/NiO-CGO hollow fibre precursor and reducing NiO in the inner layer to Ni, a CGO/Ni-CGO dual-layer hollow fibre for micro-tubular SOFC was obtained. The microstructures of the resultant CGO/Ni-CGO dual-layer hollow fibres which were co-sintered between 1450 °C and 1550 °C for 12 hours are shown in Figure 3.9. The outer diameter (OD) and the inner diameter (ID) of the dual-layer hollow fibre are measured to be of approximately 1400 and 800 µm respectively (Figure 3.9(a1-c1)) and the thicknesses of the inner and outer layers are ca. 220 µm and 80 µm. The macrostructures of the CGO/Ni-CGO dual-layer hollow fibres (Figure 3.9(a2-c2)), which are free of cracks, are almost the same as that of the CGO/NiO-CGO dual-layer hollow fibre precursor (Figure 3.7) which indicates that the co-sintering only removed the organic materials without changing general structure of the hollow fibre.

As the temperature of co-sintering increases, the porosity of the inner layer decreases as shown in Figure 3.9(a3-c3) and (a5-c5). However, the inner layer’s cross-section as well as the inner surface are still quite porous as the pores were formed during the reduction of NiO to Ni. Indeed, the porous structure in anode is desirable for the fuel gas to diffuse through without too much resistance. Similar trend is also found for the outer layer. As the increase of co-sintering temperature, the electrolyte layer becomes denser (Figure 3.9(a4-c4) while the CGO grain size becomes bigger (Figure 3.9(a6-c6)). The outer surface of the hollow fibres become smoother and the average CGO grain size, which is visually estimated from the SEM images, is of approximately 2.7, 5.9 and 9.6 µm for the co-sintering temperature at 1450, 1500 and 1550 °C, respectively.
Figure 3.9: SEM images of the reduced dual-layer hollow fibre (HF4) at different co-sintering temperatures; (a) 1450 °C, (b) 1500 °C and (c) 1550 °C, at different views; (1) Overall view of the hollow fibre, (2) Cross-section of the hollow fibre, (3) Cross-section of inner layer, (4) Cross-section of outer layer, (5) Inner surface of the hollow fibre and (6) Outer surface of the hollow fibre. The images were taken using secondary electron imaging (SEI) mode.
3.3.2 Nickel distribution and crystal phases in the dual-layer hollow fibres

For polymeric membrane, the inter-layer diffusion in the dual-layer hollow fibres is desired since it could enhance the adhesion between the layers [14, 31]. However, in ceramic membrane especially for SOFC application, the inter-layer diffusion must be prevented as it may reduce the cell efficiency by short-circuiting. Based on previous studies [14], the inter-layer diffusion phenomenon can be minimised by controlling the fabrication parameters, such as keeping low spinneret temperature (i.e. 25 °C). When the spinneret temperature is low, the viscosities of the extruded suspensions are high and the diffusion rate of the components molecules in the suspensions between the two layers would be slowed down. Therefore, in this study, the spinneret was kept at temperature below than 20 °C. The inter-layer diffusion in the electrolyte/anode dual-layer hollow fibre was analysed by energy dispersive spectrometry (EDS) and the result is shown in Figure 3.10 in which the hollow fibre sample was co-sintered at 1550 °C for 12 hours.

As can be seen in this figure, no Ni element was detected in the electrolyte outer layer which indicates that Ni in the anode layer does not pass through the interface and diffuse into the electrolyte layer during the co-extrusion process and even at 1550 °C of co-sintering. Moreover, the amount of Ni detected in the anode is about 47 wt.%, which is quite close to the calculated Ni concentration in the anode made of 60 wt.% of NiO and 40 wt.% of CGO (Ni content in reduced Ni-CGO cermet anode is about 54.1 wt.%).
Figure 3.10: Energy dispersive spectrometry (EDS) analysis of the nickel distribution near the interface between the two layers of the reduced dual-layer hollow fibres. The fibre was co-sintered at 1550 °C.

In Figure 3.11, X-ray diffraction (XRD) patterns of the anode inner layer (before and after reduction) are compared with the original CGO and NiO powders. Similar to EDS analysis, only the hollow fibre co-sintered at 1550 °C is used for XRD analysis. As can be seen in this figure, no secondary phase is found except the cubic phases of NiO and CGO in the anode after the co-sintering. Furthermore, NiO was fully reduced into Ni at 550 °C for 2.5 hours using pure hydrogen without affecting the structure of CGO. All these are in agreement with Chen’s work [32]. The outer surface of the electrolyte layer was also characterised by XRD and no Ni or NiO phase was
detected. This indicates that during the co-sintering process, there is no inter-diffusion between the layers, in good agreement with the results of EDS analysis (Figure 3.10).

**Figure 3.11**: XRD patterns of the reduced and unreduced dual-layer hollow fibres. Both reduced and unreduced fibres were co-sintered at 1550 °C and the patterns of hollow fibre were compared with that of their pure powders.
3.3.3 Effects of co-sintering temperature on the microstructures of dual-layer hollow fibres

For ceramic membranes, use of higher sintering temperature contributes normally in improving the mechanical strength of the membrane, while in the meantime decreases the porosity and increases the resistance to gas permeation. The dual-layer hollow fibre developed in this study which functions as a support for micro-tubular SOFC, requires reasonably strong mechanical property for the deposition of remaining components such as cathode and current collector, in addition to a highly porous anode and a dense electrolyte layers. As a result, the effects of the co-sintering temperature on the developed dual-layer hollow fibre have been investigated.

The effect of co-sintering temperature on the mechanical property (bending strength) of the developed CGO/Ni-CGO hollow fibre, which was investigated by a three-point bending test, is shown in Figure 3.12. As can be seen, a significant increase in the bending strength of around 38% is observed when the co-sintering temperature increases from 1450 to 1500 °C, while another increase of less than 8% is observed when the temperature is further increased to 1550 °C. At higher temperature, the ceramic particles fuse and develop into larger and closer grains with stronger bounding between them, thus giving higher mechanical strength. The mechanical strength of the developed CGO/Ni-CGO hollow fibre sintered at 1500 °C for 12 hour is approximately 141.1 MPa. This value is comparable with the Ni-YSZ tube or hollow fibre with similar size and Ni content. As an example, Ni-YSZ tube fabricated by gel casting (112.8 MPa) [33], Ni-YSZ tube made by plastic mass ram extrusion technique (130 MPa) [34] and Ni-YSZ hollow fibres made by dry-jet wet extrusion/sintering technique (118.6 MPa and 35 MPa for structures with finger-like
voids on one side (asymmetric structure) and both sides (sandwich-like structure) respectively) [7, 9].

![Figure 3.12: Bending strength of the reduced dual-layer hollow fibres measured at room temperature as a function of co-sintering temperatures (number of samples = 5).](image)

The effect of co-sintering temperature on the pore structure of the anode inner layer was investigated by a nitrogen permeation test, in which the Ni-CGO anode hollow fibre samples were fabricated using same preparation conditions as those for the dual-layer hollow fibre. As can be seen in Figure 3.13, the nitrogen permeability values are significantly higher for fibre sintered at 1450 °C than the fibre at 1500 °C and the permeability values further drop when the sintering temperature is increased to 1550 °C. Moreover, with the increase of the sintering temperature, the nitrogen permeability is less dependent on the inlet pressure, i.e. the slope of the permeability
curve is closer to 0, which shows that Knudsen diffusion flow is dominant for the hollow fibre co-sintered at higher temperature and thus indicates the average pore size in the anode layer decreases with the increase of the sintering temperature. This is also in agreement with the results in Figure 3.9.

![Figure 3.13](image)

Figure 3.13: Gas permeability of the reduced anode single-layer hollow fibres as a function of inlet pressure. The trend of the permeability of the anode fibres sintered at different co-sintering temperatures was compared.

The electrolyte layer of SOFC must be impermeable to any gas to avoid direct contact between fuel and oxidant. In order to investigate the effect of the co-sintering temperature on the outer electrolyte layer of the developed dual-layer hollow fibres, a gas-tightness test was carried out, the process of which has been described elsewhere [27]. According to Tan et al. [27], a membrane can be considered fully gas-tight if the
nitrogen permeability measured is close to $10^{-10}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$. As can be seen in Figure 3.14, the nitrogen permeability of the hollow fibres co-sintered at 1450 °C is $13.9 \times 10^{-10}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$. This value decreases dramatically to $2.02 \times 10^{-10}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$ at 1500 °C and only reduces slightly to $0.96 \times 10^{-10}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$ when the co-sintering temperature is increased to 1550 °C. This is due to the decrease of the porosity in the electrolyte layer with the increase of co-sintering temperature and indicates that the co-sintering temperature at 1500 °C is high enough to achieve a dense electrolyte layer for SOFCs.

![Figure 3.14](image-url)

**Figure 3.14:** Gas permeability of the reduced dual-layer hollow fibres measured at room temperature as a function of co-sintering temperature, with the initial pressure of 40 psig. This graph is used to describe the gas-tightness property of the electrolyte layer (number of samples = 3).
3.3.4 Effect of co-sintering temperature on the electrical conductivity

Apart from the structural characteristics discussed above, electrical conductivity of the anode is critically important to minimise the ohmic losses in the cell. In this study, the conductivity measurement of the anode which is a single layer Ni-CGO hollow fibre prepared under same conditions as those of the dual-layer hollow fibres was carried out using four-probe DC technique at room temperature. The conductivity obtained is mainly from the contribution of Ni phase in the anode as the CGO has no electronic conductivity at room temperature. Figure 3.15 shows the potential difference across the anode as a function of current. As expected, linear curves were obtained in all $I-V$ plot, which indicates ohmic behaviour of the anode.

![Figure 3.15: Current-voltage behaviour of the reduced anode single-layer hollow fibre that sintered at different temperatures. The measurement was carried out at room temperature by passing varying controlled currents (0.050, 0.075 and 0.100 A).](image-url)
The resistance calculated from the slope of the linear curves of the $I-V$ plots were then used to determine the conductivity value according to the Eq. (3.4). The electrical conductivity of the anode hollow fibres against the sintering temperature is plotted in Figure 3.16. As can be seen, the electrical conductivity increases when the sintering temperature increases from 1450 to 1550 °C. With the increase of sintering temperature, the connection between NiO particles are strengthened, forming a more continuous Ni phase after reduction which contribute to the increase in the electrical conductivity of the anode [7, 9, 35]. This result also suggests that the anode layer has almost achieved its ideal sintering temperature at 1500 °C as there is only small difference between the conductivity values at 1500 °C and 1550 °C.

**Figure 3.16**: Electrical conductivity of the reduced anode single-layer hollow fibres as a function of sintering temperature. The measurement was carried out at room temperature using 4-point DC technique.
In addition, the conductivity values obtained in this work are much higher than previous studies, for example, the conductivity of Ni-YSZ hollow fibre consisted sandwich-like structure with 50 wt.% Ni content was ca. 1700 S cm\(^{-1}\) [9] while the conductivity of Ni-YSZ hollow fibre with asymmetric structure is ca. 772 S cm\(^{-1}\) [7]. This is because of more sponge-like structure with shorter and less finger-like voids and more uniform Ni distribution in the anode layer of the dual-layer hollow fibres are developed in this study. Another reason for the higher conductivity in this study is that the hollow fibre samples are directly connected to the set-up without using any base [9] or paste connection [7]. This contributes to a lower resistance and as a result, increases the measured values of the conductivity.

Based on the discussion above on the effects of co-sintering temperature on the properties of dual-layer hollow fibre, a temperature at 1500 ℃ was chosen to co-sinter the hollow fibre for the construction of a complete micro-tubular SOFC, which will be discussed in the following section.

### 3.3.5 Electrochemical performances

A multi-layer cathode consisting of two layers of LSCF-CGO mixture and one layer of pure LSCF was brush-painted onto the electrolyte surface of HF4 co-sintered at 1500 ℃. The morphology of the sintered cathode layer was observed using SEM and the image is shown in Figure 3.17. As can be seen, the obtained cathode of approximately 40 µm is porous and uniform which greatly facilitates gas transport and oxidant reduction reaction in the cathode. The cathode layer is also in good contact with the electrolyte surface of the dual-layer hollow fibres. Furthermore, although the cathode is made of three layers, no obvious boundaries between the layers can be
observed, indicating a very low resistance for the transfer of electrons and oxygen ions.

![SEM image of cathode layer prepared using brush-painting technique and sintered at 1200 °C for 5 h.](image)

**Figure 3.17**: SEM image of cathode layer prepared using brush-painting technique and sintered at 1200 °C for 5 h. The images were taken using secondary electron imaging (SEI) mode.

The electrochemical performance of the full cell with active cell length of 10 mm, inner diameter of 0.80 mm and outer diameter of 1.44 mm was investigated at different temperatures (550-600 °C) using hydrogen gas of 15 cm$^3$ min$^{-1}$ (saturated with water vapour of 0.35 cm$^3$ min$^{-1}$ at 20 °C, 1 atm) at the anode (lumen side) and air (40 cm$^3$ min$^{-1}$ at 20 °C, 1 atm) at the cathode side (outer surface). Figure 3.18 shows the cell voltage and power density curves as a function of the current density. The open-circuit voltage (OCV) decreases with the increase of the cell operating temperature, which shows the values of ca. 0.97, 0.95, and 0.93 V at 550 °C, 570 °C and 600 °C respectively.
Figure 3.18: Voltages and power densities as functions of current density of the cell HF4 co-sintered at 1500 °C. The cell operated at temperature range of 550 to 600 °C using hydrogen flow rate of 15 cm$^3$ min$^{-1}$ (20 °C, 1 atm) and air flow rate of 40 cm$^3$ min$^{-1}$ (20 °C, 1 atm).

This can be explained by the increase of electronic conductivity in the CGO electrolyte with the increase of temperature [36], which causes more electrons in the anode transport through the electrolyte to the cathode and results in a minor short circuiting to the cell. Due to the same reason, the OCV values that were obtained in this study are also slightly lower than the Nernst voltage, $V_N$ that calculated from the equation below:
\[ V_N = \frac{-\Delta G_T}{2F} + \frac{RT}{2F} \ln \left( \frac{p_{H_2} \sqrt{p_{O_2}}}{p_{H_2O}} \right) \]  \hspace{1cm} (3.5)

where \( \Delta G_T \) is the Gibbs energy at the operational temperature, \( F \) is the Faraday constant, \( R \) is the gas constant, \( T \) is the cell temperature and \( p_{H_2}, p_{O_2} \) and \( p_{H_2O} \) are the partial pressures of hydrogen, oxygen and steam, respectively. Based on the assumptions that the cell operates at 1 atm with the fuel stream consists of 97.7 mol% \( H_2 \) + 2.3 mol% \( H_2O \) and air stream contains 21 mol% \( O_2 \), the \( V_N \) at operating temperature of 600 °C is approximately 1.16 V.

As also shown in Figure 3.18, the cell HF4 produces the maximum power densities of 0.34 W cm\(^{-2}\), 0.47 W cm\(^{-2}\) and 0.68 W cm\(^{-2}\) at 550 °C, 570 °C and 600 °C, respectively. However, the maximum power density is still about 70% lower than reported for the 10 µm electrolyte cells with similar operating temperatures [5, 37-39], largely due to the thicker electrolyte layer of the cell that is developed in this work of about 80 µm. Hence, further optimisation on the electrolyte layer thickness is expected would reduce potential losses and increase power densities of the cell significantly.

