MICRO-STRUCTURED HOLLOW FIBERS FOR MICRO-TUBULAR SOLID OXIDE FUEL CELLS

BY
TAO LI

Department of Chemical Engineering
Faculty of Engineering
IMPERIAL COLLEGE LONDON

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 composed by and originated entirely from me. Information obtained from the published and unpublished work of others has been acknowledged in the text and corresponding references are included in the thesis.

Tao Li

Imperial College London, March 2015
COPYRIGHT DECLARATION

The copyright of this thesis rests with the author and is made available under a Creative Commons Attribution Non-Commercial No Derivatives licence. Researchers are free to copy, distribute or transmit the thesis on the condition that they attribute it, that they do not use it for commercial purposes and that they do not alter, transform or build upon it. For any reuse or redistribution, researchers must make clear to others the licence terms of this work.

Tao Li

Imperial College London, March 2015
Abstract

Micro-tubular solid oxide fuel cells (MT-SOFCs) have received increasing research interest in the past decade. However, current development is restricted in R&D phase due to several technical challenges, such as expensive manufacturing route, which limits mass-scale production, and the difficulties in efficient current collection, especially from the small lumen of micro-tubes.

In terms of fabrication, conventional routes usually consist of repetitions of coating and sintering, which is both time and cost-consuming. To tackle this problem, a phase inversion-assisted co-extrusion process has been established in this study, which dramatically simplifies the fabrication process, with improved adhesion. The phase inversion process could lead to the formation of an asymmetric structure, comprising micro-channels and a sponge-like structure. The former morphology could facilitate fuel transport, while the latter provides reactive sites for electrochemical reactions. The feasibility of the new manufacturing route has been established by fabricating anode/anode functional layer (AFL)/electrolyte triple-layer hollow fibers and the results suggest that inserting an AFL could effectively improve power density by 30% due to enlarged triple-phase boundary.

As for the current collection from the lumen side, a new nickel-based current collector has been developed via co-extrusion. By controlling the fabrication parameters, a deliberate mesh-structure has been obtained with uniformly distributed entrances. Inserting this nickel-based inner layer considerably increases the electrical conductivity of anode and reduces gas diffusion resistance. After a complete cell was constructed, systematic electrochemical performance tests were undertaken. It has been illustrated that more uniform current collection has been achieved and contact
loss, which is the major contributor towards ohmic loss in conventional current collectors, has been significantly reduced to less than 10% of total ohmic loss. This result indeed highlights the features of process economy and high efficiency of the new current collection design and suggests this design to be suitable for large-scale stack construction.
The three-year PhD study has been my most memorable experience. I could not have achieved the goals without the assistance from my colleagues and friends, to whom I own large debts of gratitude.

First and for most, I'd like to express my most sincere appreciation to my supervisor, Professor Kang Li, for his continuous guidance, encouragement and supervision throughout my research. Without his help, I would not have started or finished this effort. In addition, I really appreciate that Professor Li provides me with the generous financial support, the working conditions and the opportunity to collaborate with other groups.

Secondly, I am heartily grateful to the postdoctoral fellows, Dr Zhentao Wu and Dr Bo Wang, for kindly sharing their extensive knowledge and expertise on fabrication and characterization of hollow fiber membranes. They also help in carefully reviewing my publications and reports. I will always bear in mind about their admirable work ethic and personal values. Moreover, I am indebted to all remaining colleagues and friends of Professor Li’s group: Jing Ji, Dr Xinlei Liu, Melanie Lee, Nur Hidayati Othman, Jeng Chong, Dr Jessica Lai, Farah Aba and Ana Gouveia Gil who either directly or indirectly provide generous support. A special thanks goes to Lisa Kleiminger from Professor Geoffrey Kelsall’s group for sharing her knowledge on electrochemistry. Her advice and suggestion help me gain a better insight into a new research aspect.

Last but not least, I would like to dedicate this thesis to my family, who provides both financial and emotional support throughout my time in London. Also, a special thanks to my wife, who has accompanied me even in the hardest time, for her love, patience, understanding and encouragement.
Table of Contents

Abstract.......................................................................................................................... 3

Acknowledge.................................................................................................................. 5

Table of Contents.......................................................................................................... 6

List of Tables.................................................................................................................. 11

List of Figures................................................................................................................ 13

Nomenclature.................................................................................................................. 19

Chapter 1. Introduction.................................................................................................. 21
  1.1 Background............................................................................................................. 21
  1.2 History................................................................................................................... 23
  1.3 Different Types of Fuel Cells................................................................................ 25
  1.4 PhD Objectives ..................................................................................................... 27
  1.5 Thesis structure..................................................................................................... 28

Chapter 2. Literature Review......................................................................................... 31
  2.1 SOFC Principles and Thermodynamics............................................................... 31
  2.2 SOFC components................................................................................................ 37
    2.2.1 Anode ............................................................................................................ 40
    2.2.2 Electrolyte ..................................................................................................... 44
    2.2.3 Cathode .......................................................................................................... 47
    2.2.4 Interconnect ................................................................................................... 50
  2.3 Intermediate Temperature SOFC .......................................................................... 51
2.3.1 Electrolyte materials for IT-SOFC .................................................. 52
2.3.2 Anode materials for IT-SOFC .......................................................... 56
2.3.3 Cathode materials for IT-SOFC ......................................................... 58
2.3.4 Interconnect materials for IT-SOFC .................................................. 59
2.4 Geometries classification .................................................................. 60
  2.4.1 Cell configuration ............................................................................ 60
  2.4.2 Types of stack design ...................................................................... 63
2.5 Progress in Micro-tubular SOFCs ....................................................... 66
  2.5.1 Plastic mass ram extrusion ............................................................... 67
  2.5.2 Wet spinning .................................................................................. 73
  2.5.3 Sintering Process ........................................................................... 84
2.6 Conclusion .......................................................................................... 87

Reference .................................................................................................. 88

CHAPTER 3 Single-step Fabrication and Characterisations of Triple-Layer Ceramic Hollow Fibres for MT-SOFCs ........................................................................... 107

3.1 Introduction .......................................................................................... 108
3.2 Experimental ........................................................................................ 111
  3.2.1 Materials ........................................................................................ 111
  3.2.2 Fabrication of anode/AFL/electrolyte triple-layer hollow fibers ....... 111
  3.2.3 Characterizations ............................................................................ 115
3.3 Results and Discussion ......................................................................... 120
  3.3.1 Sintering behaviours .................................................................... 120
  3.3.2 Macrostructure and porosity .......................................................... 123
3.3.3 Mechanical and gas-tightness properties................................. 127
3.3.4 Electrical conductivity ...................................................... 130
3.4 Conclusions ........................................................................ 132
References.............................................................................. 133

CHAPTER 4 Co-extrusion of Electrolyte/Anode functional layer/Anode Triple-layer Hollow Fibers for MT-SOFCs–Electrochemical Performance Study ............... 138

4.1 Introduction.......................................................................... 139

4.2 Experimental....................................................................... 141
4.2.1 Materials.......................................................................... 141
4.2.2 Fabrication of anode/AFL/electrolyte triple-layer hollow fibers ...... 142
4.2.3 Characterizations............................................................... 144

4.3 Results and Discussion........................................................ 147
4.3.1 Morphology...................................................................... 147
4.3.2 Gas-tightness and mechanical strength.............................. 151
4.3.3 Electrochemical performances............................................ 153

4.4 Conclusions ........................................................................ 158

References.............................................................................. 159

CHAPTER 5 A Dual-Structured Anode/Ni-Mesh Current Collector Hollow Fiber for Micro-Tubular SOFCs...................................................... 163

5.1 Introduction.......................................................................... 164

5.2 Experimental....................................................................... 166
5.2.1 Materials.......................................................................... 166
5.2.2 Fabrication of anode/anodic current collector hollow fibers ........................................ 166
5.2.3 Dip-coating of electrolyte ...................................................................................... 168
5.2.4 Characterizations ................................................................................................. 169
5.3 Results and Discussion ............................................................................................ 172
  5.3.1 Morphology of dual-structured hollow fibers ..................................................... 172
  5.3.2 Gas diffusion inside the dual-structured hollow fiber ....................................... 176
  5.3.3 Mechanical property .......................................................................................... 179
  5.3.4 Electrical conductivity ....................................................................................... 181
  5.3.5 Dip-coating of electrolyte .................................................................................. 182
5.4 Conclusions ............................................................................................................. 183
References ..................................................................................................................... 184

CHAPTER 6 Co-extrusion of Triple-layer Hollow Fibers with Anodic Current Collector
for MT-SOFC .................................................................................................................. 188
6.1 Introduction ............................................................................................................. 189
6.2 Experimental ......................................................................................................... 191
  6.2.1 Materials .......................................................................................................... 191
  6.2.2 Fabrication of electrolyte/anode/anodic current collector triple-layer hollow fibers ......................................................................................................................... 192
  6.2.3 Characterizations .............................................................................................. 193
  6.2.4 Modelling .......................................................................................................... 196
6.3 Results and Discussion ............................................................................................ 198
  6.3.1 Sintering behaviour .......................................................................................... 198
  6.3.2 Morphology of triple-layer hollow fibers ....................................................... 200
6.3.3 Gas-tightness and mechanical strength ........................................... 203
6.3.4 Electrochemical performances and calculation of ohmic contributions
............................................................................................................. 204
6.4 Conclusions ...................................................................................... 209
References ............................................................................................. 209

CHAPTER 7 Conclusions and Recommendations for Future Work .......... 215
7.1 General conclusions ......................................................................... 215
  7.1.1 Fabrication of anode/AFL/electrolyte triple-layer hollow fibers .... 216
  7.1.2 Effects of AFL thicknesses on electrochemical performances .... 217
  7.1.3 Fabrication of dual-structured anode/nickel-mesh hollow fibers ... 218
  7.1.4 Fabrication of triple-layer hollow fibers with high-efficiency nickel-
      composite current collector ................................................................. 219
7.2 Recommendations for Future Work ................................................ 220
  7.2.1 New multi-layer designs ............................................................... 220
  7.2.2 Hydrocarbon-fuelled MT-SOFC ................................................... 220
  7.2.3 Multi-channel design .................................................................. 221
  7.2.4 MT-SOFC stack design ................................................................. 223
References ............................................................................................. 225

List of Publications ................................................................................ 227
Appendix ................................................................................................. 229
LIST OF TABLES

Table 1.1: Features of various types of fuel cells ................................................................. 26
Table 2.1: Key requirements for different cell components of SOFCs ...................... 39
Table 2.2: Conductivity, bending strength and TEC of zirconia-based electrolytes .. 46
Table 2.3: Characteristics of different SOFC configurations [16, 78] ....................... 62
Table 2.4: Development of single micro-tubular SOFC based on plastic mass ram extrusion technique .................................................................................................................. 71
Table 2.5: Development of single micro-tubular SOFC based on dry-jet wet extrusion technique ......................................................................................................................................................... 82
Table 3. 1: Compositions of spinning suspensions ......................................................... 112
Table 3. 2: Co-extrusion parameters of the triple-layer hollow fibers .................... 113
Table 4. 1: Compositions and co-extrusion parameters of the spinning suspensions for triple-layer hollow fibers .......................................................................................................................... 144
Table 4. 2: Dimensions of triple-layer hollow fibers with different extrusion rates of AFL ........................................................................................................................................................................ 149
Table 5. 1: Compositions of spinning suspensions for dual-structured hollow fibers. ........................................................................................................................................................................ 167
Table 5. 2: Composition of dip-coating slurry ............................................................... 168
Table 5. 3: Dimensions and porosity of dual-structured hollow fibers .................... 176
Table 6. 1: Compositions of the spinning suspensions for triple-layer hollow fibers. ........................................................................................................................................................................ 192
Table 6. 2: Dimensions, gas-tightness and mechanical strength of different hollow fibers samples. .......................................................................................................................... 202

Table 6. 3: Data used in the calculation of ohmic loss contributors ....................... 208

Table 6. 4: Theoretical calculation results of different ohmic loss contributors. ..... 208
LIST OF FIGURES

Figure 1.1: Schematic diagram of an individual cell. ...................................................... 22
Figure 1.2: Comparisons between the efficiencies for fuel cells (red curve) and heat engines (black curve) as a function of temperature. [1] ................................................. 23
Figure 1.3: Overall structure of the thesis. ........................................................................... 30
Figure 2.1: Working principles of a solid oxide fuel cell.................................................... 31
Figure 2.2: Typical voltage/current plot of an operating cell.[13] ........................................... 36
Figure 2.3: Schematic diagram of a single cell unit. ............................................................. 38
Figure 2.4: Schematic diagram of a Ni/YSZ anode structure ............................................ 40
Figure 2.5: Electrical conductivity of Ni-YSZ as a function of nickel content.[17]..... 42
Figure 2.6: Illustration of a multi-layer Ni-YSZ anode structure and the variations in physical properties.[10] ........................................................................................................ 43
Figure 2.7: Conductivity of YSZ in air at 1000°C (reproduced from [9]) ....................... 45
Figure 2.8: Conductivity changes during annealing at 1273K. (a)8mole%YSZ, (b)8mole%ScSZ, (c)11mole%ScSZ.[32] .................................................................................. 47
Figure 2.9: Schematic diagram of the perovskite lattice structure. ................................. 48
Figure 2.10: Ionic conductivity of selected electrolyte materials as a function of reciprocal temperature[51]. .............................................................................................. 53
Figure 2.11: Illustration of CeO2 fluorite framework. The smaller spheres denote Ce4+ cations and larger spheres represent oxygen sites. ......................................................... 54
Figure 2.12: Illustration of single cell configurations (reproduced from [78]) .......... 61
Figure 2.13: Schematic diagram of a planar design SOFC configuration. [79]........ 63
Figure 2.14: Schematic design of a cathode-supported tubular cell developed by Siemens Westinghouse [84] ................................................................. 65

Figure 2.15: Flow chart of the fabrication process of the Ni-based anode-supported micro-tubular SOFCs ............................................................... 68

Figure 2.16: Schematic diagram of an extrusion process .................................. 68

Figure 2.17: The external view of co-extruder designed by Kendall’s group [112] .. 69

Figure 2.18: Schematic ternary phase diagram of the precipitation pathway of a solvent-polymer-precipitant system[50, 128] ................................................ 73

Figure 2.19: Ternary phase diagrams for (a) DMSO (b) NMP system. Thick lines denote binodal lines; thin lines denote spinodal lines; dashed lines represent tie-lines; dots represent solidification points. [50, 129, 130] .................................................. 75

Figure 2.20: Photographs of a typical triple-orifice spinneret. (a) image from one side; (b) image from bottom; (c) dimensions of the three orifices. [50] ........................................ 78

Figure 2.21: Schematic diagram of a typical set of spinning apparatus (insert: cross sectional diagram of a dual-orifice spinneret)[133] ........................................ 79

Figure 2.22: Example of the micro-channels and sponge-like structure in CGO-NiO hollow fiber membranes ........................................................................... 80

Figure 2.23: Cross-sectional image of a typical sandwich structure .................. 81

Figure 2.24: Diagram of a qualitative mechanism for final sintering[50] ............ 86

Figure 3.1: Schematic diagram of the phase-inversion based co-extrusion process. The inset shows the picture of the quadruple-orifice spinneret used in this study. 113

Figure 3.2: Illustration of the sintering profile ................................................. 114

Figure 3.3: Schematic diagram of the apparatus of three-point bending test. ....... 117
Figure 3.4: Schematic diagram of the set-up for gas-permeation test. 1) Gas cylinder; 2) Pressure regulator; 3) Valve; 4) Test vessel; 5) Fiber holder; 6) Pressure gauge.

Figure 3.5: Schematic diagram of experimental set-up of 4-point DC method [5].

Figure 3.6: Sintering curves of NiO, CGO and the materials of anode and AFL (Heating rate: 5 °C min⁻¹).

Figure 3.7: Sintering rate curves of NiO, CGO and the materials of AFL and anode.

Figure 3.8: SEM images (secondary electron imaging (SEI) mode) of the fiber with the AFL extrusion rate of 3 ml min⁻¹: (A) precursor fiber, (B) sintered fiber and (C) reduced fiber; (I) whole views and (II) cross-section.

Figure 3.9: SEM images (backscattered electrons (BSE) mode) of (a-I) whole view, (a-II) cross-section and (a-III) a higher magnification of cross-section of the sintered triple-layer hollow fibers, using the AFL extrusion rate at 3 ml min⁻¹.

Figure 3.10: Effect of AFL extrusion rate on the thicknesses of anode, electrolyte and AFL.

Figure 3.11: Average porosity as a function of different AFL thicknesses.

Figure 3.12: Bending strength and fracture force as a function of different AFL thicknesses.

Figure 3.13: Gas-tightness property as a function of different AFL thicknesses.

Figure 3.14: Electrical conductivity of reduced anode/AFL dual layer hollow fibers as a function of thickness ratio of AFL / (AFL+Anode).

Figure 4.1: Photographic pictures of (a) quadruple-orifice spinneret; (b) example of triple-layer precursors.
Figure 4.2: Schematic diagram of the performance test set-up

Figure 4.3: SEM images of the fiber with the AFL extrusion rate of 2 ml min⁻¹: (a) overall view, (b) cross-section, (c) electrolyte/electrode interface, (d) electrolyte outer surface.

Figure 4.4: Gas-tightness property as a function of thicknesses.

Figure 4.5: Bending strength and fracture force of reduced samples as a function of different AFL thicknesses (Number of samples=4).

Figure 4.6: Open-circuit voltage (OCV) and power density as a function of current density of samples with different AFL thickness (ER denotes the extrusion rates of AFL during co-extrusion).

Figure 4.7: Fuel utilization rates of samples with different AFL thicknesses. The values were calculated via Eq. 3.3 using the current value at the maximum power density of each cell.

Figure 4.8: Effects of AFL thickness on SEI analysis of samples under open-circuit condition.

Figure 5.1: Schematic diagram of the dip-coating setup.

Figure 5.2: Schematic diagram of the set-up for gas-permeation test.

Figure 5.3: SEM images (secondary electron imaging (SEI) mode) of the dual-layer precursor fiber with the current collector extrusion rate of 2 ml min⁻¹: (a) and (c) cross section in radial direction, (b) cross section in axial direction, (d) inner surface.

Figure 5.4: SEM images of sintered dual-layer fiber with the current collector extrusion rate of 2 ml min⁻¹: (a, b) cross-section (c, e) inner surface; (d) inner surface of reduced fiber.
Figure 5.5: EDS results of interface between the inner current collector (right side) and outer anode layer (left side).

Figure 5.6: The N₂ permeation results of anode/anodic current collector dual-structured hollow fiber.

Figure 5.7: Illustration of the H₂ diffusion pathway in the anode/anodic current collector dual-layer hollow fiber. (a) Hollow fiber with long micro-channels from outer surface in this study; (b) Hollow fiber with short micro-channels in Ref.[15].

Figure 5.8: Bending strength and fracture force as a function of different current collector thicknesses.

Figure 5.9: (a) Sintering curves of NiO and the materials of anode (Heating rate: 5 °C min⁻¹); (b) Sintering rate curves of NiO and the materials of anode.

Figure 5.10: Electrical conductivity of reduced anode/anodic current collector dual layer hollow fibers as a function of current collector thickness.

Figure 5.11: Schematic diagram of a half cell with an interior Ni-mesh.

Figure 6.1: Schematic diagram of the performance test set-up.

Figure 6.2: Schematic diagram of various radiiuses for ohmic contributor calculation.

Figure 6.3: Sintering curves of pure CGO and NiO; mixtures of anode and current collector.

Figure 6.4: SEM images of the samples with different current collector extrusion rates: (a-d) overall view, cross-section, close-up images of electrolyte and current collector of sample ER1; (e) cross-section of sample ER3; (f) cross-section of sample ER5.
Figure 6.5: Open-circuit voltage (OCV) and power density as a function of current density of samples with different current collector thicknesses. .......................... 204

Figure 6.6: Effects of current collector thickness on SEI analysis of samples under open-circuit condition. ............................................................. 206

Figure 7.1: SEM images of cross-section and sponge-like region of multi-channel hollow fibers. ................................................................. 223

Figure 7.2: Schematic diagram of MT-SOFC stack design. ......................... 224
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>area of hollow fiber</td>
<td>cm$^2$/m$^2$</td>
</tr>
<tr>
<td>$ASR$</td>
<td>area specific resistance</td>
<td>Ω cm$^2$</td>
</tr>
<tr>
<td>$B_F$</td>
<td>bending strength</td>
<td>Pa</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>charge transfer coefficient</td>
<td>/</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>electrical conductivity</td>
<td>S cm$^{-1}$</td>
</tr>
<tr>
<td>$D_i$</td>
<td>inner diameter of hollow fiber/MT-SOFC</td>
<td>cm/m</td>
</tr>
<tr>
<td>$D_o$</td>
<td>outer diameter of hollow fiber/MT-SOFC</td>
<td>cm/m</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>efficiency</td>
<td>/</td>
</tr>
<tr>
<td>$F$</td>
<td>Faraday constant</td>
<td>C mol$^{-1}$</td>
</tr>
<tr>
<td>$I$</td>
<td>current</td>
<td>A</td>
</tr>
<tr>
<td>$j$</td>
<td>current density</td>
<td>A cm$^{-2}$</td>
</tr>
<tr>
<td>$j_o$</td>
<td>exchange current density</td>
<td>A cm$^{-2}$</td>
</tr>
<tr>
<td>$j_L$</td>
<td>limiting current density</td>
<td>A cm$^{-2}$</td>
</tr>
<tr>
<td>$L$</td>
<td>length of hollow fiber sample</td>
<td>cm/m</td>
</tr>
<tr>
<td>$l_e$</td>
<td>electrolyte thickness</td>
<td>cm</td>
</tr>
<tr>
<td>$N$</td>
<td>fracture force</td>
<td>N</td>
</tr>
<tr>
<td>$n_{H_2,inlet}$</td>
<td>molar flow rate of supplied hydrogen</td>
<td>mol s$^{-1}$</td>
</tr>
<tr>
<td>$\eta_a$</td>
<td>activation polarization</td>
<td>V</td>
</tr>
<tr>
<td>$\eta_c$</td>
<td>concentration polarization</td>
<td>V</td>
</tr>
<tr>
<td>$\eta_{\Omega}/\Delta\Phi$</td>
<td>ohmic polarization/loss</td>
<td>V</td>
</tr>
<tr>
<td>$OCV$</td>
<td>open-circuit 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>$P$</td>
<td>gas permeance</td>
<td>mol m$^2$ Pa$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td>$P_{\text{elec}}$</td>
<td>electric power</td>
<td>W</td>
</tr>
<tr>
<td>$P_{d,\text{elec}}$</td>
<td>power density</td>
<td>W cm$^{-1}$</td>
</tr>
<tr>
<td>$P_{H_2}$</td>
<td>partial pressure of hydrogen</td>
<td>Pa/atm</td>
</tr>
<tr>
<td>$P_{H_2O}$</td>
<td>partial pressure of water vapour</td>
<td>Pa/atm</td>
</tr>
<tr>
<td>$P_{O_2}$</td>
<td>partial pressure of oxygen</td>
<td>Pa/atm</td>
</tr>
<tr>
<td>$p_a$</td>
<td>atmospheric pressure</td>
<td>Pa</td>
</tr>
<tr>
<td>$p_i$</td>
<td>initial pressure in test cylinder</td>
<td>Pa</td>
</tr>
<tr>
<td>$p_f$</td>
<td>final pressure in 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 resistivity</td>
<td>Ω cm</td>
</tr>
<tr>
<td>$\rho_e$</td>
<td>electrolyte resistivity</td>
<td>Ω cm</td>
</tr>
<tr>
<td>$V$</td>
<td>operating voltage</td>
<td>V</td>
</tr>
<tr>
<td>$V_C$</td>
<td>volume of test cylinder</td>
<td>m$^3$</td>
</tr>
<tr>
<td>$V_N$</td>
<td>Nernst voltage</td>
<td>V</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>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>
<tr>
<td>$E_{\text{electrolyte}}$</td>
<td></td>
<td>eV</td>
</tr>
</tbody>
</table>
Chapter 1. Introduction

1.1 Background

One of the most urgent problems facing the world today is the increasing demand for energy supply because of the fast-growing world population. To satisfy the considerable requirements for energy, numerous numbers of power plants with giga-watt of output have been constructed, even though they are criticised for their low efficiencies and severe threatening to the environment, such as global warming, air pollution and ozone depletion.