Figure 3.19 shows the impedance spectra for the cell HF4 at the temperatures 550 °C, 570 °C and 600 °C under open-circuit condition. The high frequency intercept on the real impedance axis corresponds to the ohmic area specific resistance (ASR) of the cell (ionic and electronic resistances of the electrolyte and the electrodes of the cell and some contact resistance associated with interfaces [40]), while the low frequency intercept represents the total ASR of the cell. Therefore, the difference between the high frequency and low frequency intercepts on the real axis is taken as approximating to the electrode polarisation ASR, which generates from the resistances.
of the gas diffusion and the gas conversion, i.e. fuel oxidation and oxygen reduction [40]. As expected, the ohmic ASR decreases with the operating temperature due to increase in the conductivities of the anode, electrolyte and cathode materials. The same trend is shown for the electrode polarisation ASR and this can be attributed to the increase in the kinetics of the fuel oxidation and oxidant reduction reactions in the anode and cathode respectively with the rise of cell operating temperature.

**Figure 3.19:** Impedance analysis of the cell HF4 co-sintered at 1500 °C measured under open-circuit condition at temperature range of 550 to 600 °C using signal amplitude of 10 mV at frequencies of 100 kHz to 0.01 Hz and hydrogen flow rate of 15 cm$^3$ min$^{-1}$ (20 °C, 1 atm) and air flow rate of 40 cm$^3$ min$^{-1}$ (20 °C, 1 atm).
3.4 Conclusions

Defect-free CGO/NiO-CGO dual-layer hollow fibres precursors have successfully been prepared by phase inversion-based co-extrusion technique. The chosen hollow fibres precursors were then co-sintered at a temperature range of 1450-1550 °C before a reduction process at 550 °C using hydrogen in order to form to CGO/Ni-CGO dual-layer hollow fibres. The dual-layer hollow fibres have the anode inner layer consisting of an asymmetric structure with short finger-like voids originating from the inner fibre surface and the electrolyte outer layer which has a dense structure. The experimental results obtained from the analyses conducted indicate that as the co-sintering temperature is increased, the mechanical strength, gas-tightness property of the electrolyte and electrical conductivity of the anode of the dual-layer hollow fibres are improved. On the contrary, it is found that the permeability of the anode layer decreases with the rise of the co-sintering temperature. Based on these results, the co-sintering temperature of 1500 °C is the recommended temperature to co-sinter the dual-layer hollow fibres and the micro-tubular of SOFC is developed using the hollow fibre co-sintered at this temperature. The fuel cell of the corresponding dual-layer hollow fibre produces maximum power densities of 0.68 W cm$^{-2}$ at temperature 600 °C and this is indeed shows the potential of co-extrusion/co-sintering technique in producing the support for SOFC. However, optimisation of the structure of the dual-layer hollow fibres is required to improve the performance of the micro-tubular SOFCs.

References


CHAPTER 4

Electrolyte Thickness Control and Its Effect on Electrolyte/Anode Dual-Layer Hollow Fibres for Micro-Tubular Solid Oxide Fuel Cells

Abstract
As an effective effort in improving the performance of electrolyte/anode dual-layer hollow fibres for micro-tubular solid oxide fuel cell (SOFC), high quality dual-layer hollow fibres with controllable electrolyte layer thickness have been developed in this work by adjusting the fabrication parameters of a single-step co-extrusion/co-sintering process. Uniform and defect-free outer electrolyte layer from 70 to 10 µm can be achieved when the extrusion rate is reduced from 5 to 0.5 cm$^3$ min$^{-1}$. Although the bending strength and the gas-tightness properties are reduced slightly with the decrease in electrolyte layer thickness, a significant improvement in power output of the cell is achieved. Power density as high as 1.11 W cm$^{-2}$ is obtained from the cell with the electrolyte layer of 10 µm in thickness which is 114 % higher than the one with an electrolyte layer of 65 µm.

4.1 Introduction
The micro-tubular solid oxide fuel cell (SOFC) has received considerable attention in recent years due to the advantages of this design. The reduction in the size of SOFC leads to an increase in the volumetric power density as the power density scales with the reciprocal of the tube diameter [1]. Therefore, a 2 mm diameter micro-tubular
SOFC could provide ten times of more power per stack volume than a 20 mm diameter counterpart. Another order of magnitude increase could be achieved by further reducing of the tube size to 0.2 mm diameter but this is difficult because the connections are then more challenging and problematic to apply. The most significant issue in micro-tubular SOFC is the efficiency of the current collector connection into the lumen of a small tube. Apart from enhancing power output of the fuel cell, high thermal shock resistance is also one of the major advantages of the micro-tubular design. The large-diameter tubular SOFC are prone to cracking if they are rapidly heated, whereas the micro-tubular SOFC does not crack even when heated in blow torch to their operating of about 850 °C in as fast as 5 seconds [1]. Hence, this is a marked advantage in applications where start-up time is critical.

In general, the development in the fabrication process of the micro-tubular SOFC support is critically important to ensure the success of the cell. To date, two techniques have been commonly used in fabricating support of micro-tubular SOFC, which are plastic mass ram extrusion [2,3] and dry-jet wet extrusion [4,5]. The first technique generally involves a direct extrusion of ceramic paste through a die, in which macrostructure of the obtained micro-tubular support is symmetric and does not directly affected by the extrusion process. In contrast, the latter technique involves extrusion of a ceramic-based suspension containing polymer binder dissolved in solvent through a spinneret, passing through an air gap and finally into a non-solvent external coagulation bath. Simultaneously, another non-solvent internal coagulant flows through the lumen of the micro-tubular support precursor and the contact between internal coagulant and ceramic suspension initiates the formation of some kinds of structures (i.e. sponge-like and finger-like voids structures).
In the previous chapter, the development of defect-free cerium-gadolinium oxide (CGO) electrolyte/nickel (Ni)-CGO anode dual-layer hollow fibres for micro-tubular SOFCs via a more advanced dry-jet wet extrusion technique, i.e. a single-step co-extrusion, and followed by co-sintering and easy reduction processes has been discussed. Benefiting from the advantages of this fabrication technique, great adhesion between the anode and the electrolyte layers was achieved without any crack formation during the co-sintering. The developed dual-layer hollow fibres with the outer diameter of ca. 1400 µm and inner diameter of 800 µm consisted of a fully gas-tight electrolyte outer layer (CGO) of ca. 80 µm supported on an asymmetric anode inner layer (Ni-CGO) of approximately 220 µm. After deposition of a multi-layers cathode and applying current collectors on both the anode and cathode, a micro-tubular SOFC with the maximum power densities of 0.34-0.68 W cm\(^{-2}\) at 550-600 °C was obtained. These values are still lower than those of micro-tubular SOFCs prepared by the conventional ram extrusion and sintering technique [2,6,7,8], which was attributed to several factors and one of them was relatively thick CGO electrolyte layer (around 80 µm) as the thickness of the electrolyte could affect the ohmic properties of the cells.

Therefore, the main objective of the work that is reported in this chapter is to reduce the thickness of the electrolyte layer and afterward, to investigate the effect of the electrolyte thickness on the electrochemical performance of micro-tubular SOFCs. In the meantime, a series of characterisations on hollow fibre properties such as macrostructure, mechanical strength and gas-tightness have been carried out in order to further understand the effect of the electrolyte thickness towards the quality of the obtained dual-layer hollow fibres.
4.2 Materials and Experimental methods

4.2.1 Materials
Commercially available cerium-gadolinium oxide (Ce$_{0.9}$Gd$_{0.1}$O$_{1.95}$ or CGO, surface area 35 m$^2$g$^{-1}$, $d_{50}$ 0.32 µm) and nickel oxide (NiO, surface area 5 m$^2$g$^{-1}$, $d_{50}$ 0.55 µm) were purchased from NexTech Materials Ltd. (Ohio) and they were used as supplied. Polyethersulfone (PESf) (Radel A-300, Ameco Performance, USA), dimethyl sulfoxide (DMSO) (Sigma-Aldrich), and polyethyleneglycol 30-dipolyhydroxystearate (Arlacel P135, Uniqema) were used as a polymer binder, solvent and dispersant, respectively. Tap water and de-ionized water were used as the external and internal coagulants correspondingly. Lanthanum strontium cobalt ferrite, La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_3$ (LSCF) (NexTech Materials Ltd., Ohio) and ethylene glycol (99+, Acros Organic) were used as the materials for cathode slurry.

4.2.2 Preparation of dual-layer hollow fibres with different electrolyte thicknesses
The procedure of preparing the dual-layer hollow fibres in this study has been described in detail in Chapter 3. For this batch of fibres, the spinning suspension mixtures were milled with 20 mm agate milling balls for 48 hours instead of mixing using paddle stirrer as for the previous batch of fibres. The use of ball milling technique is more advantageous due to the better dispersion of the ceramic particles and also better seal of the suspension container during the mixing, which results to the negligible contamination or evaporation of the solvent. The compositions of the spinning suspensions for fabrication of the dual-layer hollow fibres are given in Table 4.1.
Table 4.1: Compositions of the spinning suspension for dual-layer hollow fibres with different electrolyte thicknesses.

<table>
<thead>
<tr>
<th>Layer</th>
<th>Composition (wt.%)</th>
<th>Viscosity at 50 s(^{-1}) (cP)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NiO</td>
<td>CGO</td>
</tr>
<tr>
<td>Anode</td>
<td>42.00</td>
<td>28.00</td>
</tr>
<tr>
<td>Electrolyte</td>
<td>-</td>
<td>60.00</td>
</tr>
</tbody>
</table>

The suspensions were degassed at room temperature under stirring and then loaded into two stainless steel syringes. They were simultaneously co-extruded by a syringe pump (PHD 2000 Programmable, HARVARD APPARATUS) through a triple-orifice spinneret into a tap water coagulation bath with de-ionized water as the internal coagulant. The co-extrusion conditions are summarised in Table 4.2, in which the samples are named according to the extrusion rate of the electrolyte outer layer. Details about the design of the spinneret can be found in Chapter 3. The hollow fibre precursors were then co-sintered by heating in air at 1500 °C for 12 hours in a tubular furnace (TSH17/75/450, ELITE). The co-sintered dual-layer CGO/NiO-CGO hollow fibers were reduced to CGO/Ni-CGO dual-layer hollow fibres at 550 °C using pure hydrogen for 2.5 hours (MTF 12/25/250, CARBOLITE).
Table 4.2: Co-extrusion conditions of dual-layer hollow fibres with different electrolyte thicknesses.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Air gap (cm)</th>
<th>Internal coagulant flow rate (cm³ min⁻¹)</th>
<th>Inner layer extrusion rate (cm³ min⁻¹)</th>
<th>Outer layer extrusion rate (cm³ min⁻¹)</th>
<th>Electrolyte thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R-0.5</td>
<td></td>
<td></td>
<td>0.5</td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>R-1</td>
<td></td>
<td></td>
<td>1</td>
<td></td>
<td>19</td>
</tr>
<tr>
<td>R-2</td>
<td>20</td>
<td>10</td>
<td>7</td>
<td></td>
<td>35</td>
</tr>
<tr>
<td>R-3</td>
<td></td>
<td></td>
<td>3</td>
<td></td>
<td>53</td>
</tr>
<tr>
<td>R-4</td>
<td></td>
<td></td>
<td>4</td>
<td></td>
<td>65</td>
</tr>
<tr>
<td>R-5</td>
<td></td>
<td></td>
<td>5</td>
<td></td>
<td>70</td>
</tr>
</tbody>
</table>

4.2.3 Characterisations of dual-layer hollow fibres with different electrolyte thicknesses

Physica UDS-200 rheometer was used to measure viscosity of the suspension at 20 °C, prior to the co-extrusion process. The morphology of the reduced hollow fibres was examined using a JEOL JSM-5610 scanning electron microscope (SEM). The hollow fibres were snapped in order to obtain clear cross-sectional fracture and then placed on a metal holder and sputtered by gold under vacuum. High resolution images of the cross-section of the hollow fibres were taken at different magnifications using backscattered electrons (BSE) mode.

Three-point bending test using an Instron Model 5544 tensile tester with a load cell of 1 kN was employed to examine the mechanical strength of hollow fibres. The bending strength ($B_F$) is calculated using the following equation [9]:

$$B_F = \frac{8 N L D_0}{\pi (D_o^4 - D_i^4)} \quad (4.1)$$
where $N$ is the measured load at which fracture occurred (N); $L$, $D_o$, $D_i$ are the length, the outer diameter and the inner diameter of the hollow fibres (m), respectively.

Gas-tightness of the electrolyte layer of the hollow fibres was studied at room temperature using a nitrogen ($N_2$) permeation method described elsewhere [10]. The pressure change of the permeation system was monitored by a pressure transducer. The gas permeability is calculated based on the change of cylinder pressure with time:

$$P = \frac{V_c}{RT \cdot At} \ln \left( \frac{p_o - p_t}{p_t - p_a} \right)$$  \hspace{1cm} (4.2)

where $P$ is the permeability of the test membrane (mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$); $V_c$ is the volume of the test cylinder (m$^3$); $R$ is the gas constant (8.314 J mol$^{-1}$ K$^{-1}$); $T$ is the measured temperature (K); $p_o$ and $p_t$ are the initial and final measured pressures in the test cylinder (Pa); $p_a$ is the atmospheric pressure (Pa); $A$ (m$^2$) is the hollow fibre area that is $A = \pi(D_o - D_i)L]/\ln(D_o/D_i)$, where $D_o$ and $D_i$ are respectively the outer and the inner diameter of the hollow fibre (m); $L$ is the length of the hollow fibre (m); and $t$ is the time for measurement (s).

The procedures of preparing the cathode layer and fuel cell reactor for electrochemical performance are similar to the ones that have been described in Chapter 3. A multi-layers cathode (i.e. 2 layers of LSCF-CGO and 1 layer LSCF) was deposited on the electrolyte of the dual-layer hollow fibres by brush painting technique and sintered at 1200 °C for 5 hours to form a 10 mm length cathode. After applying current collectors, the resultant micro-tubular SOFC was fixed in a gas-tight alumina tube (Multilab Ceramics, UK) using a ceramic sealing paste (Aremco, USA). The complete cell reactor was inserted in the centre of a tube furnace (MTF 12/25/250, CARBOLITE). The current collectors attached to the anode and the cathode were connected to a potentiostat/galvanostat (Autolab® PGSTAT 30,
Netherlands) for measuring the current-voltage performances of the micro-tubular SOFCs at 600 °C, with 15 cm$^3$ min$^{-1}$ of hydrogen (saturated with water vapour of 0.35 cm$^3$ min$^{-1}$ using a bubbling cylinder at 20 °C, 1 atm) and air of 40 cm$^3$ min$^{-1}$ (20 °C, 1 atm) were flowed through the anode and cathode respectively in a counter-flow arrangement. A current step of approximately 1.1 second was used. The AC impedance spectra were measured on the same electrochemical workstation (0.01 Hz-100 kHz) with signal amplitude of 10 mV under open-circuit conditions at 600 °C.

4.3 Results and Discussion

4.3.1 Macrostructure

Figure 4.1 shows the SEM images of the electrolyte/anode dual-layer hollow fibres with different electrolyte thicknesses co-sintered at 1500 °C for 12 hours followed by a reduction at 550 °C for 2.5 hours. As the co-extrusion parameters for the inner layer were kept the same as reported in Chapter 3, the anode structure of the hollow fibres is similar and is composed of short finger-like voids originating from the inner surface with the rest of the anode occupied by a sponge-like structure.
Figure 4.1: SEM images of the overall view of the reduced dual-layer hollow fibres consisting of different electrolyte thicknesses. The images were taken using backscattered electrons (BSE) mode.

The formation of this kind of asymmetric structure has been explained in details by Kingsbury and Li [11] and in the Chapter 3. Each type of structures (i.e. finger-like voids and sponge-like structures) has their own effects on the anode characteristics. As an example, finger-like voids in anode is believed to have a strong effect on the
permeation of fuel as longer finger-like voids allow gas diffusion much easier through the anode. However, the presence of such macro-voids is less advantageous in terms of both mechanical strength and electrical conductivity of the anode. Based on this understanding, it is thus crucial to control the growth of the finger-like voids in the anode support and in this study, the relative length of the finger-like voids was controlled to be around 35% of the overall anode thickness.

Variation in outer electrolyte thickness of the dual-layer hollow fibres is achieved by simply adjusting the corresponding extrusion rate, without affecting the structure of the anode inner layer. Viscosity of the spinning suspension for the outer layer should not be too high in order to ensure a smooth flow of the suspension and a full and uniform coverage especially when the extrusion rate is very low. Therefore, the ceramic loading was reduced from 64 wt.% in the previous batch of fibre (fibre HF4 as shown in Chapter 3) to 60 wt.% in this work, as an effort to reduce the viscosity of the suspension. As shown in Figure 4.2, dual-layer hollow fibres with different electrolyte thicknesses were successfully produced when the extrusion rate of the outer layer was varied from 0.5 to 5 cm$^3$ min$^{-1}$. The fibre R-5 that extruded from 5 cm$^3$ min$^{-1}$ produced the thickest electrolyte layer while the thinnest electrolyte generated for the R-0.5 prepared from 0.5 cm$^3$ min$^{-1}$ of extrusion rate.
Figure 4.2: SEM images of the cross-sectional view of the reduced dual-layer hollow fibres consisting of different electrolyte thicknesses. The images were taken using backscattered electrons (BSE) mode.

Figure 4.3 presents the higher magnification images of the dual-layer hollow fibres R-0.5, R-1, R-2, R-3, R-4 and R-5 in order to further highlight the difference in the electrolyte thickness. This figure shows that all the six batches of hollow fibres have good adhesion between the inner and outer layers as all of them are free from
delamination problems. Furthermore, the electrolyte outer layer has very uniform thickness on the anode inner layer and covers the whole length of hollow fibre surface and thus, shows another advantage of co-extrusion as a deposition technique of a thin layer on the hollow fibre support.

\[ \text{Figure 4.3: Close-up SEM images of the electrolyte of the reduced dual-layer hollow fibres consisting of different electrolyte thicknesses. The images were taken using backscattered electrons (BSE) mode.} \]
The difference in the porosity between these two layers can also be observed in this figure as the anode is relatively porous due to reduction of the NiO to Ni while the electrolyte layer achieves a very dense structure. Due to the discernible difference between the inner and outer layers as shown in this figure, the thickness of the electrolyte layer was measured using these images. Table 4.2 lists the measured thickness of electrolyte of fabricated samples. From this table, it shows that the extrusion rate significantly affects the thickness of the outer layer as the thickness of the electrolyte outer layer varies from 10 to 70 µm when the extrusion rate was controlled from 0.5 to 5 cm\(^3\) min\(^{-1}\). It is also displayed that the electrolyte layer did not fully cover the anode when the extrusion rate was lower than 0.5 cm\(^3\) min\(^{-1}\). From these results, it proves that the co-extrusion is a suitable technique in producing thin and uniform electrolyte layer, comparable with other conventional and complex depositing techniques such as dip-coating and chemical vapour deposition (CVD).

### 4.3.2 Mechanical and gas-tightness properties

The mechanical property of the dual-layer hollow fibres with different electrolyte thicknesses together with the anode single-layer hollow fibre was investigated by three-point bending test, as shown in Figure 4.4. As expected, the dual-layer hollow fibre with the thinnest electrolyte layer (10 µm for R-0.5) shows the lowest bending strength of about 143 MPa, which is still about 30 % higher than the single-layer hollow fibre. Whilst, the bending strength of dual-layer hollow fibres gradually increases to 146, 151, 157, 163 and 166 MPa with the increase of thickness of the electrolyte outer layer from 19 µm (R-1), 35 µm (R-2), 53 µm (R-3), 65 µm (R-4) and 70 µm (R-5), respectively. This can be explained by the difference in the porosity between anode and electrolyte of the hollow fibres. In order to obtain high efficiency
of anode layer, a 60 wt.% of NiO was used and after reduction process, it was then turned into a mechanically weak Ni network due to the interconnected pores structure in the anode layer. The deposition of a thicker dense electrolyte layer on the anode support and thus, improves the mechanical strength of the hollow fibre.

![Figure 4.4: Bending strength of the reduced dual-layer hollow fibres measured at room temperature as a function of electrolyte thickness (number of samples = 5).](image)

In order to investigate the effect of the electrolyte thickness on the gas-tightness property of the developed dual-layer hollow fibres, a gas-tightness test was performed. As can be seen in Figure 4.5, the nitrogen permeability of the hollow fibre consisting of 10 µm electrolyte (R-1) is $11.7 \times 10^{-9}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$. This value decreases to $6.6 \times 10^{-9}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$ for the fibre consisting of 19 µm electrolyte
(R-1) and is further reduced to $4.5 \times 10^{-9}$, $2.9 \times 10^{-9}$, $2.1 \times 10^{-9}$ and $1.1 \times 10^{-9}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$ when the electrolyte thickness is increased to 35 µm (R-2), 53 µm (R-3), 65 µm (R-4) and 70 µm (R-5), respectively. This indicates that the thicker the dense layer, the better the gas-tightness property of the electrolyte is. Without electrolyte outer layer, the permeability of the nitrogen gas through the hollow fibre is $1081 \times 10^{-9}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$, which is more than two-orders of magnitude higher than the permeability of the fibre R-0.5 with the thinnest electrolyte layer.

Figure 4.5: Gas permeability of the reduced dual-layer hollow fibres measured at room temperature as a function of electrolyte thickness, with the initial pressure of 40 psig. This graph is used to describe the gas-tightness property of the electrolyte layer (number of samples = 3).
Although fibre R-0.5 shows the lowest mechanical strength and gas-tightness property among the reported dual-layer hollow fibres, the electrochemical measurement was carried out using the fuel cell that was prepared from this fibre as it is anticipated that thinner electrolyte has lower resistance. The fibres R-1, R-2 and R-4 were also tested in order to study the effect of electrolyte thickness on the electrochemical performance.

4.3.3 **Electrochemical performances**

Figure 4.6 (a) shows cell voltages and power densities as a function of current density for the single cell of micro-tubular SOFC that was prepared from R-0.5, R-1, R-2 and R-4, with 15 cm$^3$ min$^{-1}$ of hydrogen (saturated with water vapour of 0.35 cm$^3$ min$^{-1}$ at 20 °C, 1 atm) flowing through the anode and 40 cm$^3$ min$^{-1}$ (20 °C, 1 atm) of air flowing to the cathode. The operation temperature was set at 600 °C because the CGO electrolyte has very favourable ionic conductivity at temperatures as low as 600 °C [12] yet, higher temperature would cause severe reduction in CGO which lead to high electronic conductivity [13]. It is also shown in previous finding in Chapter 3 that the power output of the cell operated at 600 °C was significantly higher than the cell at 550 or 570 °C. The measured open-circuit voltage (OCV) shows an increase from 0.77 V to 0.93 V with the increase in the electrolyte thickness of the dual-layer hollow fibres from 10 µm to 65 µm. As the thicker electrolyte shows better gas-tightness property (as shown in Figure 4.5), it reduces the possibility for the fuel or oxidant to transport towards the opposite electrode and results in higher OCV. The low OCV value of the fibre R-0.5 is not only due to the gas tightness issue, but also probably because of the minor electronic current leakage across the electronic conductive path.
in the CGO electrolyte [6], resulting from the reduction of Ce$^{4+}$ to Ce$^{3+}$ at the reducing atmosphere.

The maximum power densities achieved are 0.52 W cm$^{-2}$, 0.62 W cm$^{-2}$, 0.77 W cm$^{-2}$ and 1.11 W cm$^{-2}$ for the cells R-4, R-2, R-1 and R-0.5 respectively, which increases with the decrease in the electrolyte layer thickness. In the thinner electrolyte, the travelling distance of the oxygen ion from the cathode side through the electrolyte to the anode side could be shorten and thus, reduces the ohmic resistance of the cell (will be discussed further using impedance data in the following paragraph). In order to observe a precise relationship between the maximum power density and the electrolyte thickness, the maximum power density of each cell was normalised with their electrolyte thickness and the result is shown in Figure 4.6 (b). From this figure, it can be seen that the electrolyte thickness-normalised maximum power density rise exponentially with the decrease of electrolyte thickness. One of the possible reasons to explain this trend is, the reduction of electrolyte thickness not only reduces the ohmic resistance, but also enhances the rate of the reactions in both electrodes due to the more effective oxygen ion transfer from the cathode to the anode. These results justify the need of reducing the electrolyte thickness due to the significant impact on the performance of the cell. In comparison with previous studies, the maximum power density obtained for cell R-0.5, i.e. 1.11 W cm$^{-2}$ is the best performances among those cells that were fabricated using the dry-jet wet extrusion [14-19] which again can be attributed to the reduction in the electrolyte thickness. However, this value is still lower than the ones produced by conventional ram extrusion method with similar electrolyte thickness (10 µm) which were reported to be 1.29 W cm$^{-2}$ at 600 $^o$C [6,20] and 1.31 W cm$^{-2}$ at 550 $^o$C [21,22]. The difference can be explained by the impedance data shown below.
Figure 4.6: (a) Effect of electrolyte thickness on the voltages and power densities of the cells. The cell operated at temperature of 600 °C using hydrogen flow rate of 15 cm$^3$ min$^{-1}$ (20 °C, 1 atm) and air flow rate of 40 cm$^3$ min$^{-1}$ (20 °C, 1 atm); (b) The electrolyte thickness-normalised maximum power density of the cells as a function of electrolyte thickness.
Figure 4.7 (a) shows impedance data for the cells of micro-tubular SOFCs at 600 °C which is used to investigate the effect of electrolyte thickness on the ohmic area specific resistance (ASR). The high frequency intercept on the real impedance axis represents the value of ohmic ASR in the cell which is generated from the ionic resistance in the electrolyte layer, both ionic electronic resistances in the electrodes and the contact resistant from the interfaces and current collectors [23]. From this figure, it can be seen that ohmic ASR of the cells are reduced with the decrease in the electrolyte thickness of the cells. By assuming each cell has the same ohmic resistances in their electrodes, interfaces and current collectors due to the similar material compositions, structures and fabrication techniques, it indicates that the ionic resistance in the electrolyte layer is decreased significantly by the reduction in the electrolyte thickness. This is also one of the major reasons for the higher power output of thinner electrolyte layer that shown in Figure 4.6 (a).

In order to prove that the major cause of the difference in the ohmic ASR in this work is the electrolyte thickness, the ohmic ASR of each cell was normalised with the electrolyte thickness and the trend is shown in Figure 4.7 (b). From this graph, it is shown that the electrolyte thickness-normalised ohmic ASR of each cells is still in a close range, with the average value of $0.00344 \pm 0.00036 \, \Omega \, \text{cm}^2 \, \mu\text{m}^{-1}$. This also indicates that the ohmic ASR is almost directly proportional to the electrolyte thickness for the cells consisting of similar microstructure.
Figure 4.7: (a) Effect of electrolyte thickness on impedance spectra of cells measured under open-circuit condition at temperature range of 550 to 600 \(^{\circ}\)C using signal amplitude of 10 mV at frequencies of 100 kHz to 0.01 Hz and hydrogen flow rate of 15 cm\(^3\) min\(^{-1}\) (20 \(^{\circ}\)C, 1 atm) and air flow rate of 40 cm\(^3\) min\(^{-1}\) (20 \(^{\circ}\)C, 1 atm). (b) The electrolyte thickness-normalised ohmic ASR of the cells as a function of electrolyte thickness.
The impedance data of the highest maximum power density cell, R-0.5, is compared with the previously reported cells [6,20,21,22] that consisting of similar electrolyte thickness (10 µm). As can be seen in Table 4.3, the ohmic ASR of R-0.5 is smaller than that of Suzuki’s and Sammes’s cells. Such lower ohmic ASR can be attributed to the higher temperature that was used in this work to sinter both dual-layer hollow fibre precursor (1500 °C) and cathode layer (1200 °C) which would affects the grain size and the porosity of each layer. The bigger grain size of particles (CGO, Ni, and LSCF) as well as a denser structure would result in better overall conductivity of the electrolyte and electrodes layers [24,25].

<table>
<thead>
<tr>
<th>Cell</th>
<th>Power density (W cm(^{-1}))</th>
<th>Ohmic ASR (Ω cm(^2))</th>
<th>Electrode pol. ASR (Ω cm(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>R-0.5</td>
<td>1.11 at 600 °C</td>
<td>0.032 at 600 °C</td>
<td>0.12 at 600 °C</td>
</tr>
<tr>
<td>Suzuki [6,20]</td>
<td>1.29 at 600 °C</td>
<td>-0.07 at 600 °C</td>
<td>No information available</td>
</tr>
<tr>
<td>Sammes [21,22]</td>
<td>1.31 at 550 °C</td>
<td>0.09 at 550 °C</td>
<td>0.09 at 550 °C</td>
</tr>
</tbody>
</table>

Apart from the ohmic ASR, the electrode polarisation ASR has also been compared with the previously reported cells. The electrode polarisation ASR of R-0.5, which is obtained from the difference between the high frequency and low frequency intercepts on the real axis in Figure 4.7, is approximately 0.12 Ω cm\(^2\). This value is slightly higher than that of Sammes’s cell operated at 550 °C [21,22] and thus explains the difference in the power density results. It is believed that the less effective porosity in the anode layer of hollow fibres fabricated in this study due to relatively short finger-like voids structure (~35 %) and small void entrance size is one of the major reasons
for lower power density of R-0.5 cell. Therefore, in the following Chapter 5 and 6, the improvement on the anode porosity by controlling the anode asymmetric structure will be discussed in detail.