In the past fifty years, great efforts have been undertaken into two major approaches to relieve the dependence on fossil fuels or the effects of using fossil fuels on the environment. One method is to explore energy sources which are more environmentally friendly, for example geothermal energy, tidal energy and solar energy. However, this can only provide a small portion of global supply of energy. The other approach focuses on the utilization of existing fossil fuels in a more sustainable and efficient way with less and controllable impacts on the environment. To achieve this, new techniques have been developed, such as combined heat and power system (CHP), closed-cycle gas turbine (CCGT), synthesis gas process. These techniques usually include a secondary turbine to utilize the heat generated from the combustion process of the primary turbine. In principle, chemical energy of the reactants is first converted into thermal energy and mechanical energy before being converted into electrical energy. Hence, the overall efficiency is still limited by Carnot Cycle. According to theoretical calculations, the maximum efficiency depends
on temperatures of both the cold source ($T_2$) and the thermal source ($T_1$), as shown in Equation 1.1.

$$\eta_{HE} = \frac{T_1 - T_2}{T_1}$$

(1.1)

This derivation shows that a heat engine cannot achieve 100% conversion from chemical energy to mechanical energy even under ideal conditions.

A fuel cell, whose scheme is shown in Figure 1.1, is an energy generating device that electrochemically converts chemical energy into electric energy and heat directly.

![Figure 1.1: Schematic diagram of an individual cell.](image)

The efficiency of an electrochemical energy generator is defined as the ratio between the amount of relieved electrical energy and the change in stored chemical energy. Due to the removal of combustion as an intermediate step, the efficiency of a fuel cell does not need to be subject to the Carnot limitation. Hence, a fuel cell displays much
higher conversion efficiency compared with traditional heat engines. Figure 1.2 compares the efficiencies between a heat engine (cold source of 298 K) and a fuel cell (H₂/O₂). It can be concluded that the fuel cell displays higher efficiency, especially at a lower working temperature. In addition, lower operating temperatures contribute to less investment, lower operation costs, and fewer requirements for the equipment. Due to the advantages mentioned above, fuel cell has received increasing interest and has been considered a promising energy generator of the future.

Figure 1.2: Comparisons between the efficiencies for fuel cells (red curve) and heat engines (black curve) as a function of temperature. [1]

1.2 History

The initiation of fuel cell technology could date back to 1839, when Grove first proposed the principles of a fuel cell and invented a ‘gas voltaic battery’, also known as ‘Grove cell’ [2]. His fuel cell included dilute sulphuric acid as the electrolyte and
two platinum strips as the electrodes, which were positioned separately in hydrogen and oxygen. The current was collected through the external circuit and the upper solution was adopted as a voltmeter. At the end of the 19th century, Nernst reported the application of ceramics, such as yttria-doped zirconia (called the Nernst mass), as an oxygen-ion conductor [3]. But it was not until 1935 when Schottky suggested using the Nernst mass as the electrolyte material for a fuel cell [4]. Baur, a Swiss inventor, undertook a considerable amount of study to investigate different materials, such as molten silver and clay-doped metal oxides, for the electrolyte and reported the first operational ceramic fuel cell in 1937 [5]. Bacon, a British chemist, made a significant contribution to the progress in alkali electrolyte fuel cells in 1950s. Alkaline solution was tested instead of sulphuric acid and NiO powder was adopted to fabricate the electrodes. These alterations markedly enhanced the diffusion of fuel gases, enabling better access of fuel gases to the alkaline electrolyte, subsequently improving performances. Moreover, the use of nickel lowers the cost as it is much cheaper than platinum. In 1960, as part of the Apollo space program, National Aeronautics and Space Administration (NASA) invested millions of dollars in hydrogen-based fuel cell technology to supply electricity and water on the Apollo spacecraft. Since the mid-1980s, an increasing number of government agencies have started to invest in fuel cell research and development for potential applications in transportation, portable electronic devices and power plants.
1.3 Different Types of Fuel Cells

There are various approaches of classifications based on operating temperatures, the types of fuel, and design features. The most commonly used approach is according to electrolytes materials, as listed in Table 1.1 [6-8].

The figure summarises the major fuel cell categories. The electrolyte material determines not only the name of the fuel cells, but also the range of operating temperatures. Polymer membrane fuel cells (PMFC), alkaline fuel cells (AFC) and phosphoric acid fuel cells (PAFC) are regarded as ‘low’-temperature type and necessitate the usage of high-purity hydrogen for satisfactory performance. This is because the noble metal electrode (i.e. platinum) might well get poisoned by carbon monoxide at relatively low operating temperatures. Were hydrocarbons to be applied as the fuels for low temperature fuel cells, an external processor containing a reforming reactor and a gas-cleaning system must be used to convert hydrocarbons into high-purity hydrogen, which leads to enhanced complexity and higher cost [8].

Solid oxide fuel cells (SOFC) employ a solid electrolyte that protects the fuel cell from problems such as corrosion and electrode wetting. The most attractive advantage in comparison with other types of fuel cells is the ability to utilize hydrocarbons directly without the necessity for an additional processor [9]. The superior flexibility in the selection of fuels is mainly due to the higher operating temperature which not only ensures rapid reaction rate in the absence of catalysts, but also facilitates internal reforming during which hydrocarbons are transformed into hydrogen and carbon monoxide. In addition, the high-temperature exhaust may well be used in an integrated gas turbine to enable even higher system efficiencies.
Table 1.1: Features of various types of fuel cells

<table>
<thead>
<tr>
<th></th>
<th>PEFC</th>
<th>AFC</th>
<th>PAFC</th>
<th>MCFC</th>
<th>SOFC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrode/Catalyst</td>
<td>Carbon supported noble metals</td>
<td>Carbon supported catalysts</td>
<td>Carbon supported noble metals</td>
<td>Stainless steel-supported alloy</td>
<td>Oxide perovskites or cermet</td>
</tr>
<tr>
<td>Electrolyte</td>
<td>Solid polymer 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>Charge carrier</td>
<td>H⁺</td>
<td>OH⁻</td>
<td>H⁺</td>
<td>CO₃²⁻</td>
<td>O²⁻</td>
</tr>
<tr>
<td>Electrolyte support</td>
<td>/</td>
<td>Asbestos</td>
<td>SiC</td>
<td>LiAlO₂</td>
<td>/</td>
</tr>
<tr>
<td>Operating temperature(°C)</td>
<td>80</td>
<td>~70</td>
<td>~200</td>
<td>650</td>
<td>500-1000</td>
</tr>
<tr>
<td>Operating pressure</td>
<td>1-5 atm*</td>
<td>1-10 atm</td>
<td>1-8 atm</td>
<td>1-3 atm</td>
<td>1 atm</td>
</tr>
<tr>
<td>Fuel</td>
<td>H₂, CH₃OH</td>
<td>H₂ only</td>
<td>H₂, External reformate</td>
<td>H₂, CO, CH₄</td>
<td>H₂, CO, CH₄</td>
</tr>
</tbody>
</table>

*atm=1.01×10⁵ Pa
1.4 PhD Objectives

The major objective of this work is to develop micro-structured ceramic hollow fibers for micro-tubular solid oxide fuel cells (SOFCs) operated at intermediate temperatures. The ceramic hollow fibers are fabricated through a phase inversion-based, single-step co-extrusion/co-sintering process. These multi-layer hollow fibers could have various components depending on different membrane morphology. To achieve the broad aim, the following specific objectives will be conducted.

i) To fabricate triple-layer ceramic hollow fibers with an anode functional layer (AFL) via a single step co-extrusion process

The triple-layer co-extrusion method will be established via fabricating anode/AFL/electrolyte hollow fibers. The phase inversion process could introduce long micro-channels in the anode, which can markedly reduce the diffusion resistance of the fuel gases. However, these voids also indicate reduced reactive sites. This idea of inserting a functional layer is widely accepted to help in enlarging the triple-phase boundary (TPB) and matching the thermal expansion coefficients (TEC) between different components and improving the long-term stability of SOFCs [10].

ii) To fabricate a complete single cell with an anode functional layer (AFL) and conduct characterizations on physical and electrochemical properties.

A full single cell will be fabricated by depositing a multi-layer cathode on the hollow fiber. After connecting current collectors to both electrodes, the electrochemical performance will be measured by a potentiostat/galvanostat at intermediate temperatures (500-600 °C). Characterizations of physical properties, such as
mechanical strength, gas-permeability, will also be undertaken. The effects of the thickness of the AFL will be studied. A thicker functional layer can improve the mechanical strength and provide more reactive sites, but the diffusion resistance of the fuel gases is also increased. The thickness of the AFL can be adjusted by changing the parameters during the spinning. By comparing the electrochemical performances and physical properties, a preferable thickness of the AFL will be obtained.

**iii) To fabricate hollow fibers with micro-structured nickel-mesh as current collector.**

The efficiency of current collection is one of the factors that markedly influence the cell performance. It is reported that the Ni/CGO anode fibers with an inserted meshed porous inner current collector displays significantly higher electrical conductivity compared with a single Ni/CGO anode [11]. Therefore, the idea of developing a mesh-structured nickel layer as current collector could further optimize the micro-structure which leads to improved gas permeation property.

**iv) To fabricate triple-layer ceramic hollow fibers with an inner current collector via a single step co-extrusion process**

Based on the study in previous task, a complete single-cell will be fabricated with an integrated inner current collector. Various physical and electrochemical tests will be undertaken to study the effects of new current collector design on cell performances.

**1.5 Thesis structure**

This thesis consists of 7 chapters addressing different aspects of the fabrication of the triple-layer hollow fibers, the application of these fibers as micro-tubular SOFC
and how to improve the cell performances with a new current collection design. Figure 1.3 below illustrates the overall structure of the thesis.

Chapter 1 briefly introduces the history, concept and working principle of fuel cells, the objective of the research and the overview of the thesis. Chapter 2 presents the details of literature review, including operation, thermodynamic and materials selection of solid oxide fuel cells, and background and up-to-date development of micro-tubular SOFCs. The concepts of phase inversion-assisted co-extrusion/co-sintering technique are also explained in this chapter. Chapter 3 reports the establishment of co-extrusion/co-sintering technique by successfully delivering of electrolyte/anode functional layer/anode triple-layer hollow fiber. This chapter also reports the effect of functional layer on various physical properties, such as shrinkage behaviour, gas-tightness and mechanical strength. Based on the study in Chapter 3, Chapter 4 subsequently reports the construction of a complete micro-tubular SOFC and a systematic study of the effects of AFL thicknesses on electrochemical performances. Meanwhile, Chapter 5 explains the fabrication of dual-structured anode/current collector layer hollow fibres, in which micro-channels have been dedicatedly designed to penetrate through the whole cross-section to minimize the gas-diffusion properties. A novel nickel-mesh structured current collector is also reported to have adequate electrical conductivity. Chapter 6 reports the development of triple-layer hollow fibers integrated with the novel nickel-mesh current collector which addresses both process economy and more uniform current collection to improve the cell performances. Finally, Chapter 7 concludes the progress achieved in micro-tubular SOFCs and some suggestions for future study are given.
Figure 1.3: Overall structure of the thesis.
Chapter 2. Literature Review

2.1 SOFC Principles and Thermodynamics

A solid oxide fuel cell (SOFC) is a ceramic, battery-like device which converts chemical energy of the gaseous fuels (e.g. hydrogen, oxygen and hydrocarbons) into electricity directly. However, unlike a battery, a SOFC is continuously-fuelled, so it operates as long as gaseous reactants (fuel and oxidant) are provided to the electrodes, without running down or recharging.

Figure 2.1: Working principles of a solid oxide fuel cell.

A schematic diagram of a SOFC is provided in Figure 2.1. The mechanism of generating electrical energy depends on the electrochemical combustion of the fuel. The overall reaction, which is identical to that of the combustion, is composed of two
separate electrode reactions. During operation process, gaseous fuels (e.g. hydrogen) are supplied to the anode where oxidation occurs and electrons are released. Oxidants (e.g. oxygen/air) are fed to the cathode, where the reactants ‘capture’ the electrons and get reduced to form oxygen ions. The electrons migrate from the anode to the cathode through the external circuit, during which direct current is produced. Meanwhile, the oxygen ions diffuse through the electrolyte, which contains oxygen vacancies in the crystal framework, to react with fuel molecules at the anode.

The operating principles of the SOFC have been well understood. The thermodynamic efficiency ($\epsilon$) of a SOFC is defined as the ratio of the energy output to the reaction’s chemical energy at the thermodynamic state ($T$) [12]. The energy output and chemical energy of the reaction can be expressed using Gibbs enthalpy ($\Delta G_T$) and combustion enthalpy ($\Delta H_T$) respectively.

The Gibbs enthalpy is defined as:

$$\Delta G_T = \Delta H_T - T \cdot \Delta S_T$$  \hspace{1cm} (2.1)

So thermodynamically, the efficiency is expressed as:

$$\epsilon = \frac{\Delta G_T}{\Delta H_T} = \frac{\Delta H_T - T \cdot \Delta S_T}{\Delta H_T} = 1 - \frac{T \cdot \Delta S_T}{\Delta H_T}$$  \hspace{1cm} (2.2)

Where $\Delta S_T$ is the reaction’s entropy at the temperature of $T$.

The Nernst voltage ($V_N$) is defined as the maximum voltage a SOFC could well achieve under specific conditions (temperature, partial pressures of reactant gases). Take a hydrogen-fuelled SOFC as an example, with the assumption of an ideal gas, the Nernst voltage ($V_N$) can be calculated by using equation:
\[ V_N = \frac{-\Delta G_F}{2F} + RT \ln \left( \frac{P_{H_2} \sqrt{P_{O_2}}}{P_{H_2O}} \right) \]  

(2.3)

Where \( F \) stands for Faraday constant, \( R \) is the gas constant and \( p_{H_2}, p_{O_2} \) and \( p_{H_2O} \) denote the partial pressures of \( H_2, O_2 \) and \( H_2O \), respectively.

However, the actually voltage of an operating SOFC (\( V \)) is lower than Nernst voltage, the voltage loss or overpotential is known as polarization (\( \eta \)), which is a function of current density. The overall polarization of a SOFC is composed of four different polarization types: activation polarization (\( \eta_a \)), diffusion or concentration polarization (\( \eta_d \)), reaction polarization (\( \eta_r \)) and ohmic or resistance polarization (\( \eta_\Omega \))[13].

\[ \eta = \eta_a + \eta_r + \eta_d + \eta_\Omega \]  

(2.4)

The reaction polarization (\( \eta_r \)) needs to be considered when the reaction rate is slow. Due to the high operation temperatures (500-1000°C), the reaction polarization of SOFCs is usually negligible and the three dominant polarizations are described below:

(a) Activation polarization (\( \eta_a \)) is generally caused by electrode reactions when they are the rate-determining steps. The energy barrier involved in the electrochemical reactions has to be overcome by reactants. This energy barrier, termed as the activation energy, leads to activation polarization, which can be calculated from current density (\( j \)) by the following equation:

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

(2.5)

where \( \alpha \) is the transfer coefficient and \( j_o \) denotes the exchange current density. The transfer coefficient (\( \alpha \)) is regarded as the fraction of the polarization change that results in a variation of the reaction rate constant. The exchange current density is
the rate of both forward and reverse electrochemical reactions occurring at the electrode. As has been mentioned previously, activation polarization is related with one or more rate-determining reactions, which could be adsorption/desorption of reactant/product on the electrode surface, electron conversion, or any other steps in the process. The reaction rate depends on a number of factors such as temperature, pressure and materials. As SOFCs are operated at high temperatures when the reaction rate is usually very fast, the activation polarization could well be minimized

(b) Diffusion polarization ($\eta_d$), which is also named as concentration polarization, appears when the electrochemical reactions at the electrode is inhibited by mass transportation, for instance, the feeding rate of the gaseous fuels or the removing rate of the product is slower than the value determined by the discharge current, $j$. The limiting current, $j_L$, is reached (illustrated by a rapid decline in cell voltage) when diffusion governs the electrode reaction process (due to the low reactant concentration in the feed stream). For an electrode reaction where activation polarization is negligible, the diffusion polarization can be expressed as:

$$\eta_d = \frac{RT}{nF} \ln \left( 1 - \frac{j}{j_L} \right)$$

(2.6)

The diffusion polarization depends on a number of parameters, such as the binary H$_2$-H$_2$O diffusivity ($D_{H_2-H_2O}$), microstructure (porosity, pore size distribution, tortuosity etc.), partial pressure and current density. In SOFCs, the gaseous reactants have to diffuse through the porous electrode so the structure optimization may well help to reduce this polarization. In addition, the diffusion polarization becomes more significant when conversion approaches 100% since the reaction rate is a function of reactants’ concentrations.
(c) Ohmic Polarization \( (\eta_\Omega) \) is the sum of ionic resistance (at the electrolyte), electrical resistance (at the electrodes and current collectors) and contact resistance (at the interfaces between cell components). With regards to a SOFC system, the hindrance of electrodes could be neglected when compared with that of the solid oxide electrolyte, \( \rho_e \). Based on the assumption that the contact resistance is approaching zero, which could be realized by optimizing in fabrication techniques, the ohmic polarization could be expressed as a function of electrolyte thickness \( (l_e) \) only:

\[
\eta_\Omega = j \cdot \rho_e \cdot l_e
\]  \hspace{1cm} (2.7)

The SOFC components’ resistance is usually defined as the area specific resistance (ASR). The ohmic polarization could then be written as:

\[
\eta_\Omega = j \cdot \text{ASR}_e
\]  \hspace{1cm} (2.8)

\( \text{ASR}_e \) is the electrolyte resistance per unit area:

\[
\text{ASR}_e = \rho_e \cdot l_e
\]  \hspace{1cm} (2.9)

The actual operating voltage \( (V) \) of the SOFC at a certain current density can be calculated by subtracting all the voltage losses, which are attributed to the polarizations discussed above, from the Nernst voltage \( (V_N) \) or the so-called open-circuit voltage (OCV) \[13\]. Hence, the operating voltage is expressed as:

\[
V = V_N - \eta_a - \eta_d - \eta_\Omega
\]  \hspace{1cm} (2.10)

It is worth noticing that the ohmic concentration can be simulated using an equivalent parallel circuit composed of a resistor and a zero capacitance. Therefore, the theoretical response time is essentially zero. Such fast response enables its characterization using current interruption, which is one of the basic techniques in electrochemical impedance spectroscopy (EIS).
Figure 2.2 displays a typical voltage/current plot of an operating cell. It also demonstrates the region where different types of polarizations predominate. The maximum voltage one would expect ($V_N$ or OCV) is indicated by a dotted line parallel to the current axis. As can be seen from the pattern, the major voltage loss at low current densities is from the activation polarization, as illustrated by a rapid decline in cell voltage. With the increasing of current density, ohmic resistance dominates, as demonstrated by a slight decrease. In high-current-density region, mass transportation resistivity controls the overall resistance, leading to a significant drop in cell voltage.

![Figure 2.2: Typical voltage/current plot of an operating cell.][13]

The power output ($P_{elec}$) of a SOFC can be obtained from the operating voltage ($V$) and corresponding current ($I$) produced by the cell:
\[ P_{\text{elec}} = V \times I \]  

The power density \( P_{d,\text{elec}} \), an important parameter used to evaluate the performance, is the normalization of power output by effective area. In the case of a tubular SOFC where the anode is the inner layer (or working electrode), the effective area \( A \) is calculated by:

\[ A = \pi \cdot D_i \cdot L \]  

where \( D_i \) and \( L \) denote the inner diameter (cm) and active length (cm), respectively, of the tubular SOFC. The current density \( j \) (A cm\(^{-2}\)) and power density \( P_{d,\text{elec}} \) (W cm\(^{-2}\)) are then determined by the equations:

\[ j = \frac{I}{A} \]  

\[ P_{d,\text{elec}} = \frac{P_{\text{elec}}}{A} = V \cdot j \]

### 2.2 SOFC components

Generally, a SOFC single cell is composed of a dense electrolyte positioned between a cathode layer and an anode layer. As the output voltage of a single cell under typical operating conditions is less than 1V, the actual SOFC units normally consist of a series of single cells in the form of a stack. An additional component, termed as an interconnect or a bipolar separator, is indispensable to connect the anode of one cell with the cathode of another cell. Figure 2.3 illustrates the schematic diagram of a single cell unit.
Various components are of different functions in the SOFCs and specific requirements have to be met. In addition to appropriate chemical and morphological stability in the operating environment (reducing/oxidizing), the component materials should be of compatibility and with similar thermal expansion coefficients (TEC) to prevent cracking or delamination during operation. The electrodes (anode/cathode) must be porous to facilitate the diffusion of gaseous reactants, while the electrolyte and the interconnect have to be fully dense to avoid gas mixing. Furthermore, the price of the component materials and their commercial availability are important factors that should be taken into consideration. The key requirements for different cell components are summarized in Table 2.1 [13] and each component will be briefly discussed below.
Table 2.1: Key requirements for different cell components of SOFCs.

<table>
<thead>
<tr>
<th>Component</th>
<th>Conductivity</th>
<th>Stability</th>
<th>Compatibility</th>
<th>Morphology</th>
<th>Thermal Expansion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrolyte</td>
<td>High ionic conductivity; negligible electrical conductivity</td>
<td>Chemical, phase, morphological and dimensional stability in reducing/oxidizing atmosphere</td>
<td>No damaging chemical interactions or interdiffusion with adjoining cell components</td>
<td>Fully dense</td>
<td>Thermal expansion coefficient match with adjoining components</td>
</tr>
<tr>
<td>Anode</td>
<td>High electrical conductivity</td>
<td>Chemical, phase, morphological and dimensional stability in reducing atmosphere</td>
<td>No damaging chemical interactions or interdiffusion with adjoining cell components</td>
<td>Porous</td>
<td>Thermal expansion coefficient match with adjoining components</td>
</tr>
<tr>
<td>Cathode</td>
<td>High electrical conductivity</td>
<td>Chemical, phase, morphological and dimensional stability in oxidizing atmosphere</td>
<td>No damaging chemical interactions or interdiffusion with adjoining cell components</td>
<td>Porous</td>
<td>Thermal expansion coefficient match with adjoining components</td>
</tr>
<tr>
<td>Interconnect</td>
<td>High electrical conductivity; negligible ionic conductivity</td>
<td>Chemical, phase, morphological and dimensional stability in reducing/oxidizing atmosphere</td>
<td>No damaging chemical interactions or interdiffusion with adjoining cell components</td>
<td>Fully dense</td>
<td>Thermal expansion coefficient match with adjoining components</td>
</tr>
</tbody>
</table>
2.2.1 Anode

The anode mainly serves to provide reaction sites for the electrochemical oxidation of gaseous fuels. To achieve this, the anode should be porous and gas-permeable[14]. Other important properties include chemical and morphological stability in not only the inlet reducing environment, but also the outlet oxidizing environment; sufficient electrical conductivity for minimizing the ohmic losses; good catalytic activity for electrochemical oxidation of fuels, thus lowering the reaction polarization. Furthermore, there are other requirements such as good thermal and chemical compatibility, high mechanical strength and proper manufacturability [13].

Currently, nickel is nearly exclusively applied as the anode material for SOFCs due to its low cost, high catalytic activity for fuel oxidation and proper electrical conductivity. As a standard approach, Ni is often mixed with the corresponding electrolyte materials (e.g. YSZ: yttria stabilized zirconia) to adjust thermal expansion coefficient (TEC) matching with that of the electrolyte (TEC of YSZ and Ni are \(~11 \times 10^{-6}\) [13]and \(~17 \times 10^{-6}\) [15], respectively), as shown in Figure 2.4.

![Figure 2.4: Schematic diagram of a Ni/YSZ anode structure.](image)

Figure 2.4: Schematic diagram of a Ni/YSZ anode structure.
YSZ also functions to provide mechanical strength to the anode, suppress coarsening of the metallic particles during long-term operation and enhance the triple-phase boundary (TPB) area. TPB is the region in either anode or cathode where gas phase for fuel access, ceramic phase for oxygen ion entry and metal phase for electron output contact and get involved in the electrochemical reaction, as illustrated in Figure 2.4.

Porous Ni-YSZ cermet has been widely employed as the anode material for the past decade and a numerous number of techniques are available for fabricating this cermet. In most cases, the precursor is first fabricated with nickel oxide (NiO) and YSZ, and the final anode is obtained by an in-situ reduction when the precursor is exposed to the fuel (e.g. H₂). During this reduction, the initial volume of NiO was reduced by over 25% which consequently leads to increased porosity as preferable for the anode [16]. To optimize the cell performance, tailoring and controlling the anode morphology is one of the key factors during the preparation. The morphology is influenced by a number of variables: particle size, Ni content, contiguity of the constituent components, etc. Figure 2.5 illustrates the electrical conductivity of Ni-YSZ cermet as a function of Ni content. The S-shaped curve reveals a clear threshold for the conductivity. The electrical conductivity of cermet containing 40 vol% nickel is almost three-orders of magnitude higher than cermet with 20 vol% nickel. However, in order to maintain the appropriate mechanical strength, the nickel content is normally between 40-60 vol% [17].
Some studies have reported that considerable polarization or interfacial resistance to be observed during the oxidation of dry hydrogen, whereas this polarization decreased dramatically if a mixture of hydrogen/water had been employed [18-20]. A few volume percentage of water vapour could greatly minimize the interfacial polarization [18]. However, as the H₂O/H₂ ratio continues to increase, the interfacial resistance will rise again [19]. There is yet no clear explanation on the role of water in the H₂ oxidation, and a suggestion for the possible reason is that H₂O molecules adsorbed on the YSZ surface might well enlarge the reactive sites near the TPB.