4.4 Conclusions

A series of dual-layer hollow fibres with different electrolyte thicknesses have been developed by varying the extrusion rate of the outer layer during the co-extrusion process, followed by co-sintering and simple reduction processes. With the decrease in the extrusion rate from 5 cm$^3$ min$^{-1}$ to 0.5 cm$^3$ min$^{-1}$, the electrolyte thickness is reduced from 70 µm to 10 µm. This proves the advantages of co-extrusion technique in producing thin and uniform electrolyte layer. By reducing the thickness of the electrolyte, the bending strength and gas-tightness of the dual-layer hollow fibres are reduced, indicating that both properties strongly rely on the dense electrolyte layer. Due to the very low ohmic resistance, the cell with the thinnest electrolyte layer (i.e. 10 µm) shows the highest performance among those cells that were fabricated using the dry-jet wet extrusion in the previous studies. The maximum power density of this cell reaches up to 1.11 W cm$^{-2}$. However, further optimisation on the anode porosity of the dual-layer hollow fibre has to be carried out to boost up the performance of the micro-tubular SOFCs.

References


CHAPTER 5

Morphological Studies of the Ni-CGO Anode Hollow Fibres for Micro-Tubular Solid Oxide Fuel Cells

Abstract

In this work, Ni-CGO anodes hollow fibre with controlled asymmetric structures, i.e. adjustable ratios between thickness of the outer sponge-like and the inner finger-like layers, have been developed for micro-tubular solid oxide fuel cells (SOFCs) using a combined dry-jet wet extrusion/sintering technique followed by a post-reduction process. The control over the asymmetric structure is achieved by employing ethanol as a non-solvent to adjust the initial properties of the spinning suspensions which affects the phase inversion process and results in a series of asymmetric structures, from very thin sponge-like layer supported on considerably thicker finger-like layer (0 wt.% ethanol) to the one consisting of nearly a full sponge-like structure (35 wt.% ethanol). The properties of the anode hollow fibre are markedly affected by such changes in asymmetric structures. As an example, the experimental results show that the mechanical strength and electrical conductivity are increased up to 241 MPa and 11,246 S cm$^{-1}$ respectively, but exhibit high resistance for the fuel transport for a full sponge-like structure of the fibres prepared with 35 wt.% of ethanol.
5.1 Introduction

Solid oxide fuel cells (SOFCs) are regarded as one of the most promising energy generation technologies due to their high energy conversion efficiency. In SOFCs, oxygen ions diffuse through thin ceramic electrolyte layer and react with hydrogen to produce electricity, forming water as the only product. Other sources such as natural gas, diesel, biogas, and ethanol can also be used as a fuel of SOFCs. The typical operating temperatures of SOFC are between 800 °C and 1000 °C which induces significant degradation by a variety of thermally activated processes and thus, greatly limit the choice of materials. Such disadvantages have initiated the development of intermediate temperature SOFCs (IT-SOFCs) operated at lower temperatures between 500-700°C, using cerium-gadolinium oxide (CGO) as the electrolyte [1].

The development of the micro-tubular SOFC has become important in recent years mainly due to a number of advantages of this system such as high specific surface area and rapid thermal cycling. The micro-tubular SOFC unit can be fabricated in different configurations, e.g. electrolyte, cathode or anode-supported. In micro anode-supported cell, a relative thinner electrolyte is deposited onto a thicker pre-fabricated anode tube support. Nickel (Ni) is the material that commonly used in an anode because of its high electronic conductivity, good catalytic activity and low cost. In order to minimise the thermal expansion coefficient (TEC) difference between anode and electrolyte and also to improve the ionic conductivity property and triple-phase boundary (TPB) region in the anode, it is a standard practice to mix Ni with electrolyte material for example CGO, which the resultant mixture referred as a cermet.
The concentration limit for the cermet at which there will still be a sufficient Ni to form a continuous electronically conducting path, is generally accepted to be around 40-60 wt.% Ni [2,3]. This amount is also enough for the adsorption of a large quantity of hydrogen during the oxidation reaction at the anode. Due to the advantages of Ni as mentioned above, the Ni-based anode is one of the most prominent candidates to be used as the supporting layer in micro-tubular SOFCs. Furthermore, in comparison with the electrolyte-supported configuration, anode-supported SOFC design is more suitable for operation at lower temperatures [4,5], because smaller ohmic losses and better interface contact can be realised especially when composite electrodes are used to increase the density of TPB [6,7].

Generally, the anode tube support for micro-tubular SOFCs is fabricated by plastic mass ram extrusion [8-12] and dry-jet wet extrusion [13-16]. In ram extrusion process, a symmetric structure anode with low porosity is always obtained and thus, the pore former (for example poly methyl methacrylate beads) is used to increase the electrode porosity [9,11-12]. In contrast, by using the dry-jet wet extrusion, the macrostructure of the micro-tubular SOFC support can be well controlled by simply adjusting the fabrication parameters. This technique involves the extrusion of ceramic suspension through a tube-in-orifice spinneret, followed by a process of solvent and non-solvent exchange to induce a phase inversion of the polymer binder in the suspension [17], resulting in the formation of a hollow fibre with certain macrostructures.

In ceramic systems fabricated using dry-jet wet extrusion technique, two macrostructures have so far been observed which are finger-like voids and sponge-like structure. According to Kingsbury and Li [119], finger-like voids are formed
when the suspension is in contact with non-solvent. At this stage, the solvent/non-solvent exchange takes place resulting in a rapid increase in the local suspension viscosity and instant precipitation of the polymer phase (binder). However, due to instabilities at the interface between the suspension and the non-solvent, there is a tendency for viscous fingering to occur, initiating the formation of finger-like voids. Above a critical suspension viscosity, this phenomenon is not observed and a sponge-like membrane structure is formed.

The finger-like voids and sponge-like region are both important to anode support. Finger-like voids may provide a route with less resistance for transportation of the fuel gas and the products, while the sponge-like structure provides a large number of triple-phase boundaries (TPB) for the electrochemical reactions [19] and likewise gives the major mechanical strength to the hollow fibres. However, the presence of excess finger-like voids would probably affect continuity of the electronically conducting path of Ni metal and consequently reduce the overall performance.

Concerning the significance of these two structures to the hollow fibre anode performance, the objective of this work is therefore, to study the effect of macrostructure on the characteristics of the anode. By varying ethanol as a non-solvent additive from 0 wt.% to 35 wt.% to manipulate the spinning suspension viscosity and phase inversion rate, diverse hollow fibre morphologies are obtained. The macrostructure of these anode hollow fibres were studied using scanning electron microscopy and mercury porosimetry analysis and the properties of the hollow fibres were characterised using gas permeation test, 3-point bending test and electrical conductivity measurements.
5.2 Materials and Experimental Methods

5.2.1 Materials
Commercially available cerium-gadolinium oxide (Ce\textsubscript{0.9}Gd\textsubscript{0.1}O\textsubscript{1.95} or CGO, surface area 35 m\textsuperscript{2} g\textsuperscript{-1}, \(d_{50}\) 0.32 μm) and nickel oxide (NiO, surface area 5 m\textsuperscript{2} g\textsuperscript{-1}, \(d_{50}\) 0.55 μm) were purchased from NexTech Materials Ltd. (Ohio) and they were used as supplied. Polyethersulfone (PESf) (Radel A-300, Ameco Performance, USA), N-methyl-2-pyrrolidone (NMP) (HPLC grade, Rathbone), ethanol (VWR Prolabo) and polyethyleneglycol 30-dipolyhydroxystearate (Arlacel P135, Uniqema) were used as a polymer binder, solvent, non-solvent and dispersant, respectively. Tap water and de-ionized water were used as the external and internal coagulants correspondingly.

5.2.2 Preparation of anode hollow fibres with different structures
In the preparation of the different macrostructures of anode hollow fibres, Arlacel P135, used as a dispersant, was dissolved in NMP-ethanol solutions prior to the addition of NiO and CGO. These mixtures were milled with 20 mm agate milling balls for 48 hours. The milling was further carried out for another 48 hours after the addition of PESf in order to obtain a homogeneous spinning suspension. The detailed compositions of these suspensions are listed in Table 5.1, in which the samples are named according to the concentrations of ethanol that replace NMP as the solvent in the spinning suspension.
Table 5.1: Suspension composition for anode hollow fibres with different structures.

<table>
<thead>
<tr>
<th>Fibre</th>
<th>Composition (wt.%)</th>
<th>NMP - Ethanol Composition (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NiO</td>
<td>CGO</td>
</tr>
<tr>
<td>A-0</td>
<td>42.00</td>
<td>28.00</td>
</tr>
<tr>
<td>A-5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A-10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A-15</td>
<td>42.00</td>
<td>28.00</td>
</tr>
<tr>
<td>A-20</td>
<td></td>
<td></td>
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<tr>
<td>A-25</td>
<td></td>
<td></td>
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<tr>
<td>A-30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A-35</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Prior to the extrusion, the suspension was degassed with stirring under vacuum at room temperature until no bubbles were observable. The spinning suspension was then transferred into a stainless steel syringe and was extruded (at flow rate of 6 cm$^3$ min$^{-1}$) by a syringe pump (PHD 2000 Programmable, HARVARD APPARATUS) through a tube-in-orifice spinneret (outer diameter 2.6 mm, inner diameter 1.2 mm) into an external coagulation bath containing tap water with an air-gap of 30 cm. De-ionized water was used as the internal coagulant at a flow rate of 14 cm$^3$ min$^{-1}$. The formed hollow fibre precursor was left in the external coagulation bath overnight, allowing for the completion of phase inversion process.

The fibre precursors were then dried, cut into predetermined length and calcined in static air (TSH17/75/450, ELITE) to yield NiO-CGO hollow fibres. During the sintering, the temperature was increased from room temperature to 400 °C at a rate of 2 °C min$^{-1}$ and held for 1 hour, then to 800 °C at a rate of 2 °C min$^{-1}$ and held for 2 hours and finally to 1450 °C at a rate of 5 °C min$^{-1}$ and held for 6 hours. The final sintering temperature was chosen in this study because it had been proven high
enough to guarantee the hollow fibres with sufficient mechanical strength [8]. The temperature was then reduced to room temperature at a rate of 5 °C min\(^{-1}\).

Finally, the calcined NiO-CGO hollow fibre was reduced to Ni-CGO hollow fibre in a ceramic tubular reactor using pure hydrogen gas. The tube was inserted into a horizontal furnace (MTF 12/25/250, CARBOLITE). Argon of 30 cm\(^3\) min\(^{-1}\) (20 °C, 1 atm) was used to expel the air until the reactor temperature reaches 550 °C, following which the argon flow was replaced by pure hydrogen of 20 cm\(^3\) min\(^{-1}\) (20 °C, 1 atm). After 2.5 hours of reduction, the flow of hydrogen was switched to argon until the temperature was reduced to room temperature. The heating and cooling rates were kept at 5 °C min\(^{-1}\).

5.2.3 Characterisations of anode hollow fibres with different structures

The viscosity of the suspension was measured by using Physica UDS-200 rheometer using concentric cylinder geometry at 20 °C prior to the extrusion process. The morphology of the precursor and the reduced hollow fibres was examined using a JEOL JSM-5610 scanning electron microscope (SEM). The hollow fibres were snapped in order to obtain clear cross-sectional fracture. These hollow fibre samples were then placed on a metal holder and sputtered by gold under vacuum. High resolution images of the cross-section of the hollow fibres were taken at different magnifications using secondary electron imaging (SEI) mode. Mercury porosimeter (Micromeritics, AutoPore IV, 9500) combined with Micrometrics software (version 1.09) was used for estimating the pore size distribution and overall porosity of the Ni-CGO anode hollow fibres.
The pure gas permeability of the hollow fibres was studied at room temperature using a gas permeation method described elsewhere [20]. For the test, the hollow fibre was glued and sealed into a stainless steel sample holder using epoxy resin (UKR-135 resin with UKH-136 hardener; UK Epoxy Resins, Lancashire, UK). It was then assembled into a cylinder with a volume capacity of 300 cm$^3$. Nitrogen (N$_2$) was used as a testing gas. The gas flow rate across the hollow fibre was measured using bubble flow meter. The feed gas was supplied at the bore side of hollow fibre while the permeate gas was collected at the shell side of the module. The gas permeability was determined from the following equation [20]:

$$P = \frac{Q \ln(D_o / D_i)}{\pi L(D_o - D_i) \Delta P}$$

(5.1)

where $P$, $Q$, $D_o$, $D_i$, $L$ and $\Delta P$ are the gas permeability of nitrogen (mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$), the total gas permeation rate (mol s$^{-1}$), the inner and outer diameter of the hollow fibres (m), the hollow fibre length (m) and the pressure difference across the membrane (Pa), respectively. The permeability that was obtained for these hollow fibres can be used to indicate the trend of gas flow through the hollow fibres with different macrostructures.

The mechanical strength of hollow fibres was examined by three-point bending test using an Instron Model 5544 tensile tester provided with a load cell of 1 kN. The hollow fibres were fixed on the sample holder with a 30 mm distance. The bending strength ($B_F$) is calculated using the following equation [20]:

$$B_F = \frac{8NLD_o}{\pi(D_o^4 - D_i^4)}$$

(5.2)

where $N$ is the measured load at which fracture occurred (N); $L$, $D_o$, $D_i$ are the length, the outer diameter and the inner diameter of the hollow fibres (m), respectively.
The electrical conductivities of the hollow fibres were measured using the four-probe direct-current (DC) technique at room temperature (ca. 25 °C) as described in detail in Chapter 3. The hollow fibre samples were directly connected to the set-up without using a base and the potential differences across the anode hollow fibres of 20 mm length were measured by passing varying controlled currents (50, 75 and 100 mA). Linear fits to the generated current-voltage data were used to determine fibre resistance from which the bulk conductivity of the anode (\(\sigma\), S cm\(^{-1}\)) was estimated using the equation below:

\[
\sigma = \frac{L}{\rho_a \times A}
\]

where \(\rho_a\) is the anode resistance (\(\Omega\)), \(L\) is the fibre length (cm) and \(A\) is the hollow fibre area for current flow (cm\(^2\)).

5.3 Results and Discussion

5.3.1 Macrostructure

As the objective of this study is to investigate the effect of hollow fibre morphology on the anode performance, the anode hollow fibres with various morphologies have to be prepared and this was achieved by varying the initial suspension viscosity. In this study, ethanol was used as a non-solvent additive in order to manipulate the suspension viscosity. Ethanol was chosen because it can act as a good dispersant for the mixture of NiO-CGO and as a result, the dispersion of Ni and CGO in the prepared hollow fibre would be more uniform and continuous. Controlling the viscosity by other means, such as by varying the ratio of solvent/polymer/ceramic oxide or by the introduction of additives such as polyvinylpyrrolidone (PVP), may
affect the membrane properties [18]. The addition of ethanol to spinning suspensions, measured as a percentage of the total solvent content, causes significant changes in viscosity as shown in Figure 5.1.

![Viscosity of spinning suspensions](image)

**Figure 5.1:** Viscosity of spinning suspensions as a function of ethanol content in spinning suspension (as a percentage of the total NMP-ethanol content). The data was collected at room temperature at shear rate of 50 s\(^{-1}\).

The suspension viscosity value of 19,800 cP at 0 wt.% of ethanol slightly decreases to approximately 18,800 cP when 5 wt.% of ethanol is added. Although ethanol is a poorer solvent than NMP for PESf, it is a better "solvent" for the CGO and NiO and probably also has a more favourable interaction with the dispersant on the particle surface. Therefore, this effect dominates at low ethanol concentration and causes the viscosity decreases at 5 wt.% ethanol. However, as the ethanol concentration increases to 10 wt.%, the poor interaction with the PESf dominates and the viscosity
starts to increase to 21,400 cP and this value further increases to 22100 cP and 22900 cP at 15 wt.% and 20 wt.% ethanol content respectively. The further addition of ethanol results in large viscosity increase to 33,100 cP, 35,200 cP and 39,100 cP at 25 wt.%, 30 wt.% and 35 wt.%, respectively.