At reduced working temperatures, the thermal activation for the oxidation reactions is considerably hindered, which leads to increased polarization. Therefore, graded anode structures are often advisable, with a high-porosity large-grain substrate bearing a finer-structured active functional layer to contact with the electrolyte [16].

**Figure 2.5**: Electrical conductivity of Ni-YSZ cermet (sintered at different temperatures) as a function of nickel content [17]. Copyright © 2003 Elsevier.
In 2000, the concept of AFL was first proposed by Virkar [21] during his attempt to decrease the activation/concentration polarizations by employing a dual-layer anode structure. The substrate and functional layers, which have various compositions of NiO and YSZ, are fabricated by spray coating and tape casting, respectively. The substrate layer is made coarser in terms of bigger pore size, higher porosity and wider pore distribution by controlling the properties of the slurry. Virkar (2000) has reported that the larger pore size and porosity in the substrate layer can facilitate the transport of gaseous fuels and removal of exhaust gases, which help to minimize the concentration polarization. Furthermore, the fine structure in the functional layer contributes to more TPB reactive sites so that the activation polarization may well be inhibited.

Other studies were undertaken by Muller [10] to test new techniques for the fabrication of continuously graded, multi-layer anode, during which anode layers with different compositions were pasted onto an electrolyte substrate by screen printing, as shown in Figure 2.6. In addition to maximizing the TPB length and matching TEC between anode and electrolyte, such graded multi-layer structure helps improve the long-term stability of SOFCs.

Figure 2.6: Illustration of a multi-layer Ni-YSZ anode structure and the variations in physical properties [10]. Copyright © 2002 Elsevier.
The differences in the particle size and nickel content result in a gradient in porosity, TEC and electrical conductivity across the multi-layer anode. AFL has received increased attention, especially on NiO/YSZ cermet, in the past five years [10, 22-28]. Some other fabrication techniques have been tested for such multi-layer structure, such as ink-jet printing [29], electrophoretic co-deposition [25] and die pressing [26]. All these attempts show that AFL results in dramatic improvement in cell performance. The most recent research was conducted by Suzuki’s group [28] in which a functional layer of NiO/scandia stabilized zirconia (ScSZ) was introduced between the NiO/YSZ anode and the ScSZ electrolyte by dip-coating. He reports an enhancement by 67% in power density at 650 °C using diluted hydrogen as a fuel.

2.2.2 Electrolyte

The electrolyte of SOFCs mainly functions to conduct ions between the two electrodes at elevated temperatures and prohibit direct contact between gaseous fuels and oxidants. Hence, the electrolyte should be of good thermal and chemical stability in both the reducing and oxidizing atmosphere at high temperatures, impermeable to gases, own appropriate ionic conductivity to reduce cell impedance, and negligible electrical conductivity which helps to minimize ohmic losses. Moreover, the shrinking behaviour of electrolyte has to be compatible with other components to avoid cracking or layer separation during sintering processes [13]. Stabilized ZrO₂ with fluorite structure has been most widely investigated as the electrolyte material due to its desirable ionic conductivity and stability. Pure zirconia exhibits a monoclinic structure at room temperature, converting into tetragonal crystal
structure at 1170 °C and to a cubic fluorite phase above 2370 °C. This cubic fluorite phase is preserved until the melting point of 2680 °C [16]. However, the use of certain stabilizing dopants, such as magnesia (MgO), yttria (Y₂O₃), scandia (Sc₂O₃), calcium oxide (CaO) and a number of rare-earth oxides, could stabilize the fluorite phases throughout the temperature ranging from room temperature to its melting point. Furthermore, the introduced cations (e.g. Ca²⁺, Y³⁺, Mg²⁺, Sc³⁺), whose valence is lower than zirconium ion (Zr⁴⁺), help to increase the oxygen vacancy concentration for charge compensation. For example, the substitution of zirconium ion with Sc³⁺ introduces negative net charge in the lattice and balancing this charge requires the formation of oxygen vacancies. Furthermore, the addition of dopants is beneficial for an enhancement in mechanical and thermal properties.

![Graph](image)

**Figure 2.7:** Conductivity of YSZ in air at 1000 °C (reproduced from [9]. Copyright © 2006 Elsevier.)

Yttria-stabilized zirconia (YSZ) is extensively employed as the electrolyte material for SOFCs because of the high availability and low cost. Gibson (1998) has reported that the maximum conductivity of YSZ is obtained at the yttria content of 8 mole%
and then declines at higher concentrations, as shown in Figure 2.7 [30]. This declination is believed to be caused by the decrease in defect mobility, vacancy clustering and hence a reduction in conductivity. Scandia is another promising electrolyte material, especially for intermediate temperature (600-800 °C) SOFCs. ScSZ displays better conductivity compared with YSZ as illustrated in Table 2.2.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Conductivity at 1000°C (S cm⁻¹)</th>
<th>Bending strength (MPa)</th>
<th>TEC (1/K×10⁶)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>As sintered</td>
<td>After annealing</td>
<td></td>
</tr>
<tr>
<td>3 mole% YSZ</td>
<td>0.059</td>
<td>0.05</td>
<td>1200</td>
</tr>
<tr>
<td>3 mole% ScSZ</td>
<td>0.09</td>
<td>0.063</td>
<td>/</td>
</tr>
<tr>
<td>8 mole% YSZ</td>
<td>0.13</td>
<td>0.09</td>
<td>230</td>
</tr>
<tr>
<td>8 mole% ScSZ</td>
<td>0.30</td>
<td>0.12</td>
<td>270</td>
</tr>
<tr>
<td>11 mole% ScSZ</td>
<td>0.30</td>
<td>0.30</td>
<td>255</td>
</tr>
</tbody>
</table>

Kharton (2004) has reported that the smaller diameter difference between Zr⁴⁺ and Sc³⁺, when compared with the difference between Zr⁴⁺ and Y³⁺, contributes to a decrease in the energy required for defect association, thus improves the mobility and ionic conductivity [31]. This explains why ScSZ displays a higher conductivity. However, one of the major problems that hinder the application of ScSZ (8 mole%) is the aging that causes a significant decline in the ionic conductivity, as shown in Table 2.2. The initial conductivity of 8 mole% ScSZ, which is about twice as much as that of 8 mole% YSZ, drops considerably to nearly the same value as YSZ after 5000 hours of annealing. With Raman spectroscopy, Kharton suggests that the aging problem of ScSZ may well be attributed to the conversion from a distorted fluorite phase to a
less-conductive tetragonal phase [31]. One possible solution for such aging problem is to increase the scandia content from 8 mole% to 11 mole%. The latter could maintain a stable conductivity during long-term operation, as shown in Figure 2.9. However, this approach is limited by the high cost of Scandia.

![Conductivity changes during annealing at 1273K. (a)8mole%YSZ, (b)8mole%ScSZ, (c)11mole%ScSZ][32]. Copyright © 2000 Elsevier.

2.2.3 Cathode

The cathode functions mainly to provide reaction sites for the oxidants’ electrochemical reduction, transport charged species to electrolyte and distribute electrical current generated from reduction. To realize the functions listed above, the cathode should be highly porous and gas-permeable. Other important properties include chemical and morphological stability in the oxidizing environment; sufficient
electrical/ionic conductivity for the electron/oxygen ion transport (aiming to minimize the ohmic losses), and good catalytic activity for oxygen reduction. In addition, there are desirable requirements such as chemical compatibility, appropriate robustness and manufacturability [13].

Noble metals were initially investigated as the cathode material for SOFCs since few other materials show adequate stability at high operating temperatures. However, the high cost of noble metals, such as platinum, prohibits practical applications in SOFCs for power generation. Perovskite materials have been extensively applied as cathode materials since 1960s [33]. The general formula of a perovskite-structured oxide is $\text{ABO}_3$, where A and B denote large and small cations, respectively, which have a total valence of +6. Figure 2.9 illustrates a typical idea lattice structure of perovskite, $\text{ABO}_3$.

![Figure 2.9: Schematic diagram of the perovskite lattice structure.](image)

The larger A-site cations $\text{A}^{n+}$ (e.g. La, Sr, Ca, Pb, etc.) are of lower valence and have 12 coordinated oxygen anions while the small B-site cations $\text{B}^{m+}$ (e.g. Ti, Cr, Ni, Fe, Zr and Co, etc.) have 6 oxygen anions coordinates. The possible replacement of $\text{A}^{n+}$
or $B^{m+}$ with various lower-valence cations could make the total charge $(n+m)$ less than 6, the net negative charge in the lattice is compensated by the formation of oxygen ion vacancies [34].

Lanthanum cobaltite ($\text{LaCoO}_3$) was first tested by Tedmon in 1969 and displayed satisfactory performance. However, severe degradation that was caused by interaction with the YSZ electrolyte (forming $\text{La}_2\text{Zr}_2\text{O}_7$) was observed with increasing operation time. Since 1985, investigation focus moved to lanthanum manganite ($\text{LaMnO}_3$) due to less degradation and appropriate electrical conductivity ($10^{-4}$ S cm$^{-1}$ and 0.1 S cm$^{-1}$ at room temperature and 700°C, respectively [13]). However, it is recognized that potential reactions with YSZ still exist especially during fabrication process at elevated temperatures [35]. It is generally agreed that the electrical conductivity of $\text{LaMnO}_3$ can be significantly enhanced if it is doped with alkaline earth or transition metal cations such as magnesium ($\text{Mg}^{2+}$), calcium ($\text{Ca}^{2+}$), barium ($\text{Ba}^{2+}$), strontium ($\text{Sr}^{2+}$), cobalt ($\text{Co}^{2+}$) and yttrium ($\text{Y}^{3+}$). In the last several decades, $\text{Sr}^{2+}$, as a dopant, has been intensively investigated [36-45] because its radius is similar to that of lanthanum and displays considerable electrical conductivity under oxidizing circumstance. Moreover, its TEC matches well with other cell components (TEC of LSM and YSZ are $\sim12\times10^{-6}$ and $\sim11\times10^{-6}$, respectively [13]). When the replacement of $\text{La}^{3+}$ by $\text{Sr}^{2+}$ occurs, electric hole is introduced on Mn$^{3+}$ site to maintain electroneutrality, which consequently leads to the enhancement in the electrical conductivity, as shown in the equation below [13]:

$$\text{LaMnO}_3 \xrightarrow{\text{SrO}} \text{La}_{1-x}\text{Sr}_x\text{Mn}_{1-x}\text{Mn}_x^{4+}\text{O}_3$$  \hspace{1cm} (2.15)

The electrical conductivity of LSM rises almost linearly with the doping concentration of Sr, up to a peak value at 50 mole%. However, a solid-phase interaction between
LSM and YSZ was observed to form SrZrO$_3$ when Sr content is above 30 mole% [13]. Thus, 30 mole% is accepted as the optimum substitution concentration.

### 2.2.4 Interconnect

The maximum voltage output of a single SOFC cell under general operating conditions (with fuel and oxidant of H$_2$ and O$_2$, respectively) is less than 1 V. Hence, SOFCs are practically packed into a stack in order to generate power of higher voltages. Interconnect has to be used for electrical connection between each individual single cells, and forming separate channels inside the stack for continuous flows of fuel and oxidant. Therefore, an interconnect needs to possess properties including gas tightness, good thermal and chemical stability in both reducing and oxidizing conditions, reasonably high electrical conductivity and negligible ionic conductivity, and appropriate mechanical strength. In addition, the TEC of interconnect should be compatible with other cell components [16].

All these requirements together with the additional considerations on cost and manufacturability have constrained the suitable interconnect materials to only a few choices, such as doped rare earth chromites. Lanthanum chromite (LaCrO$_3$) has been extensively tested as the interconnect material of high temperature solid oxide fuel cells since 1970s, because of the desirable properties such as appropriate electrical conductivity in both reducing and oxidizing conditions, considerable mechanical strength and stability at high operating temperatures, and adequate compatibility with other cell components. For practical applications, various dopants have been investigated to tailor and improve the properties of LaCrO$_3$. 
2.3 Intermediate Temperature SOFC

The high temperature region of 850-1000°C adopted in conventional SOFCs helps to increase electrochemical reaction kinetics, suppress polarization resistance, improve electrolyte conductivity and result in less voltage losses. Furthermore, the internal reforming at high operating temperatures enables direct use of hydrocarbons as the fuel, hence eliminating the necessity of an external fuel processor. Other benefits of elevated temperatures include enabling carbon monoxide to be used directly as a fuel, rather than an electrocatalyst poison that has been a common problem for low temperature fuel cells, such as AFC (alkaline fuel cell) and PAFC (phosphoric acid fuel cell). However, high temperatures impose strict requirements on materials and constrain the candidates to few ceramics, which may well increase the fabrication cost. Higher operating temperatures also indicate longer start-up time and can substantially increase inter diffusion and interactions between cell components. For example, the interaction between LSM cathode and YSZ electrolyte was observed at elevated temperatures, resulting in the formation of lanthanum zirconate (La$_2$Zr$_2$O$_7$) with high-resistance, hence causing a gradual decline in the cell performance [46].

For the past decade, considerable efforts have been devoted to the development of intermediate temperature SOFCs (IT-SOFCs) which are operated between 500-800 °C. By lowering the operating temperatures, the range of candidate materials is significantly extended, which allows more economical fabrication, and quicker start-up/shut-down. Other benefits of decreased operating temperature include considerably suppressed corrosion and degradation (component inter-diffusion is less severe at lower temperatures) of cell components, thus improving the durability of cells. Furthermore, by employing compressive sealants and metallic interconnects,
better construction robustness can be obtained. These advantages make IT-SOFCs more attractive than HT-SOFCs.

There are two major approaches through which IT-SOFCs can achieve a comparable performance to HT-SOFCs. One route is to reduce the thickness of the electrolyte via fabrication control for reduced ohmic losses. The other way is to employ electrolyte materials showing adequate ionic conductivity at low operating temperatures [47]. Under the operating temperature of 700 °C, the thickness of YSZ electrolyte, which is the conventional choice for HT-SOFCs, has to be decreased to less than 15 μm to provide sufficient ionic conductivity. In this case, YSZ electrolyte may be too thin to maintain proper mechanical strength to be self-supported. Thus an electrode support is usually required. However, if the temperature further declines to 500-600°C, the benefit of reducing thickness for higher conductivity would be substantially reduced. Therefore, it is essential to consider an alternative material with appropriate conductivity at intermediate temperatures.

### 2.3.1 Electrolyte materials for IT-SOFC

Similar to HT-SOFC, the electrolyte material for IT-SOFC needs to possess high ionic conductivity (typically > 1×10⁻³ S cm⁻¹) and negligible electrical conductivity for minimized ohmic losses, in addition to proper TEC that matches with contacting cell components.

A numerous number of electrolyte materials with the required conductivity have been investigated in recent years [9, 32, 48, 49]. Figure 2.10 compares the conductivity of YSZ with that of newly developed candidates, such as calcium oxide doped ceria (CDC), yttria-doped ceria (YDC), cerium-gadolinium oxide (CGO) (also known as
gadolinia-doped ceria (GDC)), yttria-stabilized bismuth oxide (YSB), etc. The mechanism of oxygen ion transport in ceramic is thermally activated, thus the conductivity depends largely on temperatures. As illustrated in the figure, most of these selected materials, except for CaSZ, display higher ionic conductivity in the temperature region of 500-700 °C than YSZ. However, it is important to note that statistics shown in the figure are just representative values (conductivity data from [8, 48]) and actual conductivities are also dependent on a number of factors such as dopant concentration, microstructure and fabrication procedures.

**Figure 2.10:** Ionic conductivity of selected electrolyte materials as a function of reciprocal temperature (CaSZ (Zr$_{0.85}$Ca$_{0.15}$O$_{1.85}$); YSZ [(ZrO$_2$)$_{0.92}$(Y$_2$O$_3$)$_{0.08}$]; CDC (Ce$_{0.9}$Ca$_{0.1}$O$_{1.8}$); YDC (Ce$_{0.8}$Y$_{0.2}$O$_{1.96}$); CGO (Ce$_{0.9}$Gd$_{0.1}$O$_{1.9}$); LSGMC (La$_{0.8}$Sr$_{0.2}$Ga$_{0.8}$Mg$_{0.115}$Co$_{0.085}$O$_{3}$); YSB [(Bi$_2$O$_3$)$_{0.75}$(Y$_2$O$_3$)$_{0.25}$]). Reproduced from [50] with permission from Othman.
Doped ceria (CeO$_2$) is suggested as one of the most promising electrolyte materials for IT-SOFC, and detailed discussions will be made in the following section. Unlike zirconia, pure ceria maintains a stable fluorite-type structure up to its melting point [51], as shown in Figure 2.11.

![Fluorite Framework of CeO$_2$](image)

**Figure 2.11:** Illustration of CeO$_2$ fluorite framework. The smaller yellow spheres denote Ce$^{4+}$ cations and larger blue spheres represent oxygen sites.

Each Ce$^{4+}$ cation has 8 coordinated oxygen anions that occupy all the tetrahedral sites, forming a cubic close packing. However, actual ceria displays different extents of oxygen deficiencies with the formula of CeO$_{2-\delta}$ ($\delta \leq 0.3$). Pure ceria exhibits n-type electronic conduction which proceeds through a small polaron hopping mechanism [13]. The electrical conductivity of pure CeO$_2$ is negligible and the absolute ionic conductivity depends on temperature and oxygen partial pressure. Like zirconia, being doped with various low-valence metal oxides, such as lanthana (La$_2$O$_3$), yttria (Y$_2$O$_3$), gadolina (Gd$_2$O$_3$) and other rare-earth oxides, markedly improves the
conductivity of ceria, which results from formation of additional oxygen vacancies. It is generally accepted that the maximum conductivity is obtained when the doping cation has the minimum mismatch in radius, therefore, samarium (Sm\(^{3+}\)) and gadolinium (Gd\(^{3+}\)) are the optimum choices in the case of Ce\(^{4+}\) [8].

Cerium-gadolinium oxide (CGO) (also known as Gd-doped CeO\(_2\) (GDC)) has been extensively investigated in the past decade as an electrolyte material for IT-SOFC. The doping mechanism of Gd\(_2\)O\(_3\) is described in the reaction below:

\[
Gd_2O_3 \xrightarrow{CeO_2} 2Gd^{3+}_{Ce} + V^{**}_O + 3O^* _O
\]  

(2.16)

As can be seen from Figure 2.11, CGO displays consistently higher conductivity than that of YSZ in the temperature ranging from 500-700 °C. However, at elevated temperatures (>700 °C) or low oxygen partial pressures (~1x10\(^{-19}\) atm, as prevalent on the anode side of an SOFC), Ce\(^{4+}\) cations in doped ceria tend to change to Ce\(^{3+}\), which subsequently expand lattice volume that may reduce the mechanical strength of the electrolyte. Moreover, the reduction from Ce\(^{4+}\) to Ce\(^{3+}\) results in 'current leakage' between the two electrodes, reducing the open-circuit voltage (OCV) of the fuel cell. Multi-layer electrolyte with a buffer layer has been suggested to overcome the problem of current leakage. Scandia-stabilized zirconia (ScSZ) [52] has been investigated as the interlayer between CGO electrolyte and the anode, while \(((Bi_2O_3)_{1-x}(Er_2O_3)Ag\) (ESB) [53] layer was inserted between the electrolyte and the cathode. Both studies note an improvement in the OCV of the fuel cells when compared with a conventional single-layer CGO electrolyte.

Similar to zirconia, the optimum ionic conductivity of CGO is obtained at a certain doping concentration. This concentration differs within the range between 10 mole% (Ce\(_{0.9}Gd_{0.1}O_{1.95}\)) and 20 mole% (Ce\(_{0.8}Gd_{0.2}O_{1.95}\)) [47, 54-56]. However, it is reported
that Ce_{0.9}Gd_{0.1}O_{1.95} is more stable than Ce_{0.8}Gd_{0.2}O_{1.95} at low oxygen partial pressures [47].

In addition to fluorite materials, pevoskite oxides have also been investigated as IT-SOFC electrolyte. Since 1994, Ishilara’s group has tested various dopants for lanthanum gallate (LaGaO_3)-based electrolytes and reported that the Sr-doped LaGaO_3 (La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_3) displays the highest ionic conductivity, which is one order of magnitude higher than that of YSZ [57, 58]. In addition, the electrical conductivity of all Ga-based perovskites is almost independent of oxygen partial pressure, illustrating that ion conduction is dominant in these materials. All these features have suggested LSGM to be suitable for intermediate temperature operation. However, compatibility problem has also been observed between LSGM and NiO at elevated temperatures, suggesting that it is difficult to deposit LSGM film directly on anode substrate. Therefore, several studies have been undertaken, in which composite electrolyte (CGO-LSGM, LDC (lanthanum-doped ceria)-LSGM) have been employed, and displayed some satisfactory performances (max. power density 1.1 W cm^{-2}) [59, 60]. Despite the superior conductivity, LSGM is substantially more costly than ceria-based materials, which consequently prevents this material from large-scale application.

2.3.2 Anode materials for IT-SOFC

Like HT-SOFC, nickel is the most preferable material for IT-SOFC due to its low cost, high catalytic activity for fuel oxidation and notable electrical conductivity. A Ni-CGO cermet is usually adopted so as to minimize the mismatch in TECs between nickel anode and CGO electrolyte.
Nickel has been used extensively as a brilliant electrocatalyst for fuel oxidation reactions. However, there exist some desirable requirements of anode material for IT-SOFC that nickel-cermet does not fully fulfil. One of these is the redox stability, which permits brief excursions to high oxygen concentrations without irreversible loss of structural coherence and electrochemical functionality. The periodical switching on/off of the fuel gases causes nickel in the anode to be oxidized then reduced, causing repeated expansion/contraction that results in a considerable decline in the catalytic activity and conductivity of the anode [16, 61]. Moreover, the volume expansion occurs during the conversion from Ni to NiO, as mentioned in Chapter 2.2.1, can well introduce defects, which is detrimental to the mechanical strength of fuel cells. Another critical issue of using nickel is carbon deposition when hydrocarbons fuels are used. The carbon formed may block active sites and lead to loss of reforming activity. In extreme cases, carbon growth can restrict gas flow of fuel supply or even result in physical blockages [62]. Macek (2007) reports that the quantity of carbon generated from the cracking/condensation of hydrocarbon fuels is strongly dependent on operating temperatures and high temperatures lead to more severe carbon formation. In addition, there is a threshold value for hydrocarbon/steam ratio below which carbon deposition is more likely to happen [62]. Hence, substantial efforts have been undertaken to explore alternative anode materials. Copper-ceria composite is accepted as a promising replacement because it is less active in catalysing hydrocarbon cracking/condensation reactions. Ceria acts as the electrochemical oxidation catalyst while the copper only functions as a matrix for electron transport [63, 64]. Due to the low melting point of copper (1085 °C) and its oxides (CuO at 1326 °C), the copper composite anode suffers severe sintering
problem. This could be tackled by fabricating a porous ion-conductor skeleton on a dense electrolyte, then deposition of copper and cerium as nitrate salts through infiltration, followed by subsequent pyrolysis [16]. In addition to the low-temperature fabrication route, the intermediate operating temperatures can also effectively inhibit this sintering and degradation problem. The other possible replacement choices are non-metallic materials such as lanthanum chromite (LaCrO$_3$) based ceramics with perovskite structure. In addition to the appropriate stability, the La site and Cr site can be easily substituted with alkali earth (e.g. strontium, calcium) and transition metal (e.g. manganese, cobalt, iron and nickel) elements, respectively, aiming to modify the electrical conductivity and catalytic activity [65-68].

2.3.3 Cathode materials for IT-SOFC

Lowering the operating temperatures to the range of 500-700°C slows down reaction kinetics and charge transport, thus increasing the polarization resistance. LSM, which is widely adopted as the cathode material for conventional HT-SOFC, can no longer provide adequate ionic conductivity for the operation at intermediate temperatures, leading to the investigations on MIEC materials. The major active sites of LSM-based cathode are concentrated at the interface between the electrolyte and cathode, whereas the application of MIEC materials could extend the triple-phase boundary to spread throughout the cathode. (La, Sr)CoO$_3$ turns out to be the most promising alternative because it shows high ionic and electronic conductivities. However, it shows poor compatibility due to a considerable mismatch between the TEC of this material and doped ceria (TEC of (La, Sr)CoO$_3$ and CGO are ~16-22×10$^{-6}$ and
~12×10^{-6}, respectively [16]). Therefore, (La, Sr)CoO_3 can hardly be used directly with CGO electrolyte. By substituting different amount of cobalt with iron, a new compound of La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-d} (LSCF) is suggested [33, 69]. It has fantastic conductivity, acceptable catalytic activity and appropriate compatibility (TEC of LSCF and CGO are ~15×10^{-6} [70] and ~12×10^{-6}, respectively), which leads to considerable amount of efforts to be devoted on this material. Recently, another mixed conducting perovskite material, Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ}, has attracted an increasing level of research interest. It is first reported by Shao and Haile [71] as a potential cathode material for IT-SOFC, exhibiting an impressing power density of 1.01 W cm^{-2} at 600°C. They also suggest BSCF to be ideally suited to ‘single-chamber’ operation mode. The progress in development and understanding of this material is systematically reviewed by Zhou [72]. BSCF is widely accepted to have excellent catalytic activity for oxygen reduction at intermediate temperature, which is ascribed to the high concentration of oxygen vacancies [72]. Some recent studies in planar SOFC have further proved BSCF to be competent as cathode materials, showing a maximum power density of 1.56 W cm^{-2} at 800°C [73] and 1.33 W cm^{-2} at 600°C [74].

2.3.4 Interconnect materials for IT-SOFC

Due to a numerous number of constraints and requirements set on interconnect materials, the options are limited to a few candidates such as ceramics or alloy with high Cr/Ni ratio; both may turn interconnect into the most expensive component of a fuel cell stack. The conventional choice is LaCrO_3-based oxides, which is commonly
doped with alkali earth elements, such as Sr and Ca, to improve the mechanical properties and conductivity. The reduction of operating temperatures of IT-SOFC allows metallic alloys to be a promising replacement for ceramic materials. Metallic interconnects possess advantages of better mechanical strength, significantly lowered cost and excellent manufacturability. Moreover, they can withstand the rapid temperature change, which is associated with reduced start-up/shut-down time of IT-SOFCs [8]. In recent years, an increasing amount of work has been undertaken to investigate metallic systems including Cr-based, Ni-based and Fe-based alloys [75-77].

2.4 Geometries classification

There is a number of ways by which SOFCs can be classified. One approach is based on the single cell configuration, which is associated with the component that functions as the structural support of the cell. Another classification is conducted according to geometrical shape (e.g. monolithic, tubular or planar). The detailed features will be discussed below.

2.4.1 Cell configuration

The SOFC single cell configurations can be classified into two main categories: self-supporting and external-supporting. For the formal supporting type, one of the cell components (anode, cathode and electrolyte) provides the major mechanical strength. While for the external supporting type, the two electrodes and the electrolyte are fabricated into thin layers and mechanically supported by distinct
components like interconnect or porous substrate, as illustrated in Figure 2.12. Winkler [16] summarized the respective advantages and disadvantages of various configurations, as listed in Table 2.3.

Figure 2.12: Illustration of single cell configurations (reproduced from [78], Copyright © 2004 Elsevier.)
Table 2.3: Characteristics of different SOFC configurations [16, 78]. Copyright © 2004 Elsevier.

<table>
<thead>
<tr>
<th>Cell configuration</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Self-supporting</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anode-supported</td>
<td>Excellent conductivity of anode</td>
<td>Potential reoxidation problem</td>
</tr>
<tr>
<td></td>
<td>Lower operating temperature due to employment of the thin electrolytes</td>
<td>Mass transport hindered by thick anode</td>
</tr>
<tr>
<td>Electrolyte-supported</td>
<td>High mechanical strength from dense electrolyte</td>
<td>Considerable resistance due to low electrolyte conductivity</td>
</tr>
<tr>
<td></td>
<td>Less vulnerable to failure caused from anode reoxidation (Ni/YSZ anode) or cathode reduction (LSM cathode)</td>
<td>High operating temperature required to minimize ohmic losses in electrolyte</td>
</tr>
<tr>
<td>Cathode-supported</td>
<td>No oxidation problems</td>
<td>Lower conductivity</td>
</tr>
<tr>
<td></td>
<td>Lower operating temperature due to employment of the thin electrolyte</td>
<td>Mass transport limited due to thick cathode</td>
</tr>
<tr>
<td><strong>External-supporting</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Interconnect-supported</td>
<td>Thin cell components for lower operating temperatures</td>
<td>Oxidation problem</td>
</tr>
<tr>
<td></td>
<td>Adequate mechanical strength from metallic interconnects</td>
<td>Flowfield design limitation due to cell support requirements</td>
</tr>
<tr>
<td>Substrate-supported</td>
<td>Thin cell components for lower operating temperatures</td>
<td>Enhanced complexity due to additional materials</td>
</tr>
<tr>
<td></td>
<td>Potential utilization of non-cell material for support to improve performance</td>
<td>Potential electronic short with metallic substrate</td>
</tr>
</tbody>
</table>
2.4.2 Types of stack design

The stack design of SOFC depends on electrical, physical and electrochemical properties of the cell components. There are mainly four types of stack design: planar, tubular, monolithic, and segmented-cell-in series design. The major differences between each design are associated with current path, gas flow configuration and manifolding, and cell-to-cell electrical connection. The detailed discussion of their features will be made below.

Planar design, also known as flat-plate design, has received probably the most interest in the past two decades due to its simple cell geometry and good manufacturability. A schematic planar design configuration is illustrated in Figure 2.13.

![Figure 2.13: Schematic diagram of a planar design SOFC configuration](79). Copyright © 2002 Elsevier.

The planar structure, in which the cell components are fabricated as flat plates with different shapes (rectangular or circular) and connected in electrical series, is also the first design that has been tested in kilowatt-level [13]. Among the various
fabrication techniques developed for making planar SOFCs, the die-pressing and tape-casting have been proved to provide better control of the electrolyte thickness, which is one of the key factors that affect the cell performance. It is reported that an electrolyte with less than 10 μm in thickness could effectively reduce the ohmic losses, thus improving the output voltage [13]. With various fabrication routes, such as chemical vapour deposition (CVD), electrochemical vapour deposition (EVD) and sol-get method, the thickness could be controlled within sub-micron range. However, the thin electrolyte can no longer be the mechanically supporting component. As a result, most current research focuses on anode or cathode-supported cells. Excellent power densities ranging from 0.8-3.3 W cm$^{-2}$ have been obtained from anode-supported planar SOFCs operated at intermediate temperatures (≤700 °C) [80-82]. The major limitations of planar design are associated with the high-temperature gas seals and interconnect materials. The non-uniform stress distribution and temperature gradients, caused by the unavoidable nature of the seals, may lead to layer cracking, and impose additional restrictions on the heating/cooling rate, resulting in undesirably long start-up/shut-down times.

In contrast, the sealing components of tubular SOFCs are commonly positioned outside the heating zone, hence eliminating the requirement of high-temperature seal to isolate the fuel from the oxidant and significantly extending the range of available materials. It is generally accepted that tubular stack design, in which cell components are configured in the form of a multi-layered cylindrical tube, could be classified into two types based on tube diameter: the conventional sealless design (diameter >15 mm) and the micro-tubular design (diameter <5 mm). The former design type, pioneered by Siemens Westinghouse (SW) Corporation, has been investigated since
the 1960s and became commercially available in 1970. Figure 2.14 displays the illustration of the SW cathode-supported tubular cell. The LaMnO$_3$-based cathode support layer is first fabricated by extrusion and subsequent sintering, forming a tube (2.2 cm diameter, 2.2 mm thickness and ~180 cm length) that has the porosity of 30-35%. Then the 10 mole% YSZ electrolyte (~40 μm thickness) is deposited on the cathode via electrochemical vapour deposition (EVD) [83] and the Ni-YSZ anode is deposited on the electrolyte by slurry dip-coating. After another sintering process, the final cell is about 150 cm in length and 2.2 cm in outer diameter.

![Diagram of tubular cell](image)

**Figure 2.14**: Schematic design of a cathode-supported tubular cell developed by Siemens Westinghouse. Reproduced from [50] with permission from Othman.

As can be seen from Figure 2.16, the air flow goes through the inside pathway while the fuel flow on the outer surface. Despite the single biggest advantage of easy sealing, tubular design displays some drawbacks, such as the relatively low area power density. The maximum power output of a Siemens single cell is ~ 200 W at 1000°C and atmospheric pressure [16], therefore the maximum power density is calculated to be 0.19 W/cm$^2$, which is almost one order of magnitude lower compared
with planar cells. In addition, the whole fabrication process is cost and time consuming compared with planar geometry. These drawbacks, together with the long start-up time of 4-6 hours, suggest that large-dimension tubular SOFCs are mainly suitable for stationary power generation and not so attractive in transportation and military applications [16, 84].

In contrast, micro-tubular design exhibits advantages including considerable enhancement in power density, rapid start-up and adequate cycling performance. Therefore, an increasing amount of work has been concentrated on developing micro-tubular SOFCs since the 1990s [16].

2.5 Progress in Micro-tubular SOFCs

The research on micro-tubular SOFCs initiated in 1990s when Kendall successfully fabricated YSZ electrolyte tubes of 1~5 mm in outer diameter and 100~200 µm in wall thickness, by using ram extrusion technique [85]. However, this novel geometry attracted little attention and it was not until 1994, when Kendall [86, 87] reported significant improvements in the start-up time, thermal shock and sealing performance, that micro-tubular design began to draw increasing interest. A theoretical calculation has been conducted based on a tubular stack arranged in a square array and the volumetric power density; $P_{Vol}$ (W cm$^{-3}$) can be calculated based on the equation below:

$$P_{Vol} = \frac{\pi Dp}{(D+g)^3} \quad (2.17)$$

where $p$ denotes power density (W cm$^{-2}$), $D$ and $g$ represent the outer diameter (cm) and gap between individual cells (cm), respectively. It is reported that micro-
tubular design has the potential to achieve 8 times better power density compared with large-dimension tubular design [88].

So far, an enormous amount of work has been undertaken to develop micro-tubular fuel cells with different configurations, including anode-supported [89-99], electrolyte-supported [100-102] and cathode-supported [103-105]. Plastic mass ram extrusion and wet spinning (also known as phase inversion-assisted extrusion) are the two major techniques employed to fabricate the support layer, which is one of the key components that determine the mechanical properties and cell performance. The detailed features of these two methods will be discussed below.

2.5.1 Plastic mass ram extrusion

Plastic mass ram extrusion has been widely adopted as a mature technique to fabricate hollow fibers. Suzuki’s group (National Institute of Advanced Industrial Science and Technology (AIST), Japan) is one of the leading groups in fuel cell preparation and applications. Figure 2.17 illustrates the flow chart of a typical process adopted by Suzuki’s group to fabricate micro-tubular fuel cells, in which plastic mass ram extrusion is employed to prepare the anode support [90]. Firstly, the materials of the support tube are mixed with binder (e.g. cellulose) and water to form a viscous precursor or paste. Then the paste is extruded through an in-house-designed die to obtain the tubular structure, as shown in Figure 2.18. After drying, the support tube is cut to a desired length, followed by the incorporation of other components (electrolyte and cathode) via dip-coating. The plastic mass ram extrusion has been widely adopted, mainly due to its advantages such as easy operation and simplicity of the
device. However, as illustrated from the figure, the extruded support tubes are usually of a symmetric structure, which leads to considerable diffusion resistance. Therefore, various degradable pore formers, such as starch [106], sucrose [107], graphite [107, 108] and poly-methyl methacrylate (PMMA) [109, 110], have been tested by adding them into the ram suspensions to introduce proper porosity.

**Figure 2.15:** Flow chart of the fabrication process of the Ni-based anode-supported micro-tubular SOFCs.

**Figure 2.16:** Schematic diagram of an extrusion process.
It is worth noticing that the manufacturing route illustrated in Figure 2.15 is composed of repetitions of coating and sintering, which makes the overall process complicated and energy-consuming. To achieve better process economy, the ram co-extruder (as shown in Figure 2.17) developed by Kendall’s group enables the extrusion of multiple pastes with matched rheology in a single-step process [88, 111], which dramatically simplifies the manufacturing route.

![Diagram of co-extruder](https://example.com/co-extruder.png)

**Figure 2.17: The external view of co-extruder designed by Kendall’s group [111].**

Copyright © 2001 Elsevier.

The driving force is applied via a force transmission plate and the lumen is formed by a central pin. The main drawback of this process is the difficulties in individual thickness control and the inflexibility in morphology tailoring.
Recent developments in micro-tubular SOFCs fabricated by plastic mass ram extrusion technique are summarized in Table 2.4. The listed content includes cell configuration, materials for the major cell components, operating conditions and the best cell performance. More detailed information can be found in the references.
### Table 2.4: Development of single micro-tubular SOFC based on plastic mass ram extrusion technique

<table>
<thead>
<tr>
<th>Cell configuration</th>
<th>Anode</th>
<th>AFL</th>
<th>Electrolyte</th>
<th>Cathode</th>
<th>Diameter (mm)</th>
<th>Fuel stream</th>
<th>Operating Temp. (°C)</th>
<th>OCV (V)</th>
<th>Max. power density (W.cm$^2$)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anode-supported</td>
<td>Ni-CGO</td>
<td>CeO$_2$</td>
<td>CGO</td>
<td>LSCF-CGO</td>
<td>1.80</td>
<td>Humidified CH$_4$-N$_2$</td>
<td>554</td>
<td>0.9</td>
<td>0.45</td>
<td>[112]</td>
</tr>
<tr>
<td>Anode-supported</td>
<td>Ni-CGO</td>
<td>/</td>
<td>CGO</td>
<td>LSCF-CGO</td>
<td>0.80</td>
<td>Humidified H$_2$-N$_2$</td>
<td>550</td>
<td>0.8</td>
<td>1.02</td>
<td>[91]</td>
</tr>
<tr>
<td>Anode-supported</td>
<td>Ni-YSZ</td>
<td>NiO-ScSZ</td>
<td>ScSZ</td>
<td>LSCF-CGO</td>
<td>1.80</td>
<td>H$_2$-Argon</td>
<td>700</td>
<td>1.0</td>
<td>0.52</td>
<td>[28]</td>
</tr>
<tr>
<td>Cathode-supported</td>
<td>Ni-CGO</td>
<td>/</td>
<td>LSM+CGO</td>
<td>LSM-CGO</td>
<td>1.60</td>
<td>Humidified H$_2$</td>
<td>750</td>
<td>1.0</td>
<td>0.38</td>
<td>[52]</td>
</tr>
<tr>
<td>Anode-supported</td>
<td>Ni-CGO</td>
<td>/</td>
<td>CGO</td>
<td>LSCF-CGO</td>
<td>1.50</td>
<td>Humidified H$_2$-N$_2$</td>
<td>550</td>
<td>0.8</td>
<td>0.40</td>
<td>[113]</td>
</tr>
<tr>
<td>Cathode-supported</td>
<td>Ni-CGO</td>
<td>/</td>
<td>ScSZ</td>
<td>LSM-CGO</td>
<td>1.60</td>
<td>Humidified H$_2$</td>
<td>750</td>
<td>1.0</td>
<td>0.45</td>
<td>[103]</td>
</tr>
<tr>
<td>Anode-supported</td>
<td>Ni-CGO</td>
<td>/</td>
<td>CGO</td>
<td>LSCF-CGO</td>
<td>0.80</td>
<td>Humidified H$_2$-N$_2$</td>
<td>550</td>
<td>0.8</td>
<td>0.35</td>
<td>[90]</td>
</tr>
<tr>
<td>Cathode-supported</td>
<td>Ni-CGO</td>
<td>/</td>
<td>CGO</td>
<td>LSCF-CGO</td>
<td>2.26</td>
<td>Humidified H$_2$</td>
<td>600</td>
<td>0.8</td>
<td>0.16</td>
<td>[104]</td>
</tr>
<tr>
<td>Cathode-supported</td>
<td>Ni-CGO</td>
<td>/</td>
<td>ScSZ</td>
<td>LSM-CGO</td>
<td>1.60</td>
<td>Humidified H$_2$</td>
<td>800</td>
<td>1.0</td>
<td>0.31</td>
<td>[105]</td>
</tr>
<tr>
<td>Anode-supported</td>
<td>Ni-YSZ</td>
<td>/</td>
<td>YSZ</td>
<td>LSCF-CGO</td>
<td>1.70</td>
<td>Humidified H₂</td>
<td>600</td>
<td>1.0</td>
<td>0.39</td>
<td>[114]</td>
</tr>
<tr>
<td>-----------------</td>
<td>---------</td>
<td>-------</td>
<td>-------</td>
<td>----------</td>
<td>------</td>
<td>---------------</td>
<td>-----</td>
<td>-----</td>
<td>------</td>
<td>------</td>
</tr>
<tr>
<td>Anode-supported</td>
<td>Ni-CGO</td>
<td>/</td>
<td>CGO</td>
<td>LSCF-CGO</td>
<td>0.40</td>
<td>Humidified H₂</td>
<td>550</td>
<td>0.8</td>
<td>0.30</td>
<td>[115]</td>
</tr>
<tr>
<td>Anode-supported</td>
<td>Ni-ScSZ</td>
<td>/</td>
<td>ScSZ</td>
<td>LSCF-CGO</td>
<td>1.90</td>
<td>Humidified H₂</td>
<td>600</td>
<td>1.0</td>
<td>1.10</td>
<td>[116]</td>
</tr>
<tr>
<td>Anode-supported</td>
<td>Ni-YSZ</td>
<td>/</td>
<td>ScSZ</td>
<td>LSCF-CGO</td>
<td>1.80</td>
<td>H₂-Argon</td>
<td>700</td>
<td>1.0</td>
<td>0.69</td>
<td>[117]</td>
</tr>
<tr>
<td>Electrolyte-supported</td>
<td>Ni-ScSZ</td>
<td>/</td>
<td>ScSZ</td>
<td>LSM-CGO</td>
<td>3.8</td>
<td>H₂-N₂</td>
<td>920</td>
<td>1.1</td>
<td>0.26</td>
<td>[118]</td>
</tr>
<tr>
<td>Anode-supported</td>
<td>Ni-CGO</td>
<td>/</td>
<td>CGO</td>
<td>LSCF-CGO</td>
<td>1.60</td>
<td>Humidified H₂</td>
<td>550</td>
<td>0.8</td>
<td>1.31</td>
<td>[119]</td>
</tr>
<tr>
<td>Anode-supported</td>
<td>Ni-CGO</td>
<td>/</td>
<td>CGO</td>
<td>LSCF-CGO</td>
<td>1.80</td>
<td>Humidified H₂</td>
<td>550</td>
<td>0.8</td>
<td>0.63</td>
<td>[120]</td>
</tr>
<tr>
<td>Anode-supported</td>
<td>Ni-CGO</td>
<td>/</td>
<td>CGO</td>
<td>LSCF-CGO</td>
<td>1.60</td>
<td>Humidified H₂</td>
<td>550</td>
<td>0.3</td>
<td>1.30</td>
<td>[121]</td>
</tr>
<tr>
<td>Anode-supported</td>
<td>Ni-CGO</td>
<td>/</td>
<td>CGO</td>
<td>LSCF-CGO</td>
<td>1.80</td>
<td>Humidified H₂</td>
<td>450</td>
<td>0.9</td>
<td>0.30</td>
<td>[122]</td>
</tr>
<tr>
<td>Anode-supported</td>
<td>Ni-BZCY</td>
<td>Ni-BZCY</td>
<td>BZCY</td>
<td>LSCF-BZCY</td>
<td>/</td>
<td>Humidified H₂</td>
<td>700</td>
<td>1.01</td>
<td>0.5</td>
<td>[123]</td>
</tr>
</tbody>
</table>

*ScSZ= (ZrO₂)₀.₈₉(Sc₂O₃)₀.₁(CeO₂)₀.₀₁; BZCY=Ba(Zr₀.₁Ce₀.₇Y₀.₂)O₃₋₅
2.5.2 Wet spinning

In 1991, Okubo et al. [124] reported the fabrication of porous ceramic hollow fibers for water desalination by using extrusion technique based on a phase inversion process. This technique was then employed to prepare asymmetric Al₂O₃ hollow fiber membranes [125, 126], and has been used to fabricate ceramic hollow fibers for various applications. In general, this technique is slightly similar with plastic ram extrusion process. The main difference is that solidification of precursors in wet spinning is initiated by solvent/non-solvent exchange. While in plastic ram extrusion process, the tubes are dried naturally as solvent evaporates.

2.5.2.1 Phase inversion

It is generally accepted that the phase inversion process can be conceptually explained by the ternary phase diagram of the solvent-polymer-precipitant system, as illustrated in Figure 2.18.

![Figure 2.18: Ternary phase diagram of the precipitation pathway of a solvent-polymer-precipitant system. Reproduced from [50] with permission from Othman.](image-url)
The three corners denote the three components: solvent, polymer, and precipitant (also known as non-solvent), while any point on the border or within the triangle denotes a mixture of two or three components, respectively. The overall phase inversion process can be illustrated by the path from A to D. Point A denotes the initial polymeric solution where no precipitant is present. After the immersion into a precipitant (non-solvent) bath, the original stable state of the polymeric solution is transformed into a metastable state due to the continuous exchange between solvent and precipitant. However, the path from A to B is still within the single-phase region, where all the compositions are miscible. If the diffusion rate of the solvent outflux is higher than that of the precipitant influx, the polymeric concentration will increase initiating the precipitation of the polymer, as illustrated by point B. Since then, the path enters the dual-phase region, where the system is separated into a polymer-rich (solid) phase and a polymer-poor (liquid) phase. The continuous exchange of solvent and non-solvent induces solidification of the polymer-rich phase and formation of the asymmetric membrane structure, as represented by point C. Finally, the phase inversion process reaches point D, where the solvent is completely exchanged by precipitant and the solid phase (denoted by point S) constitutes the framework structure.

It is important to notice that the precipitation mechanism of phase inversion depends significantly on the types of precipitant, polymer, and solvent. For example, noticeable differences could be observed when comparing the precipitation lines of the dimethyl sulphoxide (DMSO) system and the N-Methyl-2-pyrrolidone (NMP) system, as shown in Figure 2.19.
Figure 2.19: Ternary phase diagrams for (a) DMSO/PESf/Water system and (b) NMP/PESf/Water system. Thick lines denote binodal lines; thin lines denote spinodal lines; dashed lines represent tie-lines; dots represent solidification points. [50, 127, 128]. Copyright © 1988 Elsevier.

The binodal line of the DMSO/polyethersulfone (PESf)/Water system is closer to the initial polymeric solution line (0% water) when compared with that of NMP/PESf/Water system. Assuming negligible differences between the diffusion rates of the two systems, the DMSO/PESf/Water system takes shorter time before the first polymer precipitates, thus yielding marked differences in the morphologies of resultant membranes. The formation mechanisms of the various structures observed in polymeric membranes have been extensively investigated [129, 130]. However, in terms of spinning suspension containing ceramic powders, the ratio between polymers and ceramic particles must be as low as possible (generally ≤10% [131]). Due to the low polymer concentration, the understanding of the formation mechanism for the various structures of polymeric system is of limited use during ceramic membrane fabrication. Viscous fingering phenomenon has been widely accepted to explain the two morphologies observed in ceramic/polymer system, namely micro-
channels and sponge-like structure. Some intensive study has been conducted to investigate the morphology in ceramic membranes [132, 133].

2.5.2.2 Preparation of a spinning suspension

Preparing the spinning suspension (also called the dope) is the first step in wet spinning process. A dope is normally composed of ceramic powder, solvent and additives. Ceramic powder is the major constituent of the spinning suspension. Moreover, it is the most crucial factor that determines the properties and applications of the final hollow fiber membrane. Solvents should own the desired dissolvability towards the adopted organic binder. Furthermore, solvents have to display appropriate exchange rate with precipitants, as the rates of the solvent outflux and precipitant influx significantly influence the macrostructures of the membranes [126]. Additives, including dispersants, organic binders, pore formers, anti-foaming agents, etc., are employed to control and adjust the properties of the spinning suspension. Organic binders, most of which are long-chained polymers, mainly function to form the shape of membrane precursors. They must own adequate solubility in the solvent used. Additionally, binders should be completely burnt out during the subsequent sintering process, without leaving any residues (tar or ash) that are detrimental to the mechanical strength and may well result in defects or cracks. Other additives like dispersants and anti-foaming agents play an important role in controlling the surface interactions and deflocculating soft agglomerates, in order to ensure that particles are sufficiently surrounded by organic binders, thus improving the particle dispersion in the spinning suspension.
A general preparation of a spinning suspension is composed of the following steps. First, add the dispersant into the container and mixing it with the adopted solvent. It should be noted that the amount of the dispersant should be as small as possible to ensure an adequate solid loading rate (the weight percentage of ceramic powder in the spinning suspension). Then, add the selected ceramic powder to the solvent and homogenize the suspension by ball milling. Finally, add the polymer binders and required additives, followed by further milling until binders are completely dissolved and the spinning dope is homogeneous. Moreover, a degassing process, which functions to eliminate the bubbles trapped in the suspension, is required before spinning the dope. Typically, a spinning dope has a solid loading rate between 50-70 wt.% and solvent of 20-40 wt.%. The amount of polymer binder is usually no more than 10 wt.% of that of the ceramic powder, and dispersant only makes up 0.1-1.5 wt.% of the overall dope amount.