Figure 5.2 shows NiO-CGO hollow fibre precursors prepared using the suspensions with ethanol content of 0, 5, 10, 15, 20, 25, 30 and 35 wt.%. As can be seen, hollow fibres with 0 wt.% ethanol consists of an asymmetric structure of long finger-like voids originating from the inner fibre surface and occupying up to 85 % of the fibre thickness with the remaining fibre region occupied by a sponge-like layer. The morphology of fibre A-5 resulting from a 5 wt.% of ethanol content has the same asymmetric structure as in fibre A-0, with a reduced length of the finger-like voids that originates from the inner fibre surfaces to about 70 % of fibre cross-section. Although the initial viscosity for 5 wt.% ethanol is slightly lower than that of 0 wt.%, the presence of ethanol as a non-solvent results in a faster precipitation of the fibre when in contact with the internal coagulant; as the polymer phase is closer to its precipitation point and subsequently, increases the local viscosity of the nascent fibre. This faster polymer precipitation would reduce the viscous fingering effect and resulting in shorter finger-like voids length. The relative lengths of finger-like layers are further reduced to approximately 60 %, 55 % and 50 % when the ethanol content is increased to 10 wt.%, 15 wt.% and 20 wt.% respectively as shown in SEM images of A-10, A-15 and A-20. At these points, the ethanol addition has two combined effects to the spinning suspension; firstly increasing the initial suspension viscosity prior phase inversion and secondly accelerating the rate of viscosity increase during the phase inversion. Therefore, these combined effects would cause the formation of a large sponge-like structure.
Figure 5.2: SEM images of the cross-sectional view of the NiO-CGO hollow fibre precursors prepared with different ethanol contents. The images were taken using secondary electron imaging (SEI) mode.
As shown in the image for fibre A-25, the finger-like layer is abruptly reduced to about 30% when the ethanol content reaches 25 wt.%, in agreement with the significant increase of viscosity shown in Figure 5.1. Addition of 30 wt.% ethanol for fibre A-30 which has slightly higher suspension viscosity results in a further reduction in relative finger-like void length to approximately 20% of the cross-section. The formation of finger-like voids is totally inhibited when the suspension dope for fibre A-35 contains 35 wt.% ethanol and this suggests that the contact between suspension and non-solvent (coagulant, i.e. water) during the phase inversion process achieves its stable point at suspension viscosity around 39100 cP and above.

The hollow fibres were then sintered and reduced in order to form Ni-CGO anode hollow fibre. The overall view and the cross-sectional images of these hollow fibres are shown in Figure 5.3 A-0(i) to A-35(i) and A-0(ii) to A-35(ii) respectively. It can be observed that the general cross-sectional structures of the hollow fibres are largely retained after sintering and reduction processes, where all of them still have distinguished morphologies as described above. This suggests that the sintering and reduction processes do not cause any major changes in fibre macrostructure. Although the densification of hollow fibres occurs in sintering process and this would reduce the porosity, the removal of oxygen atoms from NiO by hydrogen during the reduction process allows the structure of the fibre to be more porous especially in the sponge-like region, as can be seen in Figure 5.3 A-0(iii) to A-35(iii). These SEM images also indicate that the sponge-like structure of the fibres shows similar level of porosity regardless of the ethanol content in the spinning suspensions.
Figure 5.3: SEM images of the (i) Overall view, (ii) Cross-sectional view and (iii) the sponge-like structure region of the reduced Ni-CGO anode hollow fibres. The images were taken using secondary electron imaging (SEI) mode.
5.3.2 Pore size distribution and porosity

The investigation on the macrostructure of the hollow fibres is further demonstrated by a comparison of the mercury intrusion data as shown in Figure 5.4. According to the data obtained, three types of pores have been recognised, which are (i) the entrances pores of finger-like voids, (ii) the pores survive the sintering in the sponge-like region and (iii) the one formed as a result of the reduction of NiO to Ni. For the fibres A-0, the data shows a pore size distribution consisting of a peak at approximately 1.31 µm, which represents the pores at the inner fibre surface that form the entrances to the finger-like voids. A smaller peak at 0.35 µm is believed representing the sponge-like pores and a broad peak at a range of 0.04-0.06 µm represents the pores from the reduction of NiO. As the ethanol content in the spinning suspension is increased, the peak of finger-like pores at 1.31 µm shifts to 1.05 and 0.84 µm for fibres A-5 and A-10 respectively, indicating that the entrance of the finger-like voids become smaller [18].
Figure 5.4: Pore size distributions for the reduced anode hollow fibres consisting of various asymmetric structures together with unreduced hollow fibre, measured by mercury porosimeter at absolute pressure of $1.38 \times 10^3$ Pa to $2.28 \times 10^8$ Pa.

The intensity of the peak at 0.84 µm is reduced more than half and the peak at 0.35 µm appears more significant for fibres A-15 and A-20. The peak at 0.84 µm is totally absent for A-25 and A-30 and this can be attributed to the suspension viscosity trend shown in Figure 5.1. As there is a huge increase in the viscosity after the addition of
25 wt.% ethanol in the spinning suspension, the viscous fingering phenomenon is almost inhibited during the phase inversion, resulting in the formation of a tiny finger-like voids structure that are not started from the inner surface of the fibres [18]. By observing the Figure 5.3 A-25(ii) and A-30(ii), it can be noticed that there is very thin sponge-like pores structure in the region between the inner surface and the entrance of the finger-like voids and it is expected that the size of finger-like voids entrance sizes is reduced to the similar sizes of the one in sponge-like layer. Therefore, it is believed that the peak at 0.35 µm for fibres A-25 and A-30 does not only represent the sponge-like pores but also the entrances pores for finger-like voids. As expected, only two major peaks appear for A-35, at 0.35 µm and 0.03 µm, which each represent the sponge-like pores and the pores from the reduction of NiO respectively. Figure 5.4 also shows that the unreduced fibres have relatively low intensity peaks for the entrance pore of finger-like voids and sponge-like pores as can be seen in the trend of unreduced A-10 and A-30. It indicates that the pore size for the sponge-like structure and finger-like voids structure increase after undergoing the reduction process. This also confirms that the reduction process markedly increases the porosity of the fibres although the fibres are sintered at relatively high temperature.

Figure 5.5 shows the porosity of the hollow fibres as a function of ethanol content in spinning suspension, which was also measured using mercury porosimetry analysis. Besides the sponge-like pores and the NiO reduction’s pores, the porosity value obtained is mainly from the contribution of finger-like voids. As expected, the porosity decreases with the increase of ethanol content in spinning suspension and the highest porosity is 56 % for fibre A-0 fabricated from 0 wt.% ethanol. The porosity value decreases to 47 %, 44 %, 39 % and 37 % for fibres from 5, 10, 15 and 20 wt.% ethanol respectively. A further decrease in the finger-like voids length for fibres A-25
and A-30 of ethanol content 25 and 30 wt.% correspondingly, affects the porosity of these two fibres as their porosities are below than 30 %. The finger-like voids-free structure of A-35 caused this fibre to possess the lowest porosity of 19 %. This trend is in good agreement with SEM images that are shown in Figure 5.3. The anode needs to be porous and permeable to gasses but an extremely high level of porosity often drastically decreases the cell performance [4].

![Figure 5.5](image.png)

**Figure 5.5**: Porosity of the reduced anode hollow fibres as a function ethanol content in spinning suspension, measured by mercury porosimeter at absolute pressure of $1.38 \times 10^3$ Pa to $2.28 \times 10^8$ Pa.
5.3.3 Gas permeation and mechanical properties

Apart from porosity data, nitrogen gas permeation measurement is also important in this study in order to determine the effect of anode structure on the gas diffusion behaviour. Nitrogen permeation data from fibres A-0 to A-35 is shown in Figure 5.6 and it demonstrates the progressive gas resistance from the sponge-like region of the fibre as the nitrogen permeability decreases with the increase of sponge-like region thickness.

**Figure 5.6**: Gas permeability of the reduced anode single-layer hollow fibres as a function of inlet pressure. The trend of the permeability of the anode fibres consisting of various asymmetric structures was compared.
The fibre A-0 with the thinnest sponge-like structure region has the highest nitrogen permeability, followed by A-5, A-10, A-15 and A-25. In comparison, the permeability values of fibres A-25, A-30 and A-35 are relatively small. Although the sponge-like region contains micropores, some of the pores are dead-end or closed pores which do not actually contribute to the gas permeation. The low gas permeation would cause shortage in fuel supply at TPB region and as a result, increasing the concentration polarisation in the anode. In addition, this result also suggests that the permeability of the nitrogen is also affected by the entrance pore size of the finger-like voids. By correlating to the results that were obtained in Figure 5.4, the dramatic drops in the permeability between A-5 and A-10 and also between A-20 and A-25 are believed due to the decrease in the entrance pore size of the finger-like voids. The effect of the gas pressure on the nitrogen permeability is almost similar for every fibre as the permeability is increased with the increase of inlet pressure at up to about $4.5 \times 10^5$ Pa.

The result of three-point bending test, which is used to measure the bending strength of the various hollow fibres with different morphologies, is shown in Figure 5.7. As the ethanol content in the suspension is increased in which the finger-like voids length decreases, the bending strength increases. The A-0 shows the lowest strength compared with the other fibres and the highest strength is exhibited by A-35 which is free of the finger-like voids. This indicates that the finger-like voids are likely to diminish mechanical strength of the fibre by reducing the integrity of the sponge-like structure region. Previous study on the anode hollow fibre with similar size and Ni content [14] showed that the average values of bending strength were about 130 MPa and the micro-tubular SOFCs were successfully constructed using these hollow fibre supports [16]. This suggests that the fibres which have the bending strength more than
130 MPa, in this study are referred to the fibres that are prepared using 10 wt.% of ethanol or more, are certainly suitable to be served as a support for the construction of micro-tubular SOFC.

![Figure 5.7: Bending strength of the reduced anode hollow fibres measured at room temperature as a function of ethanol content (number of samples = 5).](image)

**Figure 5.7**: Bending strength of the reduced anode hollow fibres measured at room temperature as a function of ethanol content (number of samples = 5).

### 5.3.4 Electrical conductivity

In general, anode should possess good electronic conductivity in order to provide sufficient pathway medium for electron transport. In this study, the electronic conductivity value was obtained from four-probe DC technique at room temperature and the overall conductivity of the hollow fibres is actually contributed by the Ni
Figure 5.8 shows the electronic conductivity of the anode hollow fibres against the ethanol content in the spinning suspension. As can be seen, the conductivity of the hollow fibres is dependent on the macrostructure of the fibres as the conductivity increases with the increase of ethanol content in the spinning suspension.

**Figure 5.8**: Electrical conductivity of the reduced anode single-layer hollow fibres as a function of ethanol content in spinning suspension. The measurement was carried out at room temperature using 4-point DC technique.
This can be explained by observing the conducting path of electron in the hollow fibre as illustrated in Figure 5.9 where the anode hollow fibres with thinner finger-like voids structure have shorter and easier conduction path than that of the hollow fibres with the thicker one. Therefore, the fibres that consists thicker finger-like voids structure results in lower electrical conductivity value. As also shown in this figure, the data obtained in this study is much higher than the conductivities of anode hollow fibres that were recorded in previous studies which were 772 S cm\(^{-1}\) [14] and 1700 S cm\(^{-1}\) [15]. Apart from higher sintering temperature that was used in this study, the high conductivity is majorly due to the direct connection between the hollow fibre and the set-up without using any paste connection [14] or base [15], which contributes to lower resistance and as a result, increases the measured values of the conductivity.
Figure 5.9: Illustration of the electron conduction in the Ni-CGO anode layer hollow fibres. It describes that the conduction pathway of electrons is shorter and easier for the fibres consisting of short or without finger-like voids structure than the fibres consisting of longer finger-like voids.
5.4. Conclusions

Eight different macrostructures of Ni-CGO anode hollow fibres have been successfully prepared by varying the content of ethanol as non-solvent in the spinning suspension from 0 to 35 wt.% and these suspensions were then extruded using phase inversion and followed by sintering and reduction processes. The addition of ethanol in the spinning suspension causes a large change in the viscosity as the viscosity started to increase when 10 wt.% of ethanol is added. From the morphologies of the obtained hollow fibres, it can be observed that the ethanol suppresses the formation of finger-like voids in hollow fibres and the length of this structure is reduced as the ethanol content is increased. Three types of pores, which are (i) finger-like voids, (ii) the pores survive the sintering in the sponge-like region and (iii) the one formed as a result of the reduction of NiO to Ni, have been observed in the prepared hollow fibres. The other noticeable observation on the morphologies of the hollow fibre is the porosity of the fibres decreases with the reduction of the finger-like voids length. In studying the effect of macrostructure on the anode performance, it can be seen that the fibres with longer finger-like voids length have higher gas permeation compared to those shorter ones. However, it is observed that the finger-like voids are likely to diminish mechanical strength of the fibre by reducing the integrity of the sponge-like structure and also affect the electronically conducting path of Ni metal in the hollow fibres. Therefore, it can be concluded that the presence of finger-like voids structure in the hollow fibre strongly affects the mechanical strength, gas permeation and electrical conductivity of the anode and consequently would significantly affect the overall performance of the fuel cell.
Chapter 5  
Morphological Studies of the Macrostructure of Ni-CGO Anode Hollow Fibres for Micro-Tubular Solid Oxide Fuel Cells

References


CHAPTER 6

Dual-Layer Hollow Fibres with Different Anode Structures for Micro-Tubular Solid Oxide Fuel Cells

Abstract

In this work, a high performance micro-tubular solid oxide fuel cell (SOFC) has been developed by depositing a multi-layer cathode onto an improved electrolyte/anode dual-layer hollow fibre fabricated via a single-step co-extrusion/co-sintering technique. The use of 0-20 wt.% of ethanol in the inner layer spinning suspension allows the control over the asymmetric structure of the Ni-CGO anode layer, i.e. finger-like voids structure covering about 50-85 % of the anode layer with the rest occupied by sponge-like structure and at the same time affects the morphology of the CGO electrolyte layer. The presence of finger-like voids significantly facilitates the fuel gas diffusion inside the anode and as a result, the maximum power density increases from 1.84 W m$^{-2}$ to 2.32 W cm$^{-2}$ when the finger-like voids is increased from 50% to 70% of the asymmetric anode layer. However, further growth of finger-like voids (i.e. 85% of the anode layer) dramatically reduce the conductivity and number of triple-phase boundary (TPB) region per unit area in the anode as well as the gas-tightness property of the electrolyte, which consequently decreases the maximum power density to 0.99 W cm$^{-2}$. Based on the results obtained, therefore, dual-layer hollow fibres with 50-70 % of finger-like voids in the anode layer can be considered as the ideal structure for producing high performance micro-tubular SOFCs.
6.1 Introduction

The development of anode-supported micro-tubular solid oxide fuel cells (SOFCs) using nickel (Ni) as the anode catalyst has received more and more attention recently due to a number of advantages of this configuration such as the relatively high electrical conductivity, good catalytic activity and low material cost. Suzuki et al. [1] reported in 2006 about the successful fabrication of a Ni-cerium gadolinium oxide (CGO) anode-supported micro-cell with the cell diameter of 0.8 mm by using a conventional plastic mass ram extrusion/sintering technique. This cell generated the maximum power density of over 0.30 W cm$^{-2}$ at 550 °C. As an important effort to promote gas diffusion in the anode, Suzuki et al. improved the anode structure by introducing pore former, i.e. polymethylmethacrylate beads (PMMA) [2,3]. Using the same fabrication process and materials, the maximum power density obtained by this cell was substantially increased to 1.02 W cm$^{-2}$ and 1.29 W cm$^{-2}$ at 550 °C and 600 °C, respectively. Another recent work conducted by Sammes et al. [4,5], which fabricated anode support using similar ram extrusion with bigger cell diameter (1.8 mm), also achieved outstanding power output, i.e. 1.31 W cm$^{-2}$ at 550 °C.