### 2.5.2.3 Extrusion of ceramic hollow fiber precursor

Extrusion of the precursor fiber is the second step in the wet spinning process. The morphologies (diameter, cross-sectional structure, thickness, etc.) of the extruded precursors considerably depend on parameters such as dope viscosity, extrusion rate, air gap, and flow rates of internal/external coagulant. Among all the factors, viscosity is an essential parameter that controls the forming behaviour of the tubular shape [131]. The solution exhibits spinnability when its viscosity is higher than 10 Poise (1 Pa.S) and fibers can then be extruded through an orifice [134, 135], as illustrated in Figure 2.20.
It is suggested that the preferrable spinnability is obtained when the rheological behaviour is highly shear thinning but not thixotropic [131]. To ensure a stable spinning process and prevent the extruded precursors from breaking up into droplets, the dope should possess a relatively high viscosity, which could be achieved by adjusting the solid loading and adding adequate additives.

![Figure 2.20: Photographs of a typical triple-orifice spinneret. (a) image from one side; (b) image from bottom; (c) dimensions of the three orifices. Reproduced from [50] with permission from Othman.](image)

Figure 2.21 displays a complete set of apparatus for fabricating hollow fiber membrane. Typically, the extrusion rates of the spinning suspension and the internal/external coagulants need to be controlled by adjusting either syringe pumps or pressure inside the vessels.
After the spinning suspension is compressed through the orifice, the precursor is extruded vertically downwards into the coagulation bath while phase inversion process happens with the presence of internal/external precipitants (usually water), forming two morphologies in the macrostructure, namely micro-channels and sponge-like structure, as illustrated in Figure 2.22. For wet extrusion process, the spinneret is submerged in external chemical bath that leads to the fiber to precipitate as it emerges. In some cases, a variant of wet extrusion, known as dry jet-wet extrusion, is applied during which the suspension is extruded into air and free-falls into an external bath.

Figure 2.21: Schematic diagram of a typical set of spinning apparatus (insert: cross sectional diagram of a dual-orifice spinneret)[131]
Figure 2.22: Example of the micro-channels and sponge-like structure in CGO-NiO hollow fiber membranes.

The formation of micro-channels can be explained by the phenomenon of hydrodynamically unstable viscous fingering, which occurs at the interface between fluids that have different viscosities in the first moments of mixing [132]. In normal conditions, a stable interface between two phases with various viscosities can be preserved. However, the presence of invertible polymer binder leads to an increase in the local viscosity, thus results in a significant tendency for the occurrence of viscous fingering, which initiates the formation of micro-channels. Moreover, the subsequent precipitation of the polymer phase helps to retain the conical structure, as introduced in the previous ‘phase inversion’ section [50]. The dimensions of micro-channels and sponge-like region, such as different thickness and porosity, have a considerable influence on the membranes' mechanical strength, permeation flux, etc. Therefore, it is essential to understand the formation mechanisms so that the morphology can be controlled and ceramic hollow fibers could be well tailored for specific applications [131, 132].

In the case of SOFC applications, the micro-channels which originate from the inner lumen of the tubular hollow fiber are believed to reduce the resistance for fuel
transport, while the sponge-like region provides a notable number of reactive sites, together with the mechanical strength to support the fuel cell. In addition, by adjusting the air gap length, the so-called sandwich structure, which has micro-channels from both inner and exterior surfaces and the sponge-like structure in the middle as illustrated in Figure 2.23, was fabricated and tested [136]. However, it is reported that micro-channels from the outer side reduces the conductivity and mechanical strength, subsequently decreasing the performance of the fuel cell. Therefore, the asymmetric structure with channels only from the inner lumen is more preferable for SOFC applications.

Figure 2.23: Cross-sectional image of a typical sandwich structure

Recent developments on micro-tubular SOFCs based on dry-jet wet extrusion technique are summarized in Table 2.5. The listed content includes cell configuration types, materials for the major cell components, operating conditions and the best cell performance. More detailed information can be found in the references.
Table 2.5: Development of single micro-tubular SOFC based on dry-jet wet extrusion technique

<table>
<thead>
<tr>
<th>Cell configuration</th>
<th>Anode</th>
<th>Electrolyte</th>
<th>Cathode</th>
<th>Cell diameter (mm)</th>
<th>Fuel stream</th>
<th>Operating Temp. (°C)</th>
<th>OCV (V)</th>
<th>Max. power density (W.cm⁻²)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrolyte-supported</td>
<td>Ni</td>
<td>YSZ</td>
<td>LSCF</td>
<td>1.58</td>
<td>H₂</td>
<td>800</td>
<td>1.2</td>
<td>0.018</td>
<td>[100]</td>
</tr>
<tr>
<td>Anode-supported</td>
<td>Ni-YSZ</td>
<td>YSZ</td>
<td>LSM-YSZ</td>
<td>1.70</td>
<td>Humidified H₂</td>
<td>800</td>
<td>~1.0</td>
<td>0.377</td>
<td>[96]</td>
</tr>
<tr>
<td>Anode-supported</td>
<td>Ni-YSZ</td>
<td>YSZ</td>
<td>LSM-YSZ</td>
<td>~6.0</td>
<td>Humidified H₂</td>
<td>800</td>
<td>~1.0</td>
<td>0.848</td>
<td>[137]</td>
</tr>
<tr>
<td>Anode-supported</td>
<td>Ni-YSZ-SDC</td>
<td>YSZ</td>
<td>LSM-YSZ-SDC</td>
<td>1.50</td>
<td>Humidified H₂</td>
<td>800</td>
<td>~1.03</td>
<td>0.78</td>
<td>[97]</td>
</tr>
<tr>
<td>Anode-supported</td>
<td>Ni-YSZ</td>
<td>YSZ</td>
<td>LSCM-SDC-YSZ</td>
<td>1.30</td>
<td>Humidified H₂</td>
<td>850</td>
<td>~1.03</td>
<td>0.513</td>
<td>[138]</td>
</tr>
<tr>
<td>Electrolyte-supported</td>
<td>Ni-YSZ</td>
<td>YSZ</td>
<td>LSM-YSZ</td>
<td>1.90</td>
<td>H₂-Argon</td>
<td>800</td>
<td>0.95</td>
<td>0.018</td>
<td>[102]</td>
</tr>
<tr>
<td>Anode-supported</td>
<td>Ni-YSZ</td>
<td>YSZ</td>
<td>LSM-YSZ-SDC</td>
<td>~1.50</td>
<td>Humidified H₂</td>
<td>900</td>
<td>1.3</td>
<td>1.25</td>
<td>[139]</td>
</tr>
<tr>
<td>Anode-supported</td>
<td>Ni-BZCYYb</td>
<td>BZCYYb</td>
<td>LSCF-BZCYYb</td>
<td>1.60</td>
<td>Humidified H₂</td>
<td>600</td>
<td>1.01</td>
<td>0.26</td>
<td>[140]</td>
</tr>
<tr>
<td>Anode-supported</td>
<td>Ni-BZCYYb</td>
<td>BZCYYb</td>
<td>SSC-BZCYYb</td>
<td>Humidified H₂</td>
<td>Temperature</td>
<td>Current Efficiency</td>
<td>Power Density</td>
<td>Reference</td>
<td></td>
</tr>
<tr>
<td>-----------------</td>
<td>-----------</td>
<td>--------</td>
<td>------------</td>
<td>---------------</td>
<td>-------------</td>
<td>-------------------</td>
<td>---------------</td>
<td>-----------</td>
<td></td>
</tr>
<tr>
<td>Ni-CGO CGO LSCF-CGO 1.40 Humidified H₂</td>
<td>550</td>
<td>0.9</td>
<td>0.8</td>
<td>[98]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni-CGO CGO LSCF-CGO / Humidified H₂</td>
<td>550</td>
<td>0.78</td>
<td>1.1</td>
<td>[142]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni-CGO CGO LSCF-CGO / Humidified H₂</td>
<td>600</td>
<td>0.77</td>
<td>2.32</td>
<td>[143]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni-CGO CGO LSCF-CGO / Humidified H₂</td>
<td>600</td>
<td>0.76</td>
<td>0.69</td>
<td>[144]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni-YSZ ScSZ LSM-ScSZ 1.65 Humidified H₂</td>
<td>800</td>
<td>1.1</td>
<td>1.01</td>
<td>[145]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni-ScSZ ScSZ BCFN-CGO 2.0 Humidified H₂</td>
<td>650</td>
<td>1.1</td>
<td>0.72</td>
<td>[146]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni-ScSZ ScSZ LSM-SDC-SCSZ 1.5 Humidified H₂</td>
<td>650</td>
<td>1.1</td>
<td>0.52</td>
<td>[147]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni-YSZ YSZ LSM-YSZ 1.18 Humidified H₂</td>
<td>800</td>
<td>0.84</td>
<td>0.2</td>
<td>[148]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*BCFN= Ba₀.₉Co₀.₇Fe₀.₂Nb₀.₁O₃₋₅*
2.5.3 Sintering Process

The precursors, which are fabricated via plastic mass ram extrusion or wet extrusion, are composed of ceramic particles, organic binders and additives. Moreover, a heat treatment is necessary for obtaining the desired robustness and structures. This treatment, which is more commonly known as sintering, is a process during which the precursors are converted into dense and rigid ceramic body without melting. The sintering process comprises three steps, namely pre-sintering, thermolysis and final sintering. Detailed discussion will be made in the following sections.

2.5.3.1 Pre-sintering

The pre-sintering step mainly functions to remove the residual liquid introduced during the precursor fabrication or absorbed during the storage and transportation. Moreover, this step helps vaporize the chemically combined water on the particle surface or crystal water within the inorganic phases. Li (2007) has suggested that [131] the absorbed moisture may be preserved in the hollow fiber precursors up to 200 °C. Given that the vapour pressure and different thermal expansion properties of the cell components may well result in stresses that can subsequently lead to cracking or fracturing, the heating rate should be reasonably slow.

2.5.3.2 Thermolysis

Thermolysis is a procedure during which additives, such as organic binders and dispersant, are removed. This step plays an important role in the formation of a
desired macrostructure because incomplete removal of additives can result in defects, thus affecting the membrane properties and cell performances. Take organic binder as an example, a complete burnout of the organic binder, which has the highest weight fraction of the spinning suspension compared with other additives, considerably depends on the composition of the binder, adequate sintering atmosphere, well-controlled heating program, microstructure of the selected binder, and dynamic changes during the removal. In most occasions, thermolysis is conducted between 600-800 °C [50].

2.5.3.3 Final sintering

Final sintering is considered as the major step during which ceramic particles are converted into a rigid and denser ceramic body. Generally, the final sintering initiates when the temperature exceeds approximately one half to two thirds of the melting point of the ceramic material [133]. It is widely accepted that sintering process is composed of three stages, namely the initial stage, the intermediate stage and the final stage. Figure 2.24 illustrates a schematic particle growth process during sintering process.
The initial stage comprises surface smoothing, formation of grain boundaries, and rapid inter-particle neck growth. This process continues until the bulk density reaches 65% of theoretical value while the porosity declines by 12%, and inter-particle neck grows to approximately 40-50% of the particle radius [131]. The intermediate stage, which is usually the major section of the overall sintering procedure, starts when the pores shrink to the equilibrium shapes determined by the surface and interfacial intensions [131]. A considerable drop in the mean porosity was observed during this stage due to the slow grain growth and shrinkage of the open pores formed along the grain boundaries. Meanwhile, the bulk density further increases to approximately 65%-90% of the theoretical value. With regards to the final stage, the grains continue growing rapidly while most pores are assumed to keep shrinking and gradually disappear. Nevertheless, it is also reported that pores that have larger sizes than the grains shrink at a relatively slow speed, which explains the observation that the macrostructure of the fiber precursors, such as the micro-channels above a certain
size, can be perfectly reserved after sintering, whereas the sponge-like structure can be completely dense and gas tight [131, 132].

2.6 Conclusion

In the past two decades, MT-SOFCs have attracted an increasing amount of research interest due to the considerable enhancement in volumetric power density, rapid start-up and adequate long-term stability. Some challenges still remain to be tackled, such as high fabrication cost and difficulties in current collection, which prohibits the micro-tubular design from commercialization. To summarize, new micro-tubular designs addressing process economy, high efficiency and good manufacturability are of great interest. One of the approaches to reduce fabrication cost is lowering the working temperature to the so-called ‘intermediate-temperature’ range, which dramatically extends the range of available materials. Recently, the co-extrusion technique developed in the group could allow multiple layers to be formed in a single-step process, which considerably reduces the numbers of sintering cycle and subsequently the energy consumption. In addition, the phase inversion process employed during fabrication leads to superior versatility in tailoring the morphology. Such benefits, together with the delivery of new nickel-based current collector that reduces the complexity of current collection technique from the limited lumen of micro-tubes, giving rise to great potential for the resultant micro-tubular SOFCs to be applied for mass-scale production and commercial applications.
Reference


D. J. L. Brett, A. Atkinson, D. Cumming, E. Ramirez-Cabrera, R. Rudkin, and N. P. Brandon, "Methanol as a direct fuel in intermediate temperature (500-


[70] L. Lu, Y. Guo, H. Zhang, and J. Jin, "Electrochemical performance of La_2NiO_{4+δ}-La_{0.8}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} composite cathodes for intermediate temperature solid oxide fuel cells," Materials Research Bulletin, vol. 45, pp. 1135-1140, 2010.

[72] W. Zhou, R. Ran, and Z. Shao, "Progress in understanding and development of \( \text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta} \)-based cathodes for intermediate-temperature solid-oxide fuel cells: A review," *Journal of Power Sources*, vol. 192, pp. 231-246, 2009.

[73] Z. Duan, M. Yang, A. Yan, Z. Hou, Y. Dong, Y. Chong, *et al.*, "\( \text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta} \) as a cathode for IT-SOFCs with a GDC interlayer," *Journal of Power Sources*, vol. 160, pp. 57-64, 2006.


[80] Y. JW, M. H, E. M, and I. T, "High-power SOFC using La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-δ}/Ce_{0.8}Sm_{0.2}O_{2-δ} composite film," *Electrochem and Solid-State Letters*, vol. 8, pp. A389-A391, 2005.


[140] F. Zhao, C. Jin, C. Yang, S. Wang, and F. Chen, "Fabrication and characterization of anode-supported micro-tubular solid oxide fuel cell based on BaZr0.1Ce0.7Y0.1Yb0.1O3-δ electrolyte," *Journal of Power Sources*, vol. 196, pp. 688-691, 2011.


[146] C. Yang, C. Ren, L. Yu, and C. Jin, "High performance intermediate temperature micro-tubular SOFCs with Ba0.8Co0.7Fe0.3Nb0.1O3-δ as cathode," *International Journal of Hydrogen Energy*, vol. 38, pp. 15348-15353, 2013.


CHAPTER 3

Single-step Fabrication and Characterisations of Triple-Layer Ceramic Hollow Fibers for MT-SOFCs

Abstract

In this chapter, a phase inversion-assisted co-extrusion/co-sintering technique has been established to fabricate a triple-layer ceramic hollow fiber in one step for micro-tubular solid oxide fuel cells (MT-SOFCs). The fibers developed consist of an exterior symmetric electrolyte layer (CGO), a symmetric anode functional layer (AFL, NiO(40 wt.%)/CGO(60 wt.%)) and an interior asymmetric anode layer (NiO(60 wt.%)/CGO(40 wt.%)) where radical micro-channels provide lower fuel diffusion resistance. In addition to more triple-phase boundary (TPB) for electrochemical reactions, the AFL forms a graded porosity with better conductivity and sintering behaviours, leading to greater bounding characteristics between the electrolyte and anode. The thickness of AFL could be adjusted between 19.1 and 77.5 µm by simply controlling its extrusion rate during co-extrusion, with no cracks or delamination observed after co-sintering. Moreover, the effects of AFL thickness on physical and electrochemical properties of the obtained triple-layer fibers were investigated systematically using various characterization techniques. The results illustrate that the AFL between anode and electrolyte improves the fiber’s

* The work presented in this chapter has been published; T. Li, Z. Wu, and K. Li, Journal of Membrane Science, vol. 449, pp. 1-8, 2014.
mechanical strength and gas-tightness of the electrolyte, whereas resulting in slight drops in electrical conductivity and average porosity of anode and AFL.

3.1 Introduction

Solid oxide fuel cells (SOFCs) are considered as one of the most promising technologies for sustainable generation of clean energy in the near future. As a complete solid-state device, chemical energy in fuels is directly converted into electric power without the intermediate combustion step, resulting in higher efficiencies and lower or zero emissions of pollutants (SO₂ and NOₓ) and greenhouse gases [1-3]. SOFCs can be classified into two major types according to geometric shapes, namely planar design and tubular design [2]. Planar design has received probably the most attention due to its simple cell geometry and good manufacturability, even though the high temperature sealing has been one of the major challenges associated with such design [4]. In contrast, the tubular design shows the superior benefit of easier sealing, which eliminates the necessity of using expensive, high-temperature seals to isolate oxidant from the fuel. However, its power density is limited due to less efficient packing and elongated electronic pathway. Moreover, the manufacturing cost is increased due to more complicated fabrication processes [2, 5]. The micro-tubular design has started to attract research attentions since early 1990s [6-8], due to a number of advantages such as rapid start-up/shut-down, high power density, good cycling performance and thermal shock resistance. These features make it suitable for portable applications and auxiliary power units (APUs) [9].
Initially, the incorporation of different components of a micro-tubular SOFC was achieved by many repetitions of coating and sintering, thus the overall multi-step fabrication process is time and cost-consuming. In addition, there are some other potential challenges such as inconsistent adhesion between different components, and consequently soaring ohmic and overpotential resistance [10, 11]. In contrast, the new phase inversion-assisted co-extrusion technique enables the fabrication of multi-layer micro-tubes in a single step, which dramatically simplifies the process, with improved adhesion between layers. Instead of repeated sintering conventionally used, one co-sintering step would finalize the structure, as long as mismatch in sintering behaviour between layers can be controlled and minimized [9]. Advantages of this technique have been demonstrated in fabricating dual-layer hollow fibers for micro-tubular SOFCs [12, 13].

In addition to the progress in novel feasible and cost-effective fabrication techniques, the development of micro-tubular SOFC design is also of considerable importance to realize larger scale applications. In order for improved diffusion of gaseous fuels with enlarged triple-phase boundary (TPB) inside anode, the concept of an anode functional layer (AFL) was first proposed by Virkar in 2000 [14], during his attempts to decrease the activation/concentration polarizations by employing a graded anode. By controlling the properties of the slurry, the substrate layer is coarser with a bigger pore size and higher porosity in order to facilitate the transports of gaseous fuels and exhaust gases, which helps to reduce the concentration polarization. Furthermore, a finer structure has been introduced in the subsequent layer for more reactive sites so that the activation polarization may well be inhibited. In 2002, Muller [15] reported the fabrication of a continuously graded
multi-layer structure, during which anode layers with different compositions were pasted onto an electrolyte substrate by screen printing. In addition to enlarging the TPB, such an AFL also helps in matching the thermal extension coefficient (TEC) between anode and electrolyte, which helps to improve the long-term stability of SOFCs. AFL has received an increasing level of interest in the past decade, during which some other fabrication techniques have been investigated, such as ink-jet printing [16], electrophoretic co-deposition [17] and die pressing [18]. All these attempts show that AFL results in a considerable improvement in cell performances. However, the thickness of AFL was also reported to be critically important. A thicker AFL is commonly obtained by increasing the number of coatings. Work by Chen [11] has shown that a thin AFL (5 µm), which was fabricated by slurry spin coating, could effectively promote the power density by 15%, while thicker AFLs (10 µm and 15 µm) reduce the cell performance. This is probably due to the defects and cracks formed during repeated sintering and therefore a poorer contact at the interfaces.

In this chapter, a novel co-extrusion technique has been established during which triple-layer ceramic hollow fibers were successfully fabricated in a one-step process by using a quadruple-orifice spinneret. Uniform and defect free AFL with varied thicknesses is formed continuously by adjusting its extrusion rate without introducing additional interfaces. The effects of AFL thickness on various physical properties were investigated, including porosity, gas-tightness, mechanical strength and electrical conductivity. The results of these preliminary studies could well provide comprehensive understanding and insights before a systematic performance test is conducted.
3.2 Experimental

3.2.1 Materials

Cerium-gadolinium oxide (Ce$_{0.9}$Gd$_{0.1}$O$_{1.95}$ (CGO), surface area 35.6 m$^2$ g$^{-1}$, mean particle size (d50) 0.1-0.4 μm) and nickel oxide (NiO, surface area 3.7 m$^2$ g$^{-1}$, mean particle size (d50) 0.5-1.5 μm) are commercially available (NexTech Materials Ltd. (Ohio)), and were used as supplied. Polyethersulfone (PESf) purchased from Radel A-300, Ameco Performance (USA), and dimethyl sulfoxide (DMSO) purchased from VWR International, LLC were used as the polymer binder and the solvent, respectively. Polyethyleneglycol 30-dipolyhydroxystearate (Arlacel P135, Uniqema) was used as the dispersant of the spinning suspension. During the spinning, de-ionized water and tap water were the internal and external coagulants, respectively.

3.2.2 Fabrication of anode/AFL/electrolyte triple-layer hollow fibers

Three separate spinning suspensions were prepared. Detailed compositions of different spinning suspensions are listed in Table 3.1. By power mixing 60 wt% of NiO with CGO in the anode suspension, sufficient electrical conductivity can be obtained without sacrificing too much robustness, as CGO phase is the major contributor towards the mechanical strength. The ceramic powders were first mixed with solvent (DMSO) and dispersant, and milled for 3-4 days (JARMILL, Gladstone Engineering. LTD, UK). The milling balls have two different sizes of 10 mm and 15 mm in diameter, and the rolling speed was adjusted between 60-120 rpm. The mixing continued for a further 2-3 days after adding the polymer binder (10% of the total weight of ceramic powders) in order to ensure homogeneous spinning.

111
suspending suspensions. Before being transferred into stainless steel syringes, all three spinning suspensions were degassed under vacuum with stirring, thereby eliminating air bubbles trapped inside. The triple-layer precursor fibers were fabricated by a phase-inversion assisted co-extrusion technique. The bore fluid and the suspensions for different cell components were loaded into four stainless steel syringes separately and simultaneously extruded through a custom-designed quadruple-orifice spinneret. The new spinneret design contains four feed inlets for various components. All suspensions go through a distributor and corresponding guiding channels, and concentrate at the quadruple-orifice exit. This co-extrusion process is illustrated in Figure 3.1. The extrusion rates of all the components were precisely controlled by syringe pumps (Harvard PHD22/200 HPsi and KDS410). The operating conditions adopted during spinning are summarized in Table 3.2.

**Table 3.1: Compositions of the spinning suspensions for triple-layer hollow fibers.**

<table>
<thead>
<tr>
<th></th>
<th>Anode</th>
<th>AFL</th>
<th>Electrolyte</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ceramic powders compositions</td>
<td>NiO</td>
<td>CGO</td>
<td></td>
</tr>
<tr>
<td>(wt.%)</td>
<td>40.1</td>
<td>26.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>27.0</td>
<td>40.5</td>
<td>58.0</td>
</tr>
<tr>
<td>Polymer binder (PESf)</td>
<td>6.69</td>
<td>6.76</td>
<td>5.80</td>
</tr>
<tr>
<td>Dispersant (Arlacel P135)</td>
<td>0.16</td>
<td>0.14</td>
<td>0.24</td>
</tr>
<tr>
<td>Solvent (DMSO)</td>
<td>26.2</td>
<td>25.5</td>
<td>35.9</td>
</tr>
</tbody>
</table>
Prior to the co-sintering, triple-layer precursor fibers were cut to a length of 40 cm and dried at room temperature for 2-3 days. The sintering was undertaken using a tubular furnace (CARBOLITE). Figure 3.2 displays the temperature profile adopted here, which is based on our previous studies [5].
The temperature was first increased to 400 °C at a rate of 2 °C min⁻¹, followed by a dwelling stage of 1 hour, in order to remove the residual liquid introduced during the fabrication of precursor fibers. Then the temperature was raised to 800 °C at a rate of 2 °C min⁻¹ and held for 2 hours. This procedure helps to eliminate additives, such as organic binders and dispersant. Finally, the furnace was heated up to 1500 °C at a rate of 15 °C min⁻¹, followed by another dwelling stage of 12 hours. This sintering step is critically important to the integrity of the resultant fiber, because during this step the ceramic particles are progressively converted into a more rigid and denser ceramic body [19]. In addition, the extraordinarily high heating rate (15 °C min⁻¹) was adopted to minimize the period of time during which the shrinkage rate difference is most significant. As discussed in Section 3.3.1, there exists significant difference in
the shrinkage rates of anode, ALF and electrolyte between the temperature ranges of 850-1400 °C. Therefore, a relatively high heating rate is needed to prohibit the generation of interior stress. After the sintering, the furnace was cooled down to room temperature at 3 °C min⁻¹.

For some post-sintering characterizations, the co-sintered triple-layer hollow fibers need to be reduced, converting NiO into Ni. The reduction was conducted in a pure hydrogen atmosphere by packing fibers into a stainless steel tube placed in a CARBOLITE furnace (MTF 12/25/250). Initially, argon (~30 ml min⁻¹, 25 °C, 1 atm) was used to expel air inside the tube, until the furnace temperature reached 550°C (heating rate of 5 °C min⁻¹). Then the argon flow was changed to a pure hydrogen flow (~20 ml min⁻¹, 25 °C, 1 atm) and the reduction lasted for 2.5 hours. After the reduction, the hydrogen flow was changed back to argon flow until the furnace temperature was reduced to room temperature at a rate of 5 °C min⁻¹.

3.2.3 Characterizations

Prior to the fabrication of the triple-layer ceramic hollow fibers, sintering behaviours were studied using a dilatometer (NETZSCH, model DIL 402C) to determine suitable compositions of each cell component and appropriate sintering profiles. Ceramic powders of various percentages were first mixed in ethanol, followed by a drying process at 80 °C. Then the powder mixtures were pressed into cubes of 6mm×6mm×6mm using hydraulic pressure of 2 tonnes. The tests were undertaken in static air and the chamber was heated up to 1500 °C, dwelled for 10 hours and then cooled down to room temperature.
Morphology study was conducted using a scanning electron microscope (SEM) for both precursors and sintered fibers. Prior to the observation, samples were placed on a metal holder and gold-coated under vacuum for 1.5 min at 20 mA (EMITECH Model K550). High-resolution SEM images at varying magnifications were obtained using both secondary electrons imaging (SEI) and backscattered electrons (BSE) mode (JEOL JSM-5610).

The average porosity of anode and AFL was investigated by Archimedes method using helium pycnometry (Micromeritics Accupyc 1330). The porosity ($\varepsilon$) was calculated using the following equations [20]:

$$\varepsilon = \frac{\rho_{\text{pyc}} - \rho_{\text{fiber}}}{\rho_{\text{pyc}}}$$

(3.1)

$$\rho_{\text{fiber}} = \frac{4m_{\text{sample}}}{\pi(D_o^2 - D_i^2)l_{\text{sample}}}$$

(3.2)

where $\rho_{\text{pyc}}$ denotes the skeleton density (g cm$^{-3}$) measured by pycnometry, $m$, $l$, $D_o$ and $D_i$ represent the mass, length, outer and inner diameters of the sample (cm), respectively. In addition, an assumption has been made here that each sample has a uniform structure with identical dimension all through the fiber.

The mechanical strength of the hollow fibers was measured by a tensile tester (Instron Model 5544) with a load cell of 5 kN. This measurement was conducted via a three-point bending method, as illustrated in Figure 3.3. Fiber samples were positioned onto two sample holders with a distance of 30 mm. 5 samples were taken for each data point of the bending test for each type of membrane with standard deviations of less than 15 %. The bending strength ($\sigma_b$) was calculated based on the following equation [21]:

$$\sigma_b = \frac{6F}{\pi D_i^2}$$
\[ \sigma_F = \frac{8FLD_o}{\pi(D_o^4 - D_i^4)} \]  

(3.3)

where \( F \) is the measured force when a fracture occurs (N), \( L \), \( D_o \) and \( D_i \) represent fiber length (m), the outer and inner diameters of the fiber (m), respectively.

![Figure 3.3: Schematic diagram of the apparatus of three-point bending test.](image)

The gas-tightness property of electrolyte was investigated using a N\(_2\) penetration method described elsewhere [22]. A pressure gauge was adopted to monitor the pressure change of the permeation set-up, as illustrated in Figure 3. 4. 5 samples were taken for each data point of the permeance test for each type of membrane with standard deviations of less than 10 %. The N\(_2\) permeance was calculated based on the pressure change over a certain length of time (5 hours).
\[ P = \frac{V}{RT \times A_m t} \ln \left( \frac{p_0 - p_a}{p_i - p_a} \right) \]  \hspace{1cm} (3.4)

\[ A_m = \frac{2 \pi (R_o - R_i) L}{\ln \left( \frac{R_o}{R_i} \right)} \]  \hspace{1cm} (3.5)

where \( P \) denotes the permeance of the test membrane (mol m\(^{-2}\) s\(^{-1}\) Pa\(^{-1}\)); \( V \) is the volume of the test vessel (m\(^3\)); \( R \) is the gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)); \( T \) denotes the measured temperature (K); \( p_0, p_a, p_f \) represent the initial, atmospheric and final pressure readings (Pa), respectively. \( A_m \) is the membrane area (m\(^2\)). \( R_o \) and \( R_i \) denote the outer and inner radiiuses of the electrolyte, respectively; \( L \) is the length of the fiber and \( t \) is the time for the measurement (s).

**Figure 3.4:** Schematic diagram of the set-up for gas-permeation test. 1) Gas cylinder; 2) Pressure regulator; 3) Valve; 4) Test vessel; 5) Fiber holder; 6) Pressure gauge.

The electrical conductivity of anode and AFL was measured by a modified 4-point direct current (DC) method established by Droushiotis et al. [23], as can be seen in
Figure 3. 5. The dual-layer anode and AFL fibers were fabricated under identical conditions as anode/AFL/electrolyte triple-layer hollow fibers except for the absence of electrolyte outer layer. A varying voltage (5 V, 7.5 V, 10 V) is applied between working electrode (WE) and reference electrode (RE) across a 100 ohm resistance to generate a precise current (50 mA, 75 mA, 100 mA). Counter electrode functions to complete the current circuit. Voltage drops due to the fiber (50 mm in length) resistance were measured using a multimeter. 5 samples were taken for each data point of the conductivity test for each type of membrane with standard deviations of less than 10 %. The resistance was calculated based on the linear fits of generated I-V data and bulk effective conductivity \( \sigma_{\text{fiber}}, \text{ S cm}^{-1} \) can be obtained from the equation below:

\[
\sigma_{\text{fiber}} = \frac{L_{\text{fiber}}}{A_{\text{fiber}} \times R_{\text{fiber}}}
\]

(3.6)

\[
A_{\text{fiber}} = \frac{\pi}{4} \left( D_o^2 - D_i^2 \right)
\]

(3.7)

where \( A_{\text{fiber}} \) denotes the cross-sectional area of current flow (cm²); \( L_{\text{fiber}} \) represents fiber length (ca. 5 cm); \( R_{\text{resist.an.el}} \) is the fiber resistance.
3.3 Results and Discussion

3.3.1 Sintering behaviours

Co-sintering of multi-layer ceramic hollow fibers is always challenging, especially when each layer is different in materials and compositions, showing different sintering behaviours. Prior to the co-sintering of triple-layer hollow fibers, sintering behaviours of materials involved need to be studied. Figure 3.6 illustrates the sintering curves of pure CGO (electrolyte), NiO, 40 wt.%CGO-60 wt.%NiO (anode), and 60 wt.%CGO-40 wt.%NiO (AFL).
As can be seen, the final shrinkages \( \frac{dL}{L_0} \) of the anode and AFL were 11.0\% and 12.5\%, respectively, and were lower than CGO (17.5\%) and NiO (14.0\%). This indicates that interactions between the two phases during the heat treatment tend to hinder the sintering of each phase. Such explanation agrees with the curves of sintering rate, as shown in Figure 3. 7.
Figure 3.7: Sintering rate curves of NiO, CGO and the materials of AFL and anode. (Heating rate: 5 °C min⁻¹).

The maximum sintering rate of CGO turned up at a temperature that is approximately 180 °C lower than NiO. This implies that, for a mixture of CGO and NiO, when CGO starts to shrink at a lower temperature and a higher shrinking rate, NiO always hinders the sintering of CGO. While at a certain temperature point when shrinking rate of NiO exceeds CGO, it is hindered by CGO again. This helps to explain the dual-peak sintering rate curves of both anode and AFL. Meanwhile, sintering rate peaks of anode and AFL are less in intensities and shift towards higher temperatures, when compared with CGO and NiO, which is also a result of interactions between the two phases during sintering. On the other hand, the insertion of an AFL helps in reducing the mismatch between the sintering behaviours of anode (11.0%) and electrolyte (17.5%), and could subsequently improve the densification of electrolyte.
3.3.2 Macrostructure and porosity

Figure 3.8: SEM images (secondary electron imaging (SEI) mode) of the fiber with the AFL extrusion rate of 3 ml min\(^{-1}\): (A) precursor fiber, (B) sintered fiber and (C) reduced fiber; (I) whole views and (II) cross-section.

Figure 3.8 presents a typical structure of the anode/AFL/electrolyte triple-layer hollow fiber developed, in which AFL extrusion rate of 3 ml min\(^{-1}\) was selected. As can be seen, precursor fibers, sintered fibers and reduced fibers show an
asymmetric anode structure consisting of a sponge-like layer supported on micro-channels. The micro-channels that markedly facilitate the diffusion of fuel gases into the anode layer [24] were perfectly preserved after the co-sintering and reduction. Although the anode and AFL were densified together with the exterior electrolyte during co-sintering, the following treatment in hydrogen reduced NiO into Ni and turned both asymmetric anode layer and symmetric AFL into a porous structure, generating TPB length for such SOFC design.

Some tiny micro-channels originating from the exterior surface can be observed in Figure 3. 8 B-II and C-II, which is not favourable to the mechanical strength, gas-tightness, and ionic conductivity of the micro-tubular design. But they are considered not significant in affecting cell performance [25], and can be eliminated by adjusting co-extrusion parameters, such as a higher flow rate of internal coagulant and longer air gap [26]. In order for a clearer observation on the triple-layer structure, SEM images of backscattered electrons (BSE) mode are shown in Figure 3. 9. The larger and darker particles denote NiO, while the smaller and whiter one is CGO. Based on the material composition in each layer, the interface between layers is distinguishable, and as a result, the thicknesses of anode, AFL and electrolyte can be estimated. The estimation was repeated at least 5 times for thickness of each component with standard deviations of less than 10%.
Layer thicknesses of other triple-layer fibers fabricated using different AFL extrusion rates (0-5 ml min⁻¹) are measured in the same way, and presented in Figure 3.10. As can be seen, AFL decreases from approximately 77.5 μm to 19.1 μm when the extrusion rate was reduced from 5 ml min⁻¹ to 1 ml min⁻¹. It should be noted that, when the extrusion rate of AFL was further reduced to 0.5 ml min⁻¹, the AFL can hardly be distinguished from anode in SEM images, due to the relatively big particle size of NiO.

![Figure 3.9: SEM images (backscattered electrons (BSE) mode) of (a-I) whole view, (a-II) cross-section and (a-III) a higher magnification of cross-section of the sintered triple-layer hollow fibers, using the AFL extrusion rate at 3 ml min⁻¹.](image)

![Figure 3.10: Effect of AFL extrusion rate on the thicknesses of anode, electrolyte and AFL.](image)

125
It can also be observed from Figure 3.10 that the thicknesses of electrolyte and anode slightly reduce with the increasing extrusion rates of AFL, although their extrusion rates are remained constant during the co-extrusion. This is due to the more elongation of precursor fibers when a higher AFL extrusion rate is used. With the increasing AFL extrusion rate, the precursor fiber becomes heavier, dragging the precursor fiber (especially the part within air gap) into the external coagulation bath. While for AFL, the effects of increased extrusion rate overweight the elongation, leading to a consistent increase in its thickness. When the AFL extrusion rate is reduced to zero, forming an anode/electrolyte dual-layer fiber, anode and electrolyte layers are both thinner than the triple-layer one with AFL extrusion rate of 1 ml min⁻¹. This could be linked to the interactions between the layers during the co-extrusion. The AFL has approximately the same solid loading (~67%) as the anode spinning suspension. Due to the higher weight percentage of CGO powder with smaller particle size, the spinning suspension of AFL is more viscous than anode, making it another major factor affecting the thicknesses of electrolyte and anode.

It is generally accepted that anode, together with AFL, not only provides mechanical strength, but also functions as the reaction sites for electrochemical oxidation of the fuels. However, it is difficult to balance between facilitating fuel transport and providing more TPB, both of which are the major factors that affect polarization resistance and subsequently the cell performance. Dong has suggested an ideal porosity range of anode based on a seepage theory, which is between 30% and 40% [27]. In this study, average porosity of anode and AFL was studied using a helium pycnometer and the results are illustrated in Figure 3.11.
As can be seen from the figure, the average porosity slightly decreased with the increasing of AFL thickness and the results of most samples were within the ideal range, except for the ones with AFL extrusion rates higher than 4 ml min⁻¹. This agrees with the composition of AFL that contains a higher percentage of CGO. In addition, as introduced before, the mean size of NiO particle (0.5-1.5 μm) is approximately 3-5 times bigger than CGO particle (0.1-0.4 μm). Therefore, the increasing CGO content in AFL contributes to more TPB and subsequently less polarization.

### 3.3.3 Mechanical and gas-tightness properties

Mechanical strength is one of the essential physical parameters determining life time of cells. In this study, the effect of AFL thickness on mechanical property was investigated using a three-point bending method, and is illustrated in Figure 3. 12.
As can be seen, a direct proportional relationship was observed between fracture force and AFL thickness. For the sample with the thickest AFL (approximately 80 microns), the fracture force (10.6 N) is more than twice of the one without AFL (4.6 N). Meanwhile, mechanical strength keeps increasing when the AFL thickness is increased from approximately 20 to 80 μm. Although the fracture force of the sample without AFL is less than the one with AFL of approximately 20 μm, its mechanical strength is higher due to the smaller diameter. Meanwhile, the obtained mechanical strength is quite comparable with reported dual-layer ceramic hollow fibers for micro-tubular SOFCs [5, 12].

![Figure 3.12: Bending strength and fracture force as a function of different AFL thicknesses.](image)

Gas tightness of electrolyte layer is critically important to fuel cell performance. The electrolyte of SOFC has to be impermeable to gases to prevent direct contact
between the gaseous fuels and oxidants. According to results in Figure 3.13, the nitrogen permeability of the dual-layer counterpart (no AFL) was approximately $6.43 \times 10^{-9}$ mol m$^{-2}$s$^{-1}$Pa$^{-1}$. This value decreased to $9.38 \times 10^{-10}$ mol m$^{-2}$s$^{-1}$Pa$^{-1}$ when the extrusion rate of AFL was 1 ml min$^{-1}$; but increased to $1.44 \times 10^{-9}$ mol m$^{-2}$s$^{-1}$Pa$^{-1}$, $1.85 \times 10^{-9}$ mol m$^{-2}$s$^{-1}$Pa$^{-1}$, $2.3 \times 10^{-9}$ mol m$^{-2}$s$^{-1}$Pa$^{-1}$ and $3.0 \times 10^{-9}$ mol m$^{-2}$s$^{-1}$Pa$^{-1}$ while the extrusion rate was gradually increased to 2, 3, 4 and 5 ml min$^{-1}$, respectively (corresponding electrolyte thicknesses were 29.8, 27.4, 24.7, 19.2 μm).

![Figure 3.13: Gas-tightness property as a function of different AFL thicknesses.](image)

These results are comparable with some previous studies [12]. It can be concluded that introducing an AFL contributes to better gas-tightness property of electrolyte. By selecting the sample that had an AFL extrusion rate of 2 ml min$^{-1}$, it can be observed that its gas tightness was several times better than the dual-layer counterpart while
having similar electrolyte thickness of 25 μm. This improvement proves that introducing an AFL can minimize the mismatch between the sintering behaviours of anode and electrolyte, thus facilitating the densification of electrolyte. Moreover, an inverse proportionality was illustrated between gas-tightness and the extrusion rates of AFL, implying that the thickness of electrolyte appeared to be major factor that determined gas-tightness property. According to Tan’s work [22], hollow fiber membranes could be considered fully gas-tight if the nitrogen permeability is < 10⁻¹⁰ mol m⁻² s⁻¹ Pa⁻¹. In this study, the non-ideal gas tightness of the hollow fibers could be due to the unexpected micro-channels originated from the outer surface, as discussed in Section 3.3.2.

3.3.4 Electrical conductivity

Electrical conductivity is one of the essential properties of anode and AFL as they not only provide reaction sites for electrochemical oxidation, but also function as a current collector. It is widely accepted that electrical conductivity is mainly contributed by the Ni phase in the anode and AFL, as the CGO phase has negligible electrical conductivity. In this study, the electrical conductivity measurement was conducted using a 4-point DC technique at room temperature. Figure 3.14 illustrates the obtained conductivity results as a function of thickness percentage of AFL in the whole fiber (anode and AFL).
As shown in the figure, electrical conductivity decreases with the increasing thickness percentage of AFL. This could be due to the lower percentage of NiO in the AFL (40%) compared with anode (60%), which subsequently leads to poorer continuity of Ni phase and decreased electrical conductivity. This trend is in good agreement with the work of Othman et al.[28], in which the relationship between anode conductivity and the thickness percentage of micro-channels was investigated. They suggested that the shorter the micro-channels, the better the conductivity. This is due to the calculation that micro-channels shows poorer conductivity than sponge-like region. Even though introducing an AFL appears to lower the overall electrical conductivity, they compare quite well with other studies. For example, the conductivity of Ni-CGO hollow fiber fabricated via wet spinning was around 14200 S cm⁻¹[5]. The satisfactory electrical conductivity suggests that Ni particles in anode and AFL tend to construct a continuous phase, which could help

**Figure 3.14:** Electrical conductivity of reduced anode/AFL dual layer hollow fibers as a function of thickness ratio of AFL / (AFL+Anode).
reduce ohmic resistance in the electrochemical characterization of a complete cell in the next-step work.

It is worth noticing that the overall performance of SOFC is resulted from several factors, such as thickness and micro-structure of each layer or cell component. As discussed before, the anode layer becomes thinner and average porosity is reduced with the increasing thickness of AFL, while the electrolyte layer becomes thinner but less gas-tight. All these parameters need to be considered before a proper evaluation of overall performance can be delivered. Therefore, the research has been focused on the effects of fabrication parameters, such as AFL extrusion rate, on micro-structures and physical properties of resultant hollow fibers in this chapter.

### 3.4 Conclusions

A phase-inversion assisted co-extrusion/co-sintering technique has been successfully established via fabricating anode/AFL/electrolyte triple-layer ceramic hollow fibers. By adjusting the extrusion rate of AFL during co-extrusion, different AFL thicknesses could be obtained with great adhesion between different layers. Two typical morphologies in anode layer, namely micro-channels and sponge-like structure were observed in the precursors and subsequently perfectly preserved during the co-sintering. Introducing an AFL between the anode and electrolyte improves the gas-tightness of electrolyte and mechanical strength. In addition, appropriate electrical conductivity has been preserved, which suggests that a continuous Ni phase was constructed within such hollow fibers. Although micro-channels from the outer surface were observed, which is unfavourable to the gas-tightness of electrolyte, modifications could be applied during the fabrication to
eliminate such voids, such as increasing the viscosity of spinning suspensions, using a larger air gap or increasing the flow rate of internal coagulant. As discussed before, adjusting the thickness of AFL leads to the variation in other components’ thicknesses, which subsequently results in some trade-off effects. For instance, the anode layer becomes thinner and average porosity is reduced with the increasing thickness of AFL, while the electrolyte layer becomes thinner but less gas-tight. It is worth noticing that all the parameters listed above could affect the overall performances and need to be considered before a proper evaluation of performance can be delivered. Therefore, the next chapter (Chapter 4) will be concentrated on improved control over the fabrication process, such as maintaining the electrolyte thickness when the extrusion rate of AFL is adjusted and eliminating the micro-channels from outer surface for better gas-tightness. A complete micro-tubular single cell could then be constructed and systematic studies could be undertaken to investigate the effects of AFL thickness on electrochemical performances.

References


Chapter 3  Single-step Fabrication and Characterisations of Triple-Layer Ceramic Hollow Fibers for MT-SOFC


CHAPTER 4

Co-extrusion of Electrolyte/Anode functional layer/Anode Triple-layer Hollow Fibers for MT-SOFCs

–Electrochemical Performance Study

Abstract

In this chapter, the effects of an anode functional layer (AFL) with controlled thickness on physical and electrochemical properties of a micro-tubular SOFC have been systematically studied. A series of electrolyte/AFL/anode triple-layer hollow fibers with controllable AFL thicknesses (16.9-52.7 μm) have been fabricated via a single-step phase inversion-assisted co-extrusion technique. Both robustness of the cell and gas-tightness of the electrolyte layer are considerably improved by introducing the AFL. The fracture force of the sample with the thickest AFL (9.67 N) almost doubles when compared to the electrolyte/anode dual-layer counterpart (5.24 N). Gas-tightness of the electrolyte layer is also considerably increased as AFL contributes to better-matched sintering behaviours between different components. Moreover, the formation of an AFL simultaneously with electrolyte and anode significantly improves the cell performances. The sample with the thinnest AFL (approximately 16.9 μm, 6% of the total anode thickness) leads to a 30% (from 0.89 to 1.21 W cm⁻²) increase in maximum power density, due to increased triple-phase

* The work presented in this chapter has been published;
boundaries (TPB). However, further increase in TPB from a thicker AFL is less effective for improving the cell performance, due to the substantially increased fuel diffusion resistance and subsequently higher concentration polarization. This indicates that the control over the AFL thickness is critically important in avoiding offsetting the benefits of extended TPB and consequently decreased cell performances.

4.1 Introduction

Solid oxide fuel cells (SOFCs) are a solid-state device that electrochemically converts the chemical energy in the fuels into electric power. The high working temperatures (850-1000 °C) result in high-quality excess heat, which can be further used to drive additional gas turbines or be stored in medium, thus leading to very high system efficiency [1-3]. Among various geometric designs, the micro-tubular design, which was first reported in 1990s, has attracted an increasing level of interest by exhibiting a number of desirable characteristics, such as high volumetric power density, superior thermal shock resistance and rapid start-up/shut down [4, 5]. However, there exist several challenges, such as a limited range of appropriate materials due to high working temperatures, and a lack of cost-effective manufacturing routes, which prohibit its development from early lab-scale research to commercially viable products. Therefore, there is a need to reduce the working temperature to the so-called intermediate range (500-750 °C), as defined by Steele [6], and to apply new technologies for a more economical fabrication process.
Lowering the working temperature to the intermediate temperature range markedly extends the range of available materials, which to some extent allows cheaper fabrication, interconnects and balance-of-plant (BoP) components in particular[7]. Another benefit from lowering the working temperature is a further decrease in the start-up/shut-down time, which makes this desirable advantage of micro-tubular geometric design more prominent. Co-extrusion technique was first applied in polymeric membrane systems in 1980s for more straightforward and economic fabrication [8, 9]. However, in terms of ceramic membrane system, there exist other concerns such as mismatch between rheological properties during spinning and shrinking behaviours during sintering. It was not until recent years when co-extrusion has been adopted in fabricating multi-layer micro-tubes for SOFC applications [10-15]. This technique has illustrated a number of desired characteristics over conventional multi-step processes that comprise repetitions of coating and sintering, such as great process control, better tailoring over morphologies and reduced fabrication costs. Moreover, this technique enables better adhesion between cell components, leading to a reduced ohmic loss and contact resistance. Therefore, co-extrusion has the potential to become a reliable and economical technique for mass-scale production.