As one of the first several groups employing dry-jet wet extrusion technique fabricating anode support of micro-tubular SOFC, Yang et al. [6] obtained the maximum power density of 0.38 W cm$^{-2}$ at 800 °C using Ni-yttrium stabilised zirconia (YSZ) cermet as the anode material with the resultant cell diameter of about 1.7 mm. Moreover, Yang et al. [7] demonstrated the advantages of impregnating the electrode catalyst into the porous anode and cathode matrixes formed during the phase inversion process. This improvement considerably increased the maximum power density to 0.78 W cm$^{-2}$ at 800 °C.
Another significant development in fabricating anode-supported micro-tubular SOFC has been achieved in Professor Kang Li’s laboratory, where a more advanced and accurately controlled dry-jet wet extrusion technique, i.e. co-extrusion process, is employed. By using this technique and followed by co-sintering and reduction processes, a cerium-gadolinium oxide (CGO) electrolyte/nickel (Ni)-CGO anode dual-layer hollow fibre has been developed in a single-step, as described in detail in Chapter 3. This hollow fibre can be distinguished by an electrolyte outer layer of approximately 80 µm which was supported by an asymmetric anode inner layer with the finger-like voids occupied about 35 % of the anode thickness. The resultant micro-tubular cell which also consisted of a multi-layer cathode on the dual-layer hollow fibres produced the maximum power density of 0.68 W cm\(^{-2}\) at 600 °C. Further effort to reduce the thickness of the defect-free electrolyte outer layer to as thin a 10 µm resulted in an increase of the maximum power output to 1.11 W cm\(^{-2}\) at 600 °C as shown in Chapter 4. Although this result has proved the potential of dual-layer hollow fibre as a support for micro-tubular SOFC, the value of powder density was still slightly lower than the Suzuki’s [2,3] and Sammes’s [4,5] cells with a highly porous anode and a comparable electrolyte thickness.

As reported in Chapter 5, the finger-like voids structure that formed during the phase inversion process would increase the porosity and significantly enhances the gas diffusion in the anode. Therefore, a further optimisation on the anode porosity of the dual-layer hollow fibres for micro-tubular solid oxide fuel cells (SOFCs) has been carried out in this study. By varying the ethanol content in the inner layer spinning suspension from 0 to 20 wt.%, a series of dual-layer hollow fibres containing finger-like voids structure that occupy approximately 50-85 % of the nickel (Ni)-CGO anode thickness was successfully fabricated. The three-point bending test, gas permeation
test and electrochemical measurements have been employed to investigate the effect of finger-like voids thickness on the mechanical strength, gas-tightness property and single cell performance of the dual-layer hollow fibres, respectively.

6.2 Materials and Experimental Methods

6.2.1 Materials

Commercially available cerium-gadolinium oxide (Ce$_{0.9}$Gd$_{0.1}$O$_{1.95}$ or CGO, surface area 35 m$^2$ g$^{-1}$, $d_{50}$ 0.32 µm) and nickel oxide (NiO, surface area 5 m$^2$ g$^{-1}$, $d_{50}$ 0.55 µm) were purchased from NexTech Materials Ltd. and they were used as supplied. Polyethersulfone (PESf) (Radel A-300, Ameco Performance), ethanol (VWR Prolabo) and polyethyleneglycol 30-dipolyhydroxystearate (Arlacel P135, Uniqema) were used as a polymer binder, non-solvent and dispersant, respectively. Both N-methyl-2-pyrrolidone (NMP) (HPLC grade, Rathbone) and dimethyl sulfoxide (DMSO, Sigma–Aldrich) were used as the solvents and tap water and deionized water were used as the external and internal coagulants, respectively. Lanthanum strontium cobalt ferrite, La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_3$ (LSCF) (NexTech Materials Ltd., Ohio) and ethylene glycol (99+%, Acros Organic) were used as the materials for cathode slurry.

6.2.2 Preparation of dual-layer hollow fibres with different anode structures

The procedure of preparing the dual-layer hollow fibres has been described in detail in Chapter 3 and 4 by using ball milling technique for preparing the spinning suspension. In order to achieve dual-layer hollow fibres with different anode structures, the non-solvent i.e. ethanol was added into the spinning suspension of the inner layer and the
ratio of non-solvent/solvent was varied according to the composition that used to prepare anode single-layer hollow fibres as reported in the Chapter 5. The detailed compositions of the spinning suspensions for fabricating the dual-layer hollow fibres with different anode structures in this study are listed in Table 6.1, in which the samples are named according to the ethanol content in the inner layer (anode) spinning suspension. As can also be seen in the table, different solvents were used for inner and outer layer spinning suspensions, in which NMP was for the inner and DMSO for the outer layer.

The prepared suspensions were degassed at room temperature under stirring and loaded into two stainless steel syringes. They were then simultaneously co-extruded by a syringe pump (PHD 2000 Programmable, HARVARD APPARATUS) through a triple-orifice spinneret (the extrusion rates of the inner layer and the outer layer were 6 and 0.8 cm³ min⁻¹, respectively) into a tap water coagulation bath with 20 cm air-gap length. De-ionized water was used as an internal coagulant with flow rate of 14 cm³ min⁻¹. The hollow fibre precursors were then co-sintered by heating in air at 1500 °C for 12 hours in a tubular furnace (TSH17/75/450, ELITE). The co-sintered CGO/NiO-CGO dual-layer hollow fibres were reduced to CGO/Ni-CGO dual-layer hollow fibres at 550 °C using pure hydrogen for 2.5 hours.
**Table 6.1:** Compositions of the spinning suspension for dual-layer hollow fibres with different anode structures.

<table>
<thead>
<tr>
<th>Layer</th>
<th>Fibre</th>
<th>Composition (wt.%)</th>
<th>NMP - Ethanol Composition (wt.%)</th>
<th>Viscosity (cP)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>NiO</td>
<td>CGO</td>
<td>PESf</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>E-0</td>
<td>42.00</td>
<td>28.00</td>
<td>7.00</td>
</tr>
<tr>
<td></td>
<td>E-5</td>
<td>95 – 5</td>
<td>18,800</td>
<td></td>
</tr>
<tr>
<td>Inner</td>
<td>E-10</td>
<td>90 – 10</td>
<td>21,400</td>
<td></td>
</tr>
<tr>
<td></td>
<td>E-15</td>
<td>85 – 15</td>
<td>22,100</td>
<td></td>
</tr>
<tr>
<td></td>
<td>E-20</td>
<td>80 – 20</td>
<td>22,900</td>
<td></td>
</tr>
<tr>
<td></td>
<td>E-0</td>
<td>40.00</td>
<td>60.00</td>
<td>6.00</td>
</tr>
<tr>
<td></td>
<td>E-5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Outer</td>
<td>E-10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>E-15</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>E-20</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
6.2.3 Characterisations of dual-layer hollow fibre with different anode structures

A JEOL JSM-5610 scanning electron microscope (SEM) was used to examine the morphology of the reduced hollow fibres. The hollow fibre samples were placed on a metal holder and sputtered by gold under vacuum. High resolution images of the cross-section of the hollow fibres were taken at different magnifications using backscattered electrons (BSE) and secondary electron imaging (SEI) modes.

Three-point bending test (Instron Model 5544) was carried out using a load cell of 1 kN to investigate the bending strength of the hollow fibres using the following equation to calculate the bending strength ($B_F$) [8]:

$$B_F = \frac{8NLD_o}{\pi(D_o^4 - D_i^4)} \quad (6.1)$$

where $N$ is the measured load at which fracture occurred (N); $L$, $D_o$, $D_i$ are the length, the outer diameter and the inner diameter of the hollow fibres (m), respectively.

A nitrogen ($N_2$) gas-tightness test which has been described elsewhere [9] was used to determine the integrity of the outer electrolyte layer of the hollow fibres at room temperature. The change of pressure in the system over a certain period of time was monitored by a pressure transducer. The gas permeability is calculated based on the cylinder pressure change using the following equation:

$$P = \frac{V_C}{RT \cdot At} \ln \left( \frac{p_o - p_a}{p_i - p_o} \right) \quad (6.2)$$

where $P$ is the permeability of the test membrane (mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$); $V_C$ is the volume of the test cylinder (m$^3$); $R$ is the gas constant (8.314 J mol$^{-1}$ K$^{-1}$); $T$ is the measured temperature (K); $p_o$ and $p_i$ are the initial and final measured pressures in the test cylinder (Pa); $p_a$ is the atmospheric pressure (Pa); $A$ (m$^2$) is the hollow fibre area that
is \( A = \pi(D_o - D_i)L/\ln(D_o/D_i) \), where \( D_o \) and \( D_i \) are respectively the outer and the inner diameter of the hollow fibre (m); \( L \) is the length of the hollow fibre (m); and \( t \) is the time for measurement (s).

Prior to the electrochemical performance measurement, a multi-layer cathode consisting of two layers of LSCF-CGO (50 wt.%-50 wt.%) followed by an additional layer of 100 % LSCF was coated onto the hollow fibre’s electrolyte surface by brush painting technique and sintered at 1200 °C for 5 hours. Both ends of the resultant micro-tubular SOFC were fixed into gas-tight alumina tubes (Multilab Ceramics, UK) using a ceramic sealing paste (Aremco, USA) with current collectors connected to the anode and the cathode. Another alumina tube was used to strengthen the design for practical operations which the photographic image of the reactor design is shown in Figure 3.6 in Chapter 3. The complete reactor was inserted in the centre of a tube furnace (MTF 12/25/250, CARBOLITE). The electrochemical performance of the cells was measured using a potentiostat/galvanostat (Autolab® PGSTAT 30, Netherlands) at 600 °C with 15-30 cm³ min⁻¹ of hydrogen gas (saturated with water vapour of 0.35-0.70 cm³ min⁻¹ using a bubbling cylinder at 20 °C, 1 atm) anode and a 40 cm³ min⁻¹ (20 °C, 1 atm) were flowed through the anode and cathode respectively in a counter-flow arrangement. A current step of approximately 1.1 second was used. The AC impedance spectra were measured on the same electrochemical workstation (0.01 Hz-100 kHz) with signal amplitude of 10 mV under open-circuit conditions at 600 °C.

### 6.3 Results and Discussion

In one of the previous works reported in Chapter 4, a trade-off between the power output and the open-circuit voltage (OCV) of the cells was observed when the
thickness of the electrolyte layer was reduced to a certain level by using the co-
extrusion/co-sintering technique. As can be seen in Figure 6.1 for example, there is a
big difference in the maximum power outputs between the cell R-0.5 consisting of a
10 µm electrolyte layer (outer layer extrusion rate of 0.5 cm$^3$ min$^{-1}$) and the cell R-1
consisting of a 19 µm electrolyte layer (outer layer extrusion rate of 1.0 cm$^3$ min$^{-1}$).
The first cell produced 1.11 W cm$^{-2}$ while the latter one only achieved 0.77 W cm$^{-2}$.
However, the OCV obtained for the cell R-0.5 was only 0.77 V and was enhanced to
0.85 V when the thickness of the electrolyte was increased to 19 µm for the cell R-1.
In order to achieve a new batch of cells that have high values in both OCV and power
output, the dual-layer hollow fibres with the electrolyte thickness between 10 and 19
µm were fabricated in this study by employing the outer layer extrusion rate of 0.8
cm$^3$ min$^{-1}$. 
Figure 6.1: $j$-$V$ and power density curves of previous batch dual-layer hollow fibre cells consisting of 10 µm electrolyte (R-0.5) and 19 µm electrolyte (R-1), which the detail shown in Chapter 4. The cells operated at temperature of 600 °C using hydrogen flow rate of 15 cm$^3$ min$^{-1}$ (20 °C, 1 atm) and air flow rate of 40 cm$^3$ min$^{-1}$ (20 °C, 1 atm).

6.3.1 Macrostructure

In order to control the size of the finger-like voids in the anode layer, certain amounts of ethanol (0 to 20 wt. %) as a non-solvent were employed to replace NMP and are listed in Table 6.1. In this work, NMP is used as solvent of the inner layer spinning suspension instead of DMSO (as in batches of fibres produced in Chapter 3 and 4). Due to the high freezing point of DMSO (i.e. 18.5 °C), the mixing of this solvent with...
ethanol would result in a partial solidification of DMSO and thus, reduces the potential of DMSO as a dissolving agent for the polymer binder.

Figure 6.2 shows the macrostructure of the dual-layer hollow fibres co-sintered at 1500 °C for 12 hours and reduced at 550 °C for 2.5 hours. As can be seen, the anode inner layer is of an asymmetric structure consisting of a finger-like voids layer and a sponge-like layer and the finger-like voids layer becomes shorter with the increasing amount of ethanol. Dual-layer hollow fibre without ethanol in the spinning suspension (E-0) shows the longest finger-like voids occupying about 85 % of the anode thickness. The addition of 5 wt.% ethanol confines the growth of finger-like voids to around 70 % of the anode layer thickness. The finger-like voids length is further reduced to approximately 60 %, 55 % and 50 % with the further increase of the ethanol content to 10 wt.%, 15 wt.% and 20 wt.% respectively as shown in Figure 6.2.
**Figure 6.2:** SEM images of the (i) overall view and (ii) cross-sectional of the dual-layer hollow fibres consisting of different anode structures. The images were taken using backscattered electrons (BSE) mode.
Such change in morphology is in good agreement with our previous study shown in Chapter 5 and it can be explained as; firstly, the addition of ethanol as the non-solvent would increase the initial viscosity of a spinning suspension as shown in Table 6.1, and secondly, the presence of ethanol would accelerate the precipitation of polymer binder during the phase inversion process because the polymer phase is closer to its precipitation point and subsequently, increase the local viscosity of the nascent fibre. The viscous fingering [10], which is considered as the main phenomenon for the formation of the finger-like voids in the ceramic hollow fibres, has been limited by these two effects and as a result, inhibits the growth of finger-like voids in the fibres.