The feasibility of using a phase inversion-assisted co-extrusion technique to fabricate triple-layer ceramic hollow fiber has been established in previous research [16]. In this chapter, a more controllable fabrication has been realized and the effects of AFL thicknesses on electrochemical performances have been systemically investigated. The triple-layer structure includes anode, electrolyte and an anode functional layer (AFL) between them. The benefits of employing an AFL have been
well proved and accepted, such as to introduce a gradient in conductivity and shrinkage behaviours, as well as to enlarge the triple phase boundary (TPB) by the fine structure and subsequently improve the performance of MT-SOFCs. On the other hand, the reduced porosity in this fine structure also tends to introduce considerable resistance towards the transport of fuel gases and subsequently increase the concentration polarization [17, 18]. In previous studies, a thicker AFL was normally obtained by a second coating process, forming an interface inside AFL [18, 19]. This can lead to additional issues such as problematic adhesion between layers and increased resistance at the interface between multiple coatings, which subsequently offset the benefits from introducing a thicker AFL. In this study, the single-step technique enables the fabrication of ‘interface-free’ AFL when adjusting the thicknesses, which enables the effects of a wider range of AFL thicknesses to be investigated in a more systematic way.

4.2 Experimental

4.2.1 Materials

Cerium-gadolinium oxide (Ce$_{0.9}$Gd$_{0.1}$O$_{1.95}$ (CGO), with surface area 30-40 m$^2$ g$^{-1}$, mean particle size (d50) 0.1-0.4 μm), nickel oxide (surface area 3-7 m$^2$g$^{-1}$, mean particle size (d50) 0.5-1.5 μm) and lanthanum strontium cobalt ferrite (La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_3$ (LSCF), surface area 11.79 m$^2$ g$^{-1}$) are commercially available from NexTech Materials Ltd. (Ohio), and they were used as supplied. N-methyl-2-pyrrolidone (NMP), ethanol and dimethyl sulfoxide (DMSO) (99%+, VWR International, LLC) were used as solvent. Polyethersulfone (PESf) purchased from
Radel A-300, Ameco Performance (USA) and Polyethylene glycol 30-dipolyhydroxystearate (Arlacel P135, Uniqema) were used as the polymer binder and the dispersant of the spinning suspensions, respectively. During the spinning, de-ionized water and tap water were adopted as the internal and external coagulants, respectively.

4.2.2 Fabrication of anode/AFL/electrolyte triple-layer hollow fibers

Details of the fabrication process have been described in previous chapter. Three spinning suspensions were first prepared. The CGO/NiO ratios in anode and AFL suspensions were 2:3 and 3:2, respectively. Previous research has suggested that using a mixture of NMP and ethanol as the solvent could tailor anode morphology to facilitate fuel transport [12, 20]. Therefore, NMP containing 5% ethanol was used as solvent for anode suspension and DMSO was used as the solvent for AFL and electrolyte suspensions. The ceramic powders were first mixed with solvent and dispersant, and stirred on a roll miller for 3-4 days to disperse powders uniformly. The polymer binder (10% of the total weight of ceramic powders) was subsequently added into the mixture and a further mixing of 4-5 days was undertaken to dissolve the polymer and guarantee the homogeneity of spinning suspensions. Prior to the co-extrusion process, a degassing process was conducted at room temperature, during which all three spinning suspensions were positioned in a vacuum chamber under stirring to remove trapped air bubbles which may disrupt the continuity of spinning. After degassing, precursor fibres were fabricated via a phase inversion-based co-extrusion technique, in which all components were simultaneously
extruded through a custom-designed quadruple-orifice spinneret, as illustrated in Figure 4. 1.

Figure 4. 1: Photographic pictures of (a) quadruple-orifice spinneret; (b) example of triple-layer precursors.

The extrusion rates of each component were accurately controlled by syringe pumps (Harvard PHD22/200 HPsi and KDS410). Detailed compositions of three spinning suspensions and their corresponding extrusion rates adopted during spinning are summarized in Table 4. 1.

The co-sintering was undertaken at 1500 °C for 12 hours using a tubular furnace (CARBOLITE) after triple-layer precursor fibers were cut to a certain length (~15 cm) and dried at room temperature, and the three-step sintering profile was described in previous chapter [11]. For some post-sintering characterizations, the co-sintered triple-layer hollow fibers need to be reduced, converting NiO into Ni. The reduction was conducted at 550°C in pure hydrogen atmosphere for 2.5 hours.
Table 4.1: Compositions and co-extrusion parameters of the spinning suspensions for triple-layer hollow fibers.

<table>
<thead>
<tr>
<th>Spinning components</th>
<th>Anode (wt.%)</th>
<th>AFL (wt.%)</th>
<th>Electrolyte (wt.%)</th>
<th>Bore fluid (H₂O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiO (wt.%)</td>
<td>42.0</td>
<td>25.4</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>CGO (wt.%)</td>
<td>27.9</td>
<td>38.1</td>
<td>60.0</td>
<td>/</td>
</tr>
<tr>
<td>Polymer binder (wt.%)</td>
<td>7.00</td>
<td>6.35</td>
<td>6.00</td>
<td>/</td>
</tr>
<tr>
<td>Dispersant (wt.%)</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>/</td>
</tr>
<tr>
<td>Solvent (wt.%)</td>
<td>NMP +5% Ethanol</td>
<td>DMSO</td>
<td>DMSO</td>
<td>/</td>
</tr>
<tr>
<td></td>
<td>22.85</td>
<td>30.00</td>
<td>33.85</td>
<td></td>
</tr>
</tbody>
</table>

Extrusion rates (ml/min): 7 3-0 0.8 10

4.2.3 Characterizations

Scanning electron microscopy (SEM) (JEOL JSM-5610 LV) was applied to study the morphology for both precursors and sintered fibers. A clean cross section was obtained by flexing the fibers until a fracture occurred and samples were subsequently placed vertically on a metal holder. Prior to the observation, a gold-coating was applied under vacuum for 1.5 min at 20 mA (EMITECHModel K550). Both secondary electrons imaging (SEI) and backscattered electrons (BSE) modes were adopted to obtain high-resolution images at varying magnifications.

The robustness and gas-tightness were characterized via the same process as introduced in Chapter 3. The mechanical strength of the hollow fibers was investigated via a three-point bending method using a tensile tester (Instron Model 5544) with a 5 kN load cell. Reduced fiber samples were positioned onto sample
holders with a distance of 30 mm. The bending strength ($\sigma_F$) was calculated based on the following equation [21]:

$$\sigma_F = \frac{8FLD_o}{\pi(D_o^4 - D_i^4)} \quad (4.1)$$

Where $F$ denotes the measured force when a fracture occurs; $L$, $D_o$ and $D_i$ represent fiber length (in this case, 30 mm), the outer and inner diameters (m) of the fiber, respectively.

The gas-tightness property of electrolyte was investigated using a N$_2$ permeation method described elsewhere [22]. The N$_2$ permeance was calculated based on the pressure change over a certain period of time (8 hours).

$$P = \frac{V}{RT \times A_m t} \ln \left( \frac{P_0 - P_a}{P_t - P_a} \right) \quad (4.2)$$

$$A_m = \frac{2\pi(R_o - R_in)L}{\ln\left(\frac{R_o}{R_in}\right)} \quad (4.3)$$

where $P$ denotes the N$_2$ permeance of the test membrane (mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$); $V$ is the volume of the test vessel (m$^3$); $R$ is the gas constant (8.314 J mol$^{-1}$ K$^{-1}$); $T$ denotes the measured temperature (K); $P_0$, $P_a$, $P_t$ represent the initial, atmospheric and final pressure readings (Pa), respectively. $A_m$ is the membrane area (m$^2$). $R_o$ and $R_in$ denote the outer and inner radiuses of the electrolyte, respectively; $L$ is the length of the fiber and $t$ is the time for the measurement (s).

Prior to the performance test, a multi-layer cathode with a length of 10 mm was incorporated on electrolyte surface by dip-coating. The first layer was composed of equal percentage of CGO and LSCF, while the second layer was pure LSCF. The slurry was prepared by mixing ceramic powers with solvent (DMSO) and polymer binder (PESf). The procedure was similar to that of the preparation of spinning
suspensions. The dip coating of the second layer was carried out after the first layer was dried. When both layers were dried, a heat treatment at 1200 °C for 5 hours was undertaken to obtain a complete single cell with an active cell length of 10 mm. Figure 4.2 displays a schematic diagram of the experimental set-up of electrochemical performance test. The single cell was first sealed into two gas-tight alumina tubes (Multi-lab Ltd, UK) using a ceramic sealant (Aremco, Ceramabond 552-VFG) after applying current collectors. The current collection of cathode was achieved by wrapping silver wires on cathode surface and silver paste (Silver conductive adhesive paste, Alfa Aesar) was adopted to improve the contact between cathode and silver wires. In terms of current collection from anode, silver wires were passed through the lumen, with some additional silver wool to enhance the contact between anode surface and silver wires. In addition, some silver paste was applied to fix the current collector onto the interior surface.

Figure 4.2: Schematic diagram of the performance test set-up.
Both silver wires from anode and cathode were connected to a potentiostat/galvanostat (Iviumstat, Netherlands) for I-V measurement and impedance analysis. These electrochemical performance tests were conducted at 600 °C using 20 ml min⁻¹ of pure hydrogen fed to anode as the fuel and 30 ml min⁻¹ of air fed to cathode as oxidant. The measurement was repeated for three times for each type of MT-SOFC with standard deviations of less than 5 %. Electrochemical impedance spectroscopy (EIS) analysis was undertaken in the frequency range from 100 kHz to 0.01 Hz with signal amplitude of 10 mV under open-circuit conditions. The fuel utilization rate was computed via the equation below:

\[
U_f = \frac{I}{2F \times n_{H_2, inlet}} \times 100\%
\]  

(4.4)

Where \( I \) denotes the electric current collected from the cell (A); \( F \) represents Faraday constant (A s mol⁻¹); \( n_{H_2, inlet} \) is the molar flow rate of hydrogen (mol s⁻¹). In this study, \( I \) refers to the current at maximum power density, assuming that the electric current is a linear function of the molar flow of the spent fuel.

4.3 Results and Discussion

4.3.1 Morphology

As shown in Figure 4. 3 (a), the prepared triple-layer hollow fiber displays an asymmetric structure with two typical morphologies formed during phase inversion, namely the micro-channels and sponge-like structure. Figure 4.3 (b) displays the cross-sectional SEM image of the triple-layer hollow fiber, in which the two morphologies could be more clearly observed. The micro-channels occupy
approximately 60% of the whole cross-section, with a relatively uniform distribution. Figure 4.3 (c) shows a close-up image of the electrolyte, which illustrates that the electrolyte has been properly adhered to the inner layer, together with good densification, during the co-sintering. The modified spinning process helps eliminate the micro-channels initiated from the outer surface, as no pinholes could be observed from Figure 4.3 (d), suggesting proper gas-tightness could be obtained during performance tests. The using of backscattered electrons (BSE) mode could display a discernable colour difference between CGO and NiO particles, as described elsewhere [16]. Therefore, layers with different ratios between CGO and NiO can be distinguished from each other, which subsequently helps in measuring the thicknesses of each component (Table 4.2).
Figure 4.3: SEM images of the fiber with the AFL extrusion rate of 2 ml/min: (a) overall view, (b) cross-section, (c) electrolyte/electrode interface, (d) electrolyte outer surface.

Table 4.2: Dimensions of triple-layer hollow fibers with different extrusion rates of AFL.

<table>
<thead>
<tr>
<th>Extrusion rate of AFL (ml min⁻¹)</th>
<th>OD (μm)</th>
<th>ID (μm)</th>
<th>Thickness of AFL (μm)</th>
<th>Thickness of anode (μm)</th>
<th>Thickness of electrolyte (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1465</td>
<td>883.0</td>
<td>/</td>
<td>275.8</td>
<td>15.3</td>
</tr>
<tr>
<td>1</td>
<td>1519</td>
<td>880.9</td>
<td>16.9</td>
<td>282.4</td>
<td>14.6</td>
</tr>
<tr>
<td>2</td>
<td>1540</td>
<td>878.3</td>
<td>32.6</td>
<td>284.4</td>
<td>13.9</td>
</tr>
<tr>
<td>3</td>
<td>1571</td>
<td>883.7</td>
<td>50.7</td>
<td>278.9</td>
<td>14.2</td>
</tr>
</tbody>
</table>

As shown in the table, a direct proportional relationship could be obtained between the extrusion rates of AFL and thicknesses, suggesting that a relatively precise control over the thicknesses could be achieved during co-extrusion. Moreover, a higher extrusion of AFL leads to an increase in the outer diameter of the hollow fiber, while the inner diameter remains almost the same. It is also worth noticing that the thicknesses of electrolyte are relatively constant, which to some extent eliminates the influences of the related ohmic resistance in affecting the cell performances. The obtained results are slightly different from the one in previous chapter, in which both thicknesses of anode and electrolyte vary as the extrusion rate of AFL changes. This is due to the differences in solid loadings that subsequently affect the rheology of spinning suspensions. For example, in this study, anode suspension has a markedly higher solid loading (70%) compared with
the one of AFL (63.5%), making the inner anode layer the major factor that determines the overall velocity during co-extrusion.

The effects of adding ethanol into spinning suspensions on fiber morphologies and properties have been systematically studied in previous researches [20, 23]. An ethanol concentration of 5% is also suggested as an additive to manipulate solvent properties, which has been reported to provide the best performances. NMP is a favourable solvent for phase inversion-assisted extrusion process due to several advantages, such as good mutual affinity with water, high solvent power for polymers, low toxicity and relatively high boiling point. High solubility of polymers in NMP also results in delayed precipitation of polymer binder during phase inversion, which subsequently contributes to the formation of long micro-channels with bigger diameter [23]. However, micro-channels of this type are undesired due to limited sponge-like structure, which is the major contributor to triple-phase boundary for electrochemical reactions. The introduction of ethanol as a non-solvent shortens the distance between initial polymer solution and the precipitation point, thus accelerating the phase inversion process and resulting in shorter and narrower micro-channels. Another benefit from NMP-based solvent system is a wider channel entrance at the inner surface. Some previous studies have reported that channel’s entrance size of NMP & 5% ethanol is more than 1 μm, while the value of DMSO system, which is another widely used solvent, is around 0.7 μm. Previous studies [24] have conducted some theoretical calculations about the effects of pore structure on membrane’s coefficient and concluded that the diffusion resistance through the pores could be considered negligible if the pore diameter is larger than 1 μm. This
indicates NMP solvent system could help to facilitate the diffusion of gaseous fuels and exhaust gases, which subsequently leads to reduced concentration resistance.

### 4.3.2 Gas-tightness and mechanical strength

Gas-tightness is an important property, as one of the major functions of electrolyte is to prevent the direct contact between fuel gases and oxidants. In addition, it markedly influences the open circuit voltage (OCV) during electrochemical performance test. In this study, the gas-tightness was investigated via a N$_2$ permeation method and the results are presented in Figure 4. As can be seen from the graph, the nitrogen permeance of the samples with an AFL is almost one magnitude lower than that of the dual-layer counterpart without an AFL. As introduced in Section 4.3.1, samples with different AFL extrusion rates have similar electrolyte thickness (Table 4.2), which indicates that the insertion of an AFL effectively improves the densification of electrolyte by reducing the mismatch in sintering behaviours between different components during co-sintering. This explanation matches well with the previous chapter [16]. According to Tan’s work [22], hollow fibers with its nitrogen permeance at the level of $10^{-10}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$ could be considered to be gas-tight. As shown in the figure, the gas-tightness of all samples with an AFL is located within this range. Therefore, the proper gas-tightness in this study indicates that the fabricated triple-layer hollow fibers are suitable to be constructed into a complete micro-tubular SOFC.
Mechanical strength is essential in determining the lifetime of fuel cells and was investigated using three-point bending method in this study. As shown in Figure 4.5, inserting an AFL could effectively improve the robustness of hollow fibers. Both fracture force and bending strength display a proportional relationship with the thickness of AFL due to its full-sponge structure. The fracture force of the sample with the thickest AFL (9.67 N) almost doubles compares with the dual-layer counterpart (5.24 N) without an AFL, while its bending strength shows an increment by around 40% (from 146.7 MPa to 211.7 MPa). This considerable increase in mechanical property may also be explained by that introducing an AFL facilitates the co-sintering process by reducing the mismatch in sintering behaviours between different components. However, the trend in bending strength is slightly different compared with previous chapter, in which the bending strength of samples with the AFL extrusion rates of 1 and 2 ml min⁻¹ are lower than the counterpart. This could
also be explained by the tailoring of compositions of suspensions, which leads to smaller changes in the fiber dimensions (outer and inner diameter) when the extrusion rate of AFL varies. Some previous studies have suggested that anode-supported hollow fibers with a bending strength of around 150 MPa could be well constructed into a complete single cell [25], which means triple-layer hollow fibers fabricated via co-extrusion are suitable for micro-tubular SOFC application.

![Figure 4.5: Bending strength and fracture force of reduced samples as a function of different AFL thicknesses (Number of samples=4).](image)

4.3.3 Electrochemical performances

Performance test was undertaken at 600 °C with 20 ml min⁻¹ of pure hydrogen flowing through anode as the fuel and 30 ml min⁻¹ of air as oxidant, after coating an LSCF based cathode layer. The active area used to calculate the current density is usually the area of the fuel electrode [26]. As for the micro-tubular structure in this
study, in which the anode (fuel electrode) is placed in the lumen side, an active area of 0.276 cm$^2$ was calculated using the inner diameter of the hollow fibers. Figure 4. 6 illustrates both cell voltages and power density as a function of current density for micro-tubular single cell prepared from ER1, ER2 and ER3 (ER is the abbreviation of extrusion rate of AFL), while ER0 denotes the dual-layer counterpart without an AFL. As shown in the figure, all samples with an AFL display an open-circuit voltage (OCV) of around 0.85 V at 600°C, which is slightly higher than the dual-layer counterpart (~0.8 V), due to a better gas-tightness of electrolyte (Figure 4. 4).

Figure 4. 6: Open-circuit voltage (OCV) and power density as a function of current density of samples with different AFL thickness (ER denotes the extrusion rates of AFL during co-extrusion).
The obtained OCV values are lower compared with Nernst Voltage (approximately 1.1 V based on conditions of this study), which could be due to the formation of reversible electrical conductivity of CGO at 600 °C in reducing atmosphere. This partial reduction from Ce$^{4+}$ to Ce$^{3+}$ leads to the formation of n-type conductivity and then the ‘current leakage’ between the two electrodes. However, the maximum power densities of 1.21, 1.01, 0.89 and 0.84 W cm$^{-2}$ were obtained for sample ER1, ER2, ER0 and ER3, respectively, which are comparable with other studies [12, 27]. In addition, the maximum power density from ER1 shows an increment by 30% when compared with the dual-layer counterpart, which is attributed to the increased TPB from inserting an AFL and subsequently enlarged reactive sites for electrochemical reactions. This is also in line with some previous studies [19, 28]. However, the power density shows an inverse proportional relationship with the thicknesses of AFL. Sample ER3 with the thickest AFL (~53 μm) even exhibits lower power density compared to the dual-layer counterpart, suggesting that introducing an AFL leads to a trade-off effect between enlarging TPB and increasing gas transport resistance. Fuel utilization rates were computed using the current values at the maximum power density of each cell and the obtained trend, as shown in Figure 4. 7, matches well with the power density results. The sample with the thinnest AFL displays the highest fuel utilization rate (29.1%). So far, sample with AFL thickness of approximately 17 μm (6% of anode thickness) has shown the highest power density and fuel utilization rate.
This explanation could be further proved by the EIS (electrochemical impedance spectroscopy) analysis, as shown in Figure 4.8. The first intercept on the real resistance axis (X axis) denotes the value of ohmic area specific resistance (ASR), which is composed of the internal resistances of electrolyte and electrodes, and contact resistances between different components. It can be observed that samples with AFL display slightly higher ohmic resistance than the dual-layer counterpart, which could be due to the additional resistance introduced from AFL. As described in Table 4.2, the thicknesses of anode and electrolyte maintain relatively constant when the extrusion rate of AFL varies. Moreover, the fabrication condition of cathode is almost identical. Therefore, it is reasonable to assume that differences from electrolyte, anode and cathode are considered negligible.
Figure 4.8: Effects of AFL thickness on SEI analysis of samples under open-circuit condition.

The span length between the two intercepts with X-axis represents the polarization resistance, which mainly includes concentration polarization and activation polarization. The former one is caused by mass transport resistance through electrodes and interfaces, while the latter one is associated to TPB and the number of reactive sites. A thicker AFL could extend reactive zones, which consequently reduces the activation polarization. However, the fine structure in AFL also brings significant resistance towards fuel transport. The consequent increase in polarization resistance even offsets the benefits from extended TPB and leads to decreased performances. As shown in the figure, the overall polarization ASR of sample ER3 is $0.52 \ \Omega \ \text{cm}^2$, which displays an increment by 25% compared with the dual-layer counterpart ($0.41 \ \Omega \ \text{cm}^2$). Therefore, an AFL thickness ranging between
17 and 33 μm in this study has been found to enhance the cell performances, which is around 6-11.5% of total anode thickness.

4.4 Conclusions

A series of triple-layer hollow fibers with different AFL thicknesses have been fabricated via a phase inversion-assisted co-extrusion/co-sintering technique, which dramatically simplifies the preparation process with great control over structures of each layer. Precise control over thicknesses has been achieved by adjusting the extrusion rates during co-extrusion so the effects of AFL thickness on different physical and electrochemical properties could be studied more systematically. SEM images display a typical asymmetric structure, including micro-channels and sponge-like structure. Inserting an AFL effectively improves both the cell robustness and gas-tightness of the electrolyte layer. In terms of cell performance, there exists a balance between enlarging TPB and introducing more mass transport resistance with increased AFL thickness. AFL between 17 and 33 μm (6-11.5% of total anode thickness) contributes to improved cell performance in this study, and the maximum power density of up to 1.21 W cm⁻² is obtained at 600 °C using pure H₂. To summarize, a novel triple-layer co-extrusion technique has been established during the work of Chapter 3 and 4, which provides a considerably simplified fabrication route that addresses process economy and manufacturability. In the subsequent studies, the research objective would be transferred from studying AFL to developing a low-cost, high-efficiency current collector and integrate this design into the co-extrusion process.
References


Chapter 4
Co-extrusion of Electrolyte/Anode functional layer/Anode Triple-layer Hollow Fibers for MT-SOFCs-Electrochemical performance study


CHAPTER 5

A Dual-Structured Anode/Ni-Mesh Current Collector

Hollow Fiber for Micro-Tubular SOFCs

Abstract

In this chapter, a unique dual-structured hollow fiber design has been developed for micro-tubular solid oxide fuel cells (MT-SOFCs), using a single-step phase inversion-assisted co-extrusion technique. The dual-structured design consists of an outer anode layer and an inner anodic current collecting layer, which are formed simultaneously during fabrication. Meanwhile, a plurality of micro-channels initiating from the exterior surface of the anode layer penetrate through the two layers, forming a highly asymmetric anode and a mesh-structured inner layer, which significantly facilitates the gas transport. With the increasing thickness of the current collecting layer (approximately 15 to 60 µm), electrical conductivity increases from $1.9 \times 10^4 \text{ S cm}^{-1}$ to $4.0 \times 10^4 \text{ S cm}^{-1}$, while the mechanical strength drops slightly from approximately 168 MPa to 113 MPa due to its ‘dragging effect’ during co-sintering. The benefits of improved current collection may potentially outweigh the reduced mechanical property, especially when dual-structured hollow fibers of this type are bundled together to form a stack. Moreover, benefiting from this innovative design, sustainable development of a larger scale of MT-SOFC stack or system becomes

* The work presented in this chapter has been published; T. Li, Z. Wu, and K. Li, Journal of Power Sources, vol. 251, pp. 145-151, 2014.
less challenging, since technical issues, such as concentration polarization and efficient current collection, can be well tackled.

5.1 Introduction

In the past decade, the development efforts of SOFCs have been focused on improving electrochemical performances, as well as reducing operation temperatures to the so-called intermediate temperature range (500-700 °C). Meanwhile, considerable research attention has been spent on high-performance cathode, carbon-tolerance anode, and low-cost metallic current collector [1-4]. Planar design, which receives probably the most interest due to its simple cell geometry and mature fabrication technique, has been successfully commercialized for various applications, such as domestic combined heat and power (CHP) system and auxiliary power units (APUs) [2, 5]. The micro-tubular geometric design with rapid start-up/shut-down, high power density, good cycling performance and thermal shock resistance [6] has started to attract research attentions since early 1990s. However, its development is still at R&D phase due to several technical challenges, such as the complexity in fabrication processes that limit mass-scale production and the difficulties in economically and efficiently collecting current from electrodes, especially from the small lumen of micro-tubes.

In terms of fabricating micro-tubes, co-extrusion technique [7-9] considerably simplifies the fabrication process by forming a number of layers simultaneously, as introduced in previous chapters. This is a genuine technology breakthrough when compared with conventional fabrication techniques involving repeated coating and sintering steps. With regards to scale-up, how to economically and efficiently collect
current, especially from the lumen side of each micro-tubular cell, without creating further mass transfer resistance is still a challenge, as it determines the overall performance of the corresponding MT-SOFC systems.

Various techniques have been investigated for lumen-side current collection, such as inserting nickel mesh and pin into the anodic lumen [10], connecting one end of uncovered electrode with metal wires [11-13], and sintering gold or silver layers [14]. However, reproducibility and actual contact between anode and current collector need to be considered when evaluating the overall cell performance. The cost is another concern when noble metals are selected. Recently, Lee et al. [15] have developed a combined system, in which the current collection is integrated with fuel supply by using a conductive fuel inlet pipe connected with nickel wires. A significantly increased power density and fuel utilization rate can thus be achieved, due to lower ohmic losses and contact resistance between the anode and current collector. However, a more cost-effective and efficient current collection technique addressing good manufacturability, great adhesion to anode, negligible gas transfer resistance and suitable for scaling-up is still of great interest.

This chapter demonstrates the feasibility of using a phase inversion-assisted co-extrusion technique to fabricate Ni-YSZ (yttria-stabilized zirconia, anode)/Ni (anodic current collector) dual-layer hollow fibers. Besides different materials and adjustable layer thicknesses, more benefits in designing micro-structures [8, 16], such as a highly asymmetric anode and mesh current collector, for potentially less mass transfer resistance inside anode and between the two layers have been incorporated in this study. As a result, concentration polarization could be minimized inside anode and efficient anodic current collection generated may
contribute to a more sustainable development of micro-tubular SOFC stacks and systems.

5.2 Experimental

5.2.1 Materials

Commercially available cerium-gadolinium oxide (Ce$_{0.9}$Gd$_{0.1}$O$_{1.95}$ (CGO), surface area 35.6 m$^2$ g$^{-1}$, mean particle size (d50) 0.1-0.4 μm, NexTech Materials Ltd., USA) and nickel oxide (NiO, surface area 3.7 m$^2$ g$^{-1}$, mean particle size (d50) 0.5-1.5 μm, NexTech Materials Ltd., USA) were used as supplied. Polyethersulfone (PESf) purchased from Radel A-300, Ameco Performance (USA), and dimethyl sulfoxide (DMSO) purchased from VWR International, LLC were used as the polymer binder and the solvent, respectively. Polyethylene glycol 30-dipolyhydroxystearate (Arlacel P135, Uniqema) was used as the dispersant of the spinning suspension. During the co-extrusion, DMSO and tap water were the internal and external coagulants, respectively.

5.2.2 Fabrication of anode/anodic current collector hollow fibers

Spinning suspensions of anode and anodic current collector were prepared separately, with the detailed compositions listed in Table 5.1. Typically, Arlancel P135 was dissolved in solvent (DMSO) prior to the addition of ceramic powders, and the mixture was milled for 2-3 days (JARMILL, Gladstone Engineering. LTD, UK). The mixing was further conducted for another 3-4 days after adding the organic binder (10 wt% of ceramic powders) to obtain homogeneous spinning suspensions.
Table 5.1: Compositions of spinning suspensions for dual-structured hollow fibers.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Anode (wt.%)</th>
<th>Current collector (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiO</td>
<td>40.1</td>
<td>69.6</td>
</tr>
<tr>
<td>CGO</td>
<td>26.8</td>
<td>/</td>
</tr>
<tr>
<td>Polymer binder (PESf)</td>
<td>6.69</td>
<td>6.96</td>
</tr>
<tr>
<td>Dispersant (Arlacel P135)</td>
<td>0.15</td>
<td>0.15</td>
</tr>
<tr>
<td>Solvent (DMSO)</td>
<td>26.2</td>
<td>23.3</td>
</tr>
</tbody>
</table>

Before being transferred into stainless steel syringes, both spinning suspensions were degassed under vacuum with stirring in order to eliminate air bubbles inside. The dual-layer precursors were fabricated by a phase-inversion assisted co-extrusion technique described elsewhere[17]. Pure solvent (DMSO) was adopted as the internal coagulant to obtain the mesh current collector. The extrusion rates of internal coagulant and two suspensions were accurately controlled by syringe pumps (Harvard PHD22/200 HPsi and KDS410). The extrusion rates of internal coagulant and anode were maintained at 6 and 7 ml min\(^{-1}\), respectively, while the extrusion rate of inner current collecting layer was reduced from 2 to 0 ml min\(^{-1}\) for tailoring the thickness. Precursor fibers were left in the external coagulant bath overnight to complete the solidification of polymer binder, before being cut to a length of 15 cm.

The co-sintering was undertaken in static air to yield dual-structured ceramic hollow fibers using a tubular furnace (CARBOLITE). The temperature was first increased to 400 °C at a rate of 2 °C min\(^{-1}\) and held for 1h, then to 800 °C at a rate of 2 °C min\(^{-1}\) and held for 2 hours, and finally to 1500 °C at a rate of 15 °C min\(^{-1}\) and held for 12 hours. The temperature was then decreased to room temperature at the rate of 3 °C
min⁻¹. For post-sintering characterizations, the co-sintered hollow fibers need to be reduced, converting NiO into Ni. The reduction was conducted in 20 ml min⁻¹ of pure hydrogen for 2.5 hours using a tubular furnace (CARBOLITE, MTF 12/25/250).

5.2.3 Dip-coating of electrolyte

The incorporation of electrolyte was conducted via dip-coating technique. The coating slurry was prepared via a two-step milling process. The blend that is composed of ceramic powder (CGO), solvent (azeotropic mixture of toluene and ethanol) and dispersant (Arlancel P135) was first roll milled for 2 days. After adding the PVB as the polymer binder (Butvar®B-98, Sigma-Aldrich, M.W. 40,000-70,000), the mixing was further conducted for 2-3 days to obtain a homogeneous suspension. Details of the composition are summarized in Table 5.2.

<table>
<thead>
<tr>
<th>Composition (wt.%)</th>
<th>Electrolyte</th>
<th>CGO</th>
<th>Ethanol</th>
<th>Toluene</th>
<th>Arlacel</th>
<th>PVB</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>47.22</td>
<td>35.07</td>
<td>12.06</td>
<td>0.94</td>
<td>4.71</td>
<td></td>
</tr>
</tbody>
</table>

Figure 5.1 illustrates the schematic diagram of the dip-coating process. Both precursor fibers and sintered fibers have been attempted. A pump was employed to precisely control the withdraw speed to adjust electrolyte thicknesses. After the coated layer was dried, the electrolyte was sintered at 1500 °C for 10 hours for proper densification.
Figure 5. 1: Schematic diagram of the dip-coating setup.

5.2.4 Characterizations

Prior to the co-sintering, shrinking behaviours of both anode and current collector materials were studied using a dilatometer (NETZSCH, model DIL 402C). Powder mixtures were compressed into bars of 6mm×6mm×6mm by using a custom-designed mould. The measurements were carried out in static air and the system was heated up to 1500 °C at 5 °C min⁻¹.

The morphology of the dual-layer hollow fibers was investigated using scanning electron microscopy (SEM) characterization (JEOL JSM-5610). Samples were gold-coated under vacuum for 1.5 min at 20 mA (EMITECH Model K550) and SEM images with different magnification were collected under both secondary electrons imaging (SEI) and backscattered electrons (BSE) modes. Energy dispersive spectrometry (EDS, JEOL JSM-6400 electron microscope) analyses was also undertaken to investigate the elemental distribution inside the fibers.

The average porosity was studied using a pycnometer (Micromeritics Accupyc 1330) via Archimedes method. The skeleton density of the hollow fibers $\rho_{pyc}$ (g cm⁻³) was
first determined by changing pressures of helium in a calibrated volume. The average porosity ($\varepsilon_v$) was then calculated using the equations below:

$$\varepsilon_v = \frac{\rho_{pyc} - \rho_{fiber}}{\rho_{pyc}}$$  \hspace{1cm} (5.1)

$$\rho_{fiber} = \frac{4m_{sample}}{\pi(D_o^2 - D_i^2)_sample}$$  \hspace{1cm} (5.2)

where $m$, $l$, $D_o$ and $D_i$ represent the mass (g), length, outer and inner diameters of the sample (cm), respectively.

Mechanical strength was studied by a three-point bending method using a tensile tester (Instron Model 5544) with a load cell of 5 kN. Samples were cut to a certain length (~50 mm) and placed on two sample holders with a gap of 30 mm. The fracture force was obtained and the bending strength was then calculated using the following equation:

$$\sigma_F = \frac{8FLD_o}{\pi(D_o^4 - D_i^4)}$$  \hspace{1cm} (3)

where $F$ denotes the measured fracture force (N), $L$, $D_o$ and $D_i$ represent the length(m), the outer and inner diameters of the fiber (m), respectively.

Gas permeability was investigated using $N_2$ permeation method at room temperature, details of which have been described elsewhere [18]. Hollow fiber samples were sealed into the system using epoxy resin and the feed pressures were adjusted using a pressure regulator, as illustrated in Figure 5.2. The flow rate of $N_2$ was measured using a bubble flow meter and the gas permeance was then calculated using the equation below:

$$P = \frac{Q \cdot \ln(D_o/D_i)}{\pi L(D_o^2 - D_i^2) \cdot \Delta p}$$  \hspace{1cm} (5.4)
where $P$ denotes the permeance of $N_2$ (mol m$^2$ s$^{-2}$ Pa$^{-1}$), $L$, $D_o$ and $D_i$ represent fiber length (m), the outer and inner diameters of the fiber (m), respectively, and $\Delta P$ is the pressure difference across the hollow fiber (Pa).

![Diagram of gas permeation test](image)

**Figure 5.2:** Schematic diagram of the set-up for gas-permeation test.

The electrical conductivity of the dual-layer hollow fiber was measured using a four-point direct current method at room temperature, details of which can be found elsewhere [16]. Silver wires were inserted into both ends for a depth of ~5 mm and attached to the lumen using silver paste. Samples were subsequently connected in the circuit. Voltage drop across the samples of 50 mm were obtained using a multimeter by passing controlled currents (50 mA, 75 mA and 100 mA). Bulk conductivity ($\sigma_{fiber}$, S cm$^{-1}$) of the dual-structured hollow fibers was then estimated using the equation below:

$$\sigma_{fiber} = \frac{L_{fiber}}{A_{fiber} \times R_{fiber}}$$

(5.5)
\[ A_{fiber} = \frac{\pi}{4} \left( D_o^2 - D_i^2 \right) \]  

(5.6)

where \( A_{fiber} \) represents the cross-sectional area (cm\(^2\)); \( L_{fiber} \) is the fiber length (50 mm); \( R_{resistance} \) denotes the fiber resistance calculated based on the linear fits of obtained I-V data.

5.3  Results and Discussion

5.3.1  Morphology of dual-structured hollow fibers

Figure 5.3 presents the cross-sectional morphologies of a selected precursor fiber. Micro-channels originating from the outer surface have penetrated through the entire cross section (Figure 5.3 (a) and (c)), which is a result of zero air gap and using solvent as the internal coagulant. It has been generally accepted that the formation of the micro-channels is resulted from hydrodynamically unstable viscous fingering phenomenon [19], which takes place at the interface between two fluids of different viscosities at the first moment of mixing. When the spinning suspension is in contact with non-solvent (H\(_2\)O), the solvent/non-solvent exchange leads to the increase in dynamic viscosity of suspension and the precipitation of the polymer phase. However, there exists a critical viscosity threshold above which the formation of micro-channels is completely suppressed despite the non-solvent influx. In other words, viscous fingering only occurs when the initial viscosity of spinning suspensions is below the threshold and the growth of micro-channels will be halted once the dynamic viscosity is above the threshold. By using solvent (DMSO) as the internal coagulant, the dynamic viscosity of suspensions at the front of micro-channels is maintained at a value below the threshold, so the growth of the micro-
channels can continue until penetrating through the entire cross section of the fiber, resulting in the mesh structure on the inner surface, as shown in Figure 5.3. The holes on the inner surface were estimated at around 20 μm in precursor fibers.

Figure 5.3: SEM images (secondary electron imaging (SEI) mode) of the dual-layer precursor fiber with the current collector extrusion rate of 2 ml min⁻¹: (a) and (c) cross section in radial direction, (b) cross section in axial direction, (d) inner surface.
Figure 5.4: SEM images of sintered dual-layer fiber with the current collector extrusion rate of 2 ml min⁻¹: (a, b) cross-section (c, e) inner surface; (d) inner surface of reduced fiber.

Figure 5.4 illustrates the SEM images of the co-sintered dual-structured hollow fiber. The micro-channels were well preserved during the sintering (Figure 5.4 (a) and (b)) and the holes on the inner surface were reduced to around 10 μm (Figure 5.4 (c) and (d)). Meanwhile, the two layers could be clearly distinguished (Figure 5.
3(b)), due to the remove of polymer binder in precursor counterpart. The darker layer denotes the inner current collector, while the lighter-colour layer is anode. After reducing NiO into Ni, the mesh-like structure in the current collecting layer is more distinct (Figure 5. 4(e)). The inter-layer diffusion during cell fabrication needs to be minimized, since it reduces cell efficiency [7]. EDS analysis shown in Figure 5. 5 proves that no observable inter-layer diffusion can be found at the interface between anode and current collector. While because NiO exist in both anode and current collecting layer and the two layers are extruded and sintered simultaneously, superior adhesion can thus be formed.

![Figure 5. 5: EDS results of interface between the inner current collector (right side) and outer anode layer (left side).](image)

Detailed dimensions of the dual-structured hollow fibers fabricated at controlled inner layer extrusion rates (0, 0.5, 1 and 2 ml min⁻¹) are listed in Table 5. 3. The thickness of the inner current collecting layer increases from approximately 15 to 60
μm when the extrusion rate is increased from 0.5 to 2 ml min⁻¹. Meanwhile, outer diameter of the fabricated fibers is maintained at a nearly constant value, due to the instant precipitation of the polymer binder at the outer surface when it is in contact with the excessive external coagulant (zero air gap).

### Table 5.3: Dimensions and porosity of dual-structured hollow fibers

<table>
<thead>
<tr>
<th>Extrusion rate of current collector (ml min⁻¹)</th>
<th>OD (μm)</th>
<th>ID (μm)</th>
<th>Thickness of current collector (µm)</th>
<th>Thickness of anode (µm)</th>
<th>Current collector/overall thickness (%)</th>
<th>Average porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1069.8</td>
<td>693.0</td>
<td>/</td>
<td>189.5</td>
<td>/</td>
<td>32.2</td>
</tr>
<tr>
<td>0.5</td>
<td>1064.9</td>
<td>679.6</td>
<td>15.2</td>
<td>177.5</td>
<td>7.9</td>
<td>34.7</td>
</tr>
<tr>
<td>1</td>
<td>1066.3</td>
<td>658.9</td>
<td>28.3</td>
<td>175.3</td>
<td>13.9</td>
<td>36.3</td>
</tr>
<tr>
<td>2</td>
<td>1068.9</td>
<td>633.0</td>
<td>59.9</td>
<td>158.0</td>
<td>27.5</td>
<td>40.6</td>
</tr>
</tbody>
</table>

### 5.3.2 Gas diffusion inside the dual-structured hollow fiber

Some previous research [20] has studied the theoretical effects of membrane pore structure parameters, such as pore size, pore size distribution and effective surface porosity, on the membrane’s coefficient. They concluded that when the pore radius is greater than 1μm, membrane’s coefficient is governed solely by the continuum diffusion coefficient. Since the “pores” in our inner current collecting layer are around 10 μm, fuel diffusion resistance across this layer is negligible.
Figure 5. 6 shows the experimental results of gas permeation. The gas permeance test was conducted using N₂ at room temperature to determine the gas transport behaviour. As can be seen, samples with different current collector extrusion rates display very similar gas permeation behaviour, indicating that the thickness of anodic current collect has a negligible influence on gas permeation. This agrees well with the conclusion in other studies [20] and indicates that the resistance of fuel diffusion through the mesh current collecting layer is negligible. When compared with the anode support from previous researches [16], the N₂ permeability obtained in this study is around 10 times higher, which is probably due to the considerable decrease in the thickness of sponge-layer resulted from the modified fabricating conditions.
Additionally, micro-channels (well wider than 2 μm) inside the anode layer play an important role in affecting the diffusion pathways and distribution of fuels (normally H₂). Previous studies [1, 16] have proved that the micro-channels inside anode layer significantly reduced mass transfer related concentration polarization. This is also considered as one of the major reasons for the high cell performance achieved (2.3 W cm⁻² at 600 °C) [1]. This advantage has been incorporated into the dual-structured hollow fiber design in this study, and its effects on H₂ diffusion pathways and distribution are schematically presented in Figure 5. 7, and compared with our previous anode/current collector design [21].

![Diagram of H₂ diffusion pathway](image)

**Figure 5. 7:** *Illustration of the H₂ diffusion pathway in the anode/anodic current collector dual-layer hollow fiber. (a) Hollow fiber with long micro-channels from outer surface in this study; (b) Hollow fiber with short micro-channels in Ref.[15].*

The beneficial effect of the long micro-channels results in that H₂ not only can diffuse easily into the anode layer, but also distribute evenly inside the anode of this type. This contributes to a possibly much lower mass transfer related concentration polarization when compared with our previous design, in which H₂ needs to diffuse
through a nearly full sponge-like structure with an average pore size of 0.3 μm. Reactive sites are thus more accessible to H₂ due to a shorter and less tortuous pathway. For conventional symmetric anode, there exists a trade-off between a large quantity of accessible reactive sites and a low fuel transport resistance. Porosity is one of the parameters to evaluate the balance of the two factors. Dong et. al. [22] has suggested an ideal anode porosity ranging from 30%-40% based on a seepage theory. The average porosity of the dual-structured hollow fiber in this study (Table 5. 2) increases with the current collector thickness and locates well within the suggested porosity. Moreover, the substantially decreased mass transfer resistance would benefit further in the development of larger stacks with higher system efficiencies.

### 5.3.3 Mechanical property

Mechanical strength is one of the essential aspects that determine the life of fuel cells. For the dual-structured hollow fiber, both fracture force and bending strength decrease when the thickness of current collector is increased (Figure 5. 8). This is due to the reduced anode thickness as shown in Table 5. 2, which is the main provider of the mechanical strength, and excessive shrinking behaviour of the inner layer. As can be seen in Figure 5. 9 (a), NiO (inner layer material) starts to shrink at a lower temperature, and finishes at a higher shrinkage when compared with the anode material (60 wt.%NiO-40 wt.%CGO). Meanwhile, the maximum sintering rate of NiO is higher and turns up at a lower temperature (Figure 5. 9 (b)).
Figure 5. 8: Bending strength and fracture force as a function of different current collector thicknesses.

Figure 5. 9: (a) Sintering curves of NiO and the materials of anode (Heating rate: 5oC/min); (b) Sintering rate curves of NiO and the materials of anode.

All these indicate that the inner layer keeps “dragging” the outer layer during the co-sintering, hindering the proper densification of anode layer and subsequently leads to reduced mechanical strength. Moreover, such a kind of dragging effect is more significant with a thicker current collecting layer. The maximum bending strength at the thinnest current collecting layer (15 µm) is approximately 168 MPa and is
comparable with previous studies [16, 21, 23], in which asymmetric anode supported designs were fabricated via a similar method. In addition, Yang et. al. [24] have suggested that, for an anode supported design, bending strength of around 150 MPa could be well applied for the construction of micro-tubular SOFCs, and when bundled together, mechanical strength of a micro-tubular stack can be significantly improved.

5.3.4 Electrical conductivity

In general, this study aims at developing an effective and sustainable way of collecting current from the lumen side of MT-SOFCs, and therefore, the electrical conductivities of the dual-structured hollow fibers are illustrated in Figure 5. 10.

![Figure 5. 10: Electrical conductivity of reduced anode/anodic current collector dual layer hollow fibers as a function of current collector thickness.](image)
As can be seen from the figure, the conductivity of the single-layer counterpart (current collector extrusion rate is 0 ml min⁻¹) agrees quite well with other studies [7, 16]. By adding an inner current collecting layer, the bulk conductivity is increased markedly. The conductivity of the sample with the thickest current collecting layer (4.1×10⁴ S cm⁻¹) doubles the value of the single-layer counterparts, which proves the feasibility of using such design for further development of MT-SOFC stacks. However, it is still lower than our previous anode/current collector design (7.7×10⁴ S cm⁻¹). This indicates that the long micro-channels facilitate fuel diffusion inside anode, meanwhile reduces bulk conductivity.

By combining the advantages of long micro-channels inside anode [8] and efficient current collection, the dual-structured anode/anodic current collector design is suitable to be applied for the construction of a complete micro-tubular SOFC. Moreover, the simplified and reliable single-step fabrication process presented in this study is promising for mass-scale production and would contribute to further in the development of MT-SOFC stacks and systems.

### 5.3.5 Dip-coating of electrolyte

Figure 5. 11 displays the schematic diagram of a half-cell with mesh-structured nickel layer. However, the sintered current collector/anode/electrolyte fibers were highly brittle and could not survive the subsequent coating of cathode layer. This poor mechanical strength could be due to excessive shrinkage of the inner layer (NiO) as discussed in Section 5.3.3, and consequently the improper densification of anode layer, which is the major contributor towards robustness. Therefore, the
composition of inner current collector needs to be further tailored for better-matched shrinking behaviours between different components.

![Schematic diagram of a half cell with an interior Ni-mesh.](image)

**Figure 5.11:** Schematic diagram of a half cell with an interior Ni-mesh.

### 5.4 Conclusions

In this chapter, dual-structured Ni/Ni-CGO hollow fibers have been successfully fabricated via a phase inversion-assisted co-extrusion/wet-spinning technique. By applying solvent as internal coagulant, micro-channels originating from the outer surface have penetrated the whole cross-section resulted in a mesh structure with long micro-channels, which can substantially reduce the fuel transport resistance, as the long micro-channels inside anode provide more evenly distributed and easier pathways for H\(_2\) diffusion. By adjusting the extrusion rates, precise control over the thickness of current collecting layer can be achieved with good adhesion between the two layers. Increasing the thickness of current collector leads to an increased average porosity and electrical conductivity, but a decreased mechanical strength. By combining the advantages of the reduced fuel mass transfer resistance and
efficient current collection, such micro-structured current collector creates more possibilities for sustainable development of MT-SOFCs. The major problem hindering the further construction of a complete cell is associated with the mismatch in shrinking behaviours between various components and will be tackled in the following chapter.

References


[17] B. Zydorczak, Z. Wu, and K. Li, "Fabrication of ultrathin La0.6Sr0.4Co0.2Fe0.8O3–δ hollow fibre membranes for oxygen permeation," *Chemical Engineering Science*, vol. 64, pp. 4383-4388, 2009.


CHAPTER 6

Co-extrusion of Triple-layer Hollow Fibers with Anodic Current Collector for MT-SOFC

Abstract

High manufacturing cost and low-efficient current collection have been the two major bottlenecks that prevent micro-tubular SOFCs from large-scale application. In this work, a new nickel-based composite anode current collector has been developed for anode-supported MT-SOFC, addressing reduced cost, manufacturability and current collection efficiencies. Triple-layer hollow fibers have been successfully fabricated via a phase inversion-assisted co-extrusion process, during which a thin nickel-based inner layer was uniformly coated throughout the interior anode surface for improved adhesion with superior process economy. 10 wt.% CGO was added into the inner layer to prevent the excessive shrinkage of pure NiO, thus helping to achieve the co-sintering process. The electrochemical performance tests illustrate that samples with the thinnest anodic current collector (15 % of the anode thickness) displayed the highest power density (1.07 W cm⁻²). The impedance analysis and theoretical calculations suggest that inserting the anodic current collector could dramatically reduce the percentage of contact loss down to 6-10 % of the total ohmic loss (compared to 70 % as reported in literatures), which proves the high efficiencies of new current collector design. Moreover, the superior manufacturability

* The work presented in this chapter has been published;
and process economy suggest this composite current collector suitable for mass-scale production.

6.1 Introduction

Solid oxide fuel cells (SOFCs) have been considered as a promising solution towards energy shortage and environmental pollution [1-3]. Among different geometric designs of SOFCs, the micro-tubular (MT) design was first reported in early 1990s by Kendall’s group [4], displaying some unique features, such as rapid start-up/shut-down, high volumetric power density, good cycling performance and thermal shock resistance [5]. However, several bottlenecks have to be tackled before MT-SOFCs