The outer electrolyte layer, as can be seen in Figure 6.2, is well-bounded to the inner layer although different solvents were used for preparing the spinning suspensions of the two layers. The electrolyte layer of approximately 15 µm in thickness can be achieved when the extrusion rate of 0.8 cm$^3$ min$^{-1}$ is used as shown in Figure 6.3. Moreover, although finger-like voids are observed in the electrolyte layer of fibre E-0, they are nearly eliminated in the E-5 and are totally removed in the fibre E-10. As every type of hollow fibres was fabricated using the same procedure except for the amount of ethanol in the inner anode layer suspension, the variation in the morphology of the outer electrolyte layer should be the result of the presence of ethanol that changes the process of phase inversion. For fibre E-0, the diffusion of NMP into the outer layer where DMSO was the solvent contributes to the decrease in the freezing point of DMSO and slowing down the precipitation of polymer binder. This results in a low viscosity of the outer layer suspension when it is in contact with the external coagulation and allows the viscous fingering phenomenon to occur, leading to the formation of finger-like voids in the electrolyte outer layer.
Figure 6.3: Close-up SEM images of the interface electrolyte/anode of the dual-layer hollow fibres. This figure shows the various electrolyte structures were obtained when different ethanol contents were used. The images were taken using backscattered electrons (BSE) mode.
The use of ethanol in the inner layer spinning suspension in fibres E-5, E-10, E-15 and E-20 has caused the diffusion of a mixture of ethanol-NMP into the DMSO region. The presence of ethanol as a non-solvent seems to be more effective in speeding up the polymer precipitation in DMSO, resulting in a higher viscosity of the outer layer suspension that inhibits the formation or growth of finger-like voids. Therefore, the higher the ethanol content in the inner layer suspension, the faster the precipitation of the outer layer suspension can be, until there is no finger-like voids can be formed in the outer electrolyte layer. When the content of ethanol is at or above 25 wt.%, the polymer binder in the outer layer is almost fully precipitated when in contact with the inner layer suspension (well before being immersed in the external coagulation bath) and blocks the outer orifice of the spinneret and therefore, the dual-layer hollow fibres for the such ethanol contents cannot be achieved. This further proves the effects of ethanol (in the inner layer suspension) on changing the phase inversion process of the outer layer suspension during the co-extrusion.

### 6.3.2 Mechanical and gas-tightness properties

In this study, the mechanical property of the developed dual-layer hollow fibres was investigated by three-point bending test. The bending strength was then calculated using equation (6.1). Figure 6.4 shows the bending strength of the dual-layer hollow fibres as a function of ethanol content in the inner layer spinning suspension. As can be seen, the bending strength increases markedly with the enhancement of the ethanol content in the inner layer suspension (from 0 wt.% to 20 wt.%). It should be noted that, besides the size of the finger-like structure in the anode layer, the voids in the electrolyte layer also affect the bending strength of the resultant dual-layer hollow fibres. Consequently, the fibre using 0 wt.% ethanol which has the longest finger-like
voids in the anode and contains plenty of micro-voids in the electrolyte region, shows the lowest bending strength of about 72 MPa. The bending strength increases substantially with higher amounts of ethanol in the inner layer suspension and reaches the highest value of 245 MPa when 20 wt.% of ethanol is employed, as the formation of finger-like voids were reduced notably in both inner and outer layers.

Figure 6.4: Bending strength of the reduced dual-layer hollow fibres measured at room temperature as a function of ethanol content in anode spinning suspension (number of samples = 5).

Besides the bending strength, the finger-like voids in the outer layer can be considered as certain sort of defect and affect the gas-tightness property of the electrolyte layer of
dual-layer hollow fibres. As the sponge-like structure area in the anode inner layer is relatively porous due to the reduction of NiO into Ni, it is believed that the anode layer does not give significant influence on the gas-tightness property of the dual-layer hollow fibres, which is measured based on the pressure change of the system. Figure 6.5 shows the gas-tightness of the dual-layer hollow fibres against the ethanol content in the inner layer suspension.

**Figure 6.5:** Gas permeability of the reduced dual-layer hollow fibres measured at room temperature as a function of ethanol content in anode spinning suspension, with the initial pressure of 40 psig. This graph is used to describe the gas-tightness property of the electrolyte layer (number of samples = 3).
Based on the graph above, nitrogen permeability is reduced with the increase of ethanol content. The fibre using 0 wt.% ethanol shows the highest gas permeability, namely the poorest gas-tightness of $6.4 \times 10^{-7}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$ due to the presence of finger-like voids in the outer layer region, allowing an easier diffusion of nitrogen gas. The elimination of some finger-like voids in the electrolyte layer by increasing the ethanol content to 5 wt.% has significantly reduced the pathway for gas diffusion through the electrolyte and led to a sudden drop of nitrogen permeability to $4.1 \times 10^{-8}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$. The further addition of ethanol, which means a denser electrolyte layer was produced, improves the gas-tightness property of the electrolyte by further decrease in nitrogen permeability to as low as $1.2 \times 10^{-8}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$ when 20 wt.% ethanol is used.

### 6.3.3 Electrochemical performances

A multi-layer cathode was brush-painted onto the dual-layer hollow fibre and sintered at 1200 °C for 5 hours. The approximate dimensional of resultant cells is listed in Table 6.2.

<table>
<thead>
<tr>
<th>Cell</th>
<th>Inner diameter (mm)</th>
<th>Outer diameter* (mm)</th>
<th>Cathode thickness (mm)</th>
<th>Active cathode length (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E-0</td>
<td>0.945</td>
<td>1.490</td>
<td></td>
<td></td>
</tr>
<tr>
<td>E-5</td>
<td>0.932</td>
<td>1.467</td>
<td></td>
<td></td>
</tr>
<tr>
<td>E-10</td>
<td>0.918</td>
<td>1.444</td>
<td>0.040</td>
<td>1.0</td>
</tr>
<tr>
<td>E-15</td>
<td>0.880</td>
<td>1.405</td>
<td></td>
<td></td>
</tr>
<tr>
<td>E-20</td>
<td>0.865</td>
<td>1.385</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Diameter of the cells (dual-layer hollow fibres with cathode)
After applying current collectors and built into a micro-tubular SOFC reactor, the electrochemical performance of the full cell was investigated at 600 °C using humidified hydrogen gas at the anode (lumen side) and air at the cathode side (outer surface). Figure 6.6 shows the current density-voltage (j-V) and power density curves of the cell made from fibre E-20 (approximately 50 % of the finger-like structure in the anode together with a 15 µm electrolyte layer) with hydrogen flow rates of 15 and 30 cm³ min⁻¹ (saturated with water vapour of 0.35 and 0.70 cm³ min⁻¹ respectively using a bubbling cylinder at 20 °C, 1 atm) and air flow rate of 40 cm³ min⁻¹ (20 °C, 1 atm). This cell shows an open-circuit voltage (OCV) of about 0.81 V when the hydrogen flow rate is 15 cm³ min⁻¹. This value is lower than the Nernst voltage of 1.16 V at 600 °C which is probably due to the possible minor diffusion of molecular hydrogen from the anode side to the oxidant (i.e. oxygen) region in the cathode side through the thin electrolyte thickness of only 15 µm, leading to the direct contact of these two gases. Furthermore, minor electronic conduction of the CGO electrolyte which basically creates short circuit pathways for the electrons is also one of the possible reasons for the lower OCV.

Although lower than the theoretical value, the OCV value obtained in this study is in very good agreement with our previous batch of fibres presented in Figure 6.1, in which the OCV of the cell E-20 with a 15 µm electrolyte (0.81 V) fabricated in this work is between the OCV of the cell R-0.5 with 10 µm electrolyte (0.77 V) and the cell R-1 with 19 µm electrolyte (0.85 V). This is another evidence of the influence of electrolyte thickness on the OCV value of the cell. As shown in Figure 6.6, the OCV of the cell E-20 reduces to 0.79 V with the increase of the hydrogen flow rate to 30 cm³ min⁻¹ probably due to the higher pressure in the lumen side that increases the hydrogen permeation across the electrolyte layer.
Figure 6.6: $j$-$V$ and power density curves of the cell E-20. The cells operated at temperature of 600 °C using two different hydrogen flow rates, i.e. 15 cm$^3$ min$^{-1}$ (20 °C, 1 atm) and 30 cm$^3$ min$^{-1}$ (20 °C, 1 atm), and air flow rate of 40 cm$^3$ min$^{-1}$ (20 °C, 1 atm).

In terms of the maximum power density of the cell, the E-20 produces approximately 1.25 W cm$^{-2}$ and 1.84 W cm$^{-2}$ when the hydrogen flow rates were 15 and 30 cm$^3$ min$^{-1}$ respectively. This difference can be explained by comparing the fuel utilisation in each cell. The fuel utilisation ($U_f$) has been computed using the equation (6.3) as shown below [11]:

$$U_f = \frac{I}{2F \times n_{H_2,\text{inlet}}} \times 100 \%$$  \hspace{1cm} (6.3)

where $I$ is the electric current provided by the cell (A), $F$ is the Faraday constant (As mol$^{-1}$) and $n_{H_2,\text{inlet}}$ is the hydrogen molar flow rate provided to the cell (mol s$^{-1}$). The
current value in this study is referred to the current at the maximum power density, based on the assumption that the electric current is a linear function of the molar flow of the spent fuel [12].

For the cell with 15 cm$^3$ min$^{-1}$ of hydrogen, 34.9% of the fuel was utilised. When the hydrogen flow rate was increased to 30 cm$^3$ min$^{-1}$, the fuel utilisation remains at about 34.5%, which indicates that more hydrogen volume diffuses into the small pores in the sponge-like structure in the anode where the major TPB region is located [13] and therefore, results in the higher power output. Due to the same reason, the hydrogen flow rate of 30 cm$^3$ min$^{-1}$ is used in the following experiments.

Figure 6.7 presents the results of the fuel cell test of the E-0, E-5, E-10, E-15 and E-20 at 600 °C using 30 cm$^3$ min$^{-1}$ of hydrogen. It can be seen that the cell E-0 with the longest finger-like voids in the anode shows a very low OCV of only about 0.54 V, which can be attributed to the severe gas leakage across the electrolyte layer due to the presence of the finger-like voids in the thin electrolyte layer. In contrast, the cells E-5, E-10, E-15 and E-20 which possess much better gas-tightness property (Figure 6.5) show considerably higher OCVs between 0.77 and 0.79 V. Although the obtained OCVs are still lower than the Nernst voltage, they are in very good agreement with the OCVs of the CGO-based micro-tubular SOFCs that were previously reported in literatures [1-5,14-19].

As also presented in Figure 6.7, the power density of the cells is closely related to the anode structure. The cell E-20 consists only 50% finger-like voids length of the anode thickness shows the maximum power density of 1.84 W cm$^{-2}$, which increases slightly to 1.98 W cm$^{-2}$ for the cell E-15 with 55% voids structure length. With the increasing sizes of the finger-like voids, the maximum power density keeps increasing.
to 2.03 and 2.32 W cm\(^{-2}\) for E-10 (with 60% void of the anode thickness) and E-5 (with 70% voids of the anode thickness) respectively. As shown in Figure 5.4 and 5.6 in Chapter 5, longer finger-like voids normally have bigger finger-like voids entrance pore which results to a lower resistance of fuel gas diffusion into the finger-like voids zone. Furthermore, it is believed that the finger-like voids function as a set of hundreds micro-channels [20] in the anode and thus, the presence of longer voids enhances fuel gas mixing and facilitates better fuel gas diffusion to the TPB in the sponge-like region, the area where the oxidation reaction of hydrogen takes place and consequently accelerates the rate of the reaction in the anode.

However, the finger-like voids of this type also markedly reduce the conductivity and number of TPB region per unit area in the anode, as explained in Chapter 5. When the finger-like voids are further increased to 85% of anode thickness, i.e. the cell E-0, a big drop in the cell performance is observed and the maximum power density is only 0.99 W cm\(^{-2}\). Moreover, the low OCV of the cell as the result of gas diffusion across the electrolyte is also one of the main reasons for the low electrochemical performance of this cell.

As a result of the optimised cell structure, four out of five cells developed in this study, i.e. E-5, E-10, E-15 and E-20, show outstanding performances and their maximum power densities at 600 °C are significantly higher than our previous results, i.e. around 1.11 W cm\(^{-2}\) at 600 °C for the cell R-0.5 with 35% finger-like voids length in the anode and the ones reported by Suzuki et al. [2,3] (about 1.29 W cm\(^{-2}\) at 600 °C) and Sammes et al. [4,5] (about 1.31 W cm\(^{-2}\) at 550 °C), which further demonstrates the advantages of the co-extrusion/co-sintering process in fabricating high quality dual-layer hollow fibres for better cell performance.
Figure 6.7: $j$-$V$ and power density curves of the cells consisting of different anode structures. The cells operated at temperature of 600 °C using hydrogen flow rate of 30 cm$^3$ min$^{-1}$ (20 °C, 1 atm) and air flow rate of 40 cm$^3$ min$^{-1}$ (20 °C, 1 atm).
Figure 6.8 shows the fuel utilisation in the anode as a function of ethanol content in
the inner layer spinning suspension. As aforementioned, the fuel utilisation percentage
in this study was calculated based on value of the current at the maximum power
density. As can be seen, the cell E-0 that using 0 wt.% ethanol shows the lowest fuel
utilisation in the anode of only about 21.2 %. The reasons for this are similar to the
explanation for the lowest maximum power density achieved by this cell, i.e. possible
gas diffusion across the electrolyte and less TPB per unit area in the anode. While
much higher fuel utilisations between 34.5 % and 38.9 % can be achieved for E-5 to
E20. However, the fuel utilisation of the cells obtained in this study is still
considerably low when compared to the fuel utilisation level of the commercial fuel
cell (about 85 %) [21].
Figure 6.8: Fuel utilisation percentage as a function of ethanol content in the inner layer spinning suspension. The values were calculated based on equation (6.3) using the current value at the maximum power density of each cell.

In order to get a clear picture on the effect of finger-like voids on the resistance of each component of the cells, an impedance analysis has been carried out. Figure 6.9(a) shows impedance analysis for the micro-tubular SOFCs at 600 °C which is to determine the area specific resistance (ASR) of the cells. According to Mogensen and Hendriksen [22], total ASR of the cell may be divided into ohmic ASR and electrode polarisation ASR. As shown in the graph, the distance from high frequency intercept to the zero value on the real impedance axis represents the ohmic ASR in the cell, while the distance between high frequency and low frequency intercepts shows the electrode polarisation ASR. In order to study the effect of cell macrostructures on the
cell resistance, the values of ohmic ASR, electrode polarisation ASR and total ASR obtained from this graph are then employed to plot the graph of ASR against the ethanol content in the inner layer spinning suspension as presented in Figure 6.9(b).

As can be seen in Figure 6.9(b), the ohmic ASR of the cells reduces slightly with the addition of ethanol in the inner layer spinning suspension. According to Mogensen and Hendriksen [22], the ohmic ASR originates from the electrolyte, the electrode materials and the current collection arrangement. As the current collector and cathode in this study are built in a similar way for each cell, it can be assumed that the effects of current collection and cathode on the ohmic ASR are almost negligible. Meanwhile for the anode, the ohmic ASR from the electrolyte is much higher than the one in the anode [23] and therefore, the different anode structure does not greatly affect the total ohmic ASR value and it is believed that the trend of the ohmic ASR that was obtained in this study is largely resulted from the electrolyte. Although the specific resistivity of the electrolyte is identical because of the use of the same material (i.e. CGO), the electrolyte resistance of each cell varies due to their macrostructure difference. The presence of macro-voids at 0 wt.% or low ethanol concentration has reduced the effective cross-sectional area in the electrolyte and has led to the high ohmic resistance of the cells. Thus, the ohmic resistance of the cells in this work decreases with the increase of ethanol content.
Figure 6.9: (a) Impedance spectra of the cells with different anode structure measured under open-circuit condition using signal amplitude of 10 mV at frequencies of 100 kHz to 0.01 Hz and hydrogen flow rate of 30 cm$^3$ min$^{-1}$ (20 °C, 1 atm) and air flow rate of 40 cm$^3$ min$^{-1}$ (20 °C, 1 atm); (b) The area specific resistance (ASR) as a function of ethanol content in the inner layer spinning suspension.
For the electrode polarisation ASR, it represents several types of resistances [22] such as the resistance from the gas phase diffusion and the resistance due to gas conversion, i.e. fuel oxidation and oxygen reduction. Based on this understanding, it is strongly believed that the variation in the anode structure would affect very much the value of the electrode polarisation ASR. As can be seen in the Figure 6.9(b), the electrode polarisation ASR is decreased with the increase of ethanol content from 0 wt.% to 5 wt.% probably due to the smaller TPB region per unit area that results to the less fuel oxidation reaction of the cell that using 0 wt.% ethanol (85 % finger-like voids thickness) compared to the cell that using 5 wt.% ethanol (70 % in thickness). However, the resistance from the fuel gas diffusion in the anode seems to be more dominant for the cell with finger-like voids thickness of 60 %, 55 % and 50 % (which fabricated from 10 wt.%, 15 wt.% and 20 wt.% of ethanol respectively in the inner layer suspension) since the value of electrode polarisation ASR of the cells increases as a function of ethanol content. This shows that the finger-like voids are really beneficial in promoting the gas diffusion in the anode and subsequently, minimises the electrode polarisation ASR in the cell.

In addition, the line of total ASR as a function of ethanol content is almost identical to the electrode polarisation ASR trend and this indeed shows that the difference in the anode structure in this study has bigger effect on the cell performance than the ohmic ASR. In comparison to other cells reported in previous works [1,2,4,5,7,24-25], the resistances of the cells in this study are much lower and thus, explaining the outstanding power outputs of the obtained cells.
6.4 Conclusions

This work demonstrates the advantages of co-extrusion/co-sintering process in developing high quality dual-layer hollow fibres. A set of dual-layer hollow fibres with 50% to 85% of the finger-like voids thickness in the anode inner layer has been successfully fabricated by varying the ethanol content in the inner layer spinning suspension from 0 to 20 wt.%. The use of ethanol in the inner layer spinning suspension does not only affect the structure of the anode but also the structure of the electrolyte due to the formation of macro-voids in the outer layer when lesser ethanol is used. The difference in the structures in both inner and outer layers of the dual-layer hollow fibres gives a big impact to the bending strength of the fibres, while the gas-tightness property of the hollow fibres is markedly affected by the outer layer structure. In term of electrochemical performance, the maximum power density of the cells fabricated in this study varies with the anode structure. The bigger finger-like voids entrance size in the anode with longer finger-like voids would results in a lower resistance of fuel gas diffusion into the finger-like voids zone. It is also believed that the finger-like voids structure in the anode act as a set of hundreds micro-channels that improve the fuel mixing and diffusion in the anode triple-phase boundary (TPB) region. Therefore, it is found that the maximum power density increases significantly with the increase of finger-like voids thickness and reaches the highest value at 2.32 W cm\(^{-2}\) for the cell with 70% finger-like voids thickness. This study also proves that the structure of the anode has huge impact to the resistance of the cells and suggests that the anode structure is one of the major parameters that have to be considered in order to produce a high performance micro-tubular SOFC. The results obtained in this study can be used for the development of other functional dual-layer hollow fibres in various applications.
References


7.1 General Conclusions

This thesis mainly focuses on the single-step fabrication of electrolyte/anode dual-layer hollow fibres and the use of such fibres as a support for micro-tubular solid oxide fuel cells (SOFCs). It has been demonstrated in this thesis that the structure and performance of the developed dual-layer hollow fibres can be controlled by adjusting a number of variables of the fabrication process such as the properties of the spinning suspensions and operating parameters of the co-extrusion/co-sintering process. In order to understand the effects of the fabrication parameters on the quality of the obtained dual-layer hollow fibres, a series of characterisations have been carried out such as macrostructure, sintering behaviour, anode porosity and gas permeability, mechanical strength, electrolyte gas-tightness, electrical conductivity and fuel cell test. The results obtained have been used as a guidance to improve the electrochemical performance of the micro-tubular SOFCs.

7.1.1 Fabrication of novel electrolyte/anode dual-layer hollow fibres

Defect-free electrolyte/anode dual-layer hollow fibres precursors have been successfully prepared by a phase inversion-based co-extrusion process. As a solvent for the spinning suspensions, dimethyl sulfoxide (DMSO) with the high freezing point (18.5 °C) possesses better effect in suppress the over-growth of finger-like voids when
compared with N-methyl-2-pyrrolidone (NMP) and as a result, leads to the formation of asymmetric anode inner layer with nicely sharp, short finger-like voids originating from the inner surface. Due to the different sintering behaviours of the inner and the outer layer materials, a heating rate of 15 °C min⁻¹ was used to co-sinter the hollow fibre precursor, below which the fibres can hardly survive the co-sintering. By varying the co-sintering temperature from 1450 to 1550 °C followed by the reduction at 550 °C, the porosities of the both inner and outer layers decreases and affects the mechanical strength of the hollow fibre, permeability and electrical conductivity of the anode inner layer and gas-tightness of the electrolyte outer layer. However, the general cross-sectional macrostructure of the hollow fibres are largely retained after co-sintering and reduction processes.

After depositing the cathode and applying the current collectors, the fuel cell of the corresponding dual-layer hollow fibre was investigated at different temperatures. The obtained open-circuit voltage (OCV) decreases while the maximum power density increases with the increase of the cell operating temperatures. These can be respectively explained by the increase in the electronic conductivity of the cerium-gadolinium oxide (CGO) electrolyte layer and the increase in the kinetics of the oxidation and reduction reactions and overall conductivities of the cell when the temperature is increased.

### 7.1.2 Effect of the electrolyte thickness on the dual-layer hollow fibres

By controlling the extrusion rate of the outer layer suspension, the thickness of the electrolyte outer layer of dual-layer hollow fibres can be varied without affecting the structure of the anode inner layer. Viscosity of the spinning suspension for the outer layer should not be too high in order to ensure a smooth flow of the suspension and a
full and uniform coverage especially when the extrusion rate is very low. This proves the advantages of the co-extrusion as a suitable technique in producing thin and uniform electrolyte layer, which is comparable with the other conventional and complex depositing techniques such as dip-coating and chemical vapour deposition (CVD).

By reducing the thickness of the electrolyte, the bending strength and gas-tightness of the dual-layer hollow fibres are reduced, indicating that both properties strongly rely on the dense electrolyte layer. Based on the obtained electrochemical data, a trade-off between the OCV and power density of the cells is observed when the thickness of the electrolyte layer is reduced. The OCV of the cells reduces with the decrease of the electrolyte thickness which can be explained by the decrease of the gas-tightness properties and the rise in the electronic leakage across the thinner CGO electrolyte. However, the cell with the thinner electrolyte layer shows higher maximum power density. In the thinner electrolyte, oxygen ions from the cathode side could transport more rapid to the anode side and this would accelerate the rate of the reactions in both electrodes. These results justify the need of reducing the electrolyte thickness due to the significant impact on the performance of the cell.

7.1.3 Preparation of different asymmetric structures of anode hollow fibres

The anode hollow fibres with different asymmetric structures can be prepared by varying the initial suspension viscosity. In this study, ethanol was used as a non-solvent additive in order to manipulate the suspension viscosity. Ethanol was chosen because it can act as a good dispersant for the mixture of NiO-CGO and as a result, the dispersion of Ni and CGO in the prepared hollow fibre would be more uniform and continuous. By increasing the content of ethanol in the spinning suspension, the
length of the finger-like voids structure is reduced. It has been found that the ethanol addition has two combination effects on the spinning suspension; firstly, the addition of ethanol as a non-solvent would increase the initial viscosity of a spinning suspension and secondly, the presence of ethanol would accelerate the precipitation of polymer binder during the phase inversion process because the polymer phase is closer to its precipitation point and subsequently, increase the local viscosity of the nascent fibre. These combined effects would cause the formation of a thick sponge-like structure.

In Ni-CGO anode hollow fibre, three types of pores, which are finger-like voids, the pores that survive the sintering in the sponge-like region, and the one that is formed as a result of the reduction of NiO to Ni, have been observed. The other observation of the structure of the hollow fibre is the porosity of the fibres decreases with the reduction of the finger-like voids length. The properties of the anode hollow fibre is markedly affected by such changes in asymmetric structures. The increase of the finger-like voids length does not only result in higher gas permeation but also reduces the mechanical strength and electrical conductivity of the anode hollow fibre. Therefore, the length of the finger-like voids length should be properly controlled as their presence would determine the overall performance of the fuel cell.

### 7.1.4 Effects of the asymmetric structures in the anode inner layer on dual-layer hollow fibres

In order to vary the asymmetric structure of the anode inner layer of dual-layer hollow fibre, ethanol has been used as a non-solvent. However, the mixing of ethanol with DMSO (the solvent that used in previous batches of dual-layer hollow fibres) would result in a partial solidification of DMSO and thus, reduces the potential of DMSO as
a dissolving agent for the polymer binder. Therefore, NMP is used to replace DMSO as the solvent of the inner layer spinning suspension. As expected, the addition of ethanol confines the growth of finger-like voids in the anode layer. However, the use of ethanol and NMP in the inner layer spinning suspension does not only affect the anode structure but also change the phase inversion process in the outer layer. In the system with 0 wt.% ethanol, the diffusion of NMP into the outer layer where DMSO is the solvent, decreases the freezing point of DMSO and slows down the precipitation of polymer binder. This results in a lower viscosity of the outer layer suspension when in contact with the external coagulation and allows the viscous fingering phenomenon to occur, leading to the formation of finger-like voids in the electrolyte outer layer. The use of ethanol in the inner layer spinning suspension has caused the diffusion of a mixture of ethanol-NMP into the DMSO region. The presence of ethanol as a non-solvent seems to be more effective in speeding up the polymer precipitation in DMSO, resulting in a higher viscosity of the outer layer suspension that inhibits the formation or growth of finger-like voids. Therefore, the higher the ethanol content in the inner layer suspension, the faster the precipitation of the outer layer suspension can be, until there is no finger-like void formed in the outer electrolyte layer.

The formation of macro-voids in both the inner and the outer layer markedly affects the properties of the hollow fibre. By increasing the ethanol content in the inner layer spinning suspension, the bending strength and gas-tightness property of the hollow fibres increase. In terms of the electrochemical performance, the difference in the anode structure does not give significant impact on the OCV. Only hollow fibre fabricated with 0 wt.% ethanol shows a very low OCV, which can be attributed to the gas leakage across the electrolyte layer due to the presence of the large finger-like voids in the thin electrolyte layer. The power output of the cell is closely related to the
anode structure as the maximum power density increases with the increase of finger-like voids length. Longer finger-like voids normally have bigger finger-like voids entrance size which results to a lower resistance of fuel gas diffusion into the finger-like voids zone. Furthermore, it is believed that the finger-like voids function as a set of hundreds micro-channels in the anode and thus, the presence of longer voids enhances fuel gas mixing and facilitates better gas diffusion to the TPB in the sponge-like region, the area where the oxidation reaction of hydrogen takes place and consequently accelerates the rate of the reaction in the anode. However, at a certain point, the finger-like voids also markedly reduce the number of TPB region and conductivity of the anode.

7.2 Recommendations for Future Work

7.2.1 Nano-grain size CGO particles

It has been shown in this study that the porosity of the anode inner layer strongly influences the cell performance. Although the gas diffusion in the anode has been improved by the presence of large finger-like voids, it is beneficial to further increase the porosity of the sponge-like region of the anode where most of TPB located. The use of nano-grain size CGO particle would reduce the densification temperature of the electrolyte outer layer [1-3] and thus, a much lower co-sintering temperature can be applied for a higher porosity of the anode inner layer.

7.2.2 Pore former

Apart from using nano-grain size CGO particle to reduce the co-sintering temperature, another effective and popular way in increasing the porosity of the sponge-like region
of anode is by adding pore formers to the inner layer spinning suspension. Flour, rice or corn starch, graphite and spherical polymers are widely used as pore formers [4-8] and the pore former is burned out during the sintering process. The microstructure and pore structure are significantly influenced by the size, shape and quantity of the pore formers [9,10] and the pores are normally uniformly connected to each other.

7.2.3 Bilayer electrolyte

The OCV of the cells obtained in this study is lower than the theoretical Nernst voltage which is not only due to the gas tightness issue but also because of the minor electronic current leakage across the electronic conductive path in the CGO electrolyte when Ce$^{4+}$ is reduced to Ce$^{3+}$ in the reducing atmosphere. The use of bilayer electrolyte is believed to be able to overcome this electronic currents leakage issue in the CGO electrolyte, as have been shown in previous studies [11-13].

7.2.4 Fuel cell durability

During the cell operation, micro-tubular SOFCs are subjected to cycling of both temperature and electrochemical conditions [14] which both can cause damage in the cell’s microstructure and thus, reducing cell performance. Cycling in SOFCs can be divided into two types. Firstly, the temperature gradient leads to the degradation during thermal cycling due to the different expansion coefficients between components [15]. Secondly, redox cycling (where the fuel flow is interrupted then restarted, at a constant temperature) is shown can cause damage to the cell due to the expansion of the nickel particle [16]. This repeated expansion and contraction would lead to the formation of micro-cracks in the cell. The durability and stability of the
micro-tubular SOFC developed in this work can be studied by operating the cell in both thermal and redox cycling.

7.2.5 Operation on hydrocarbon fuel

Unlike other types of fuel cells, SOFCs are operated at a high enough temperature for internal reforming of hydrocarbons to occur on the anode surface [14]. SOFCs can therefore use hydrocarbons as the fuel. Running directly on hydrocarbon fuels, however, results in carbon deposition on the anode surface and impairs cell performance. Therefore, the tolerance of the cell to fuels other than hydrogen can be investigated on the dual-layer hollow fibre SOFC by operating the cell on hydrocarbon fuel such as methane and butane.

7.2.6 Triple-layer hollow fibre

The development of triple-layer hollow fibre consists of thin cathode and electrolyte layers supported on thick anode hollow fibre can be achieved by phase inversion-based co-extrusion/co-sintering if a number of obstacles can be overcome. One of the major issues that may rise during the fabrication is the sintering temperature mismatch between the electrolyte and cathode materials. Co-sintering of the triple-layer hollow fibre at a high temperature (e.g. 1450 °C) would results in a very dense structure of cathode and also solid state reaction of some cathode materials (e.g. lanthanum manganite, LSM). Moreover, the macrostructure and thickness of the cell especially the middle layer (i.e. electrolyte) is more difficult to control during the co-extrusion process due to a more complex phase inversion process.
Reference


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Publications


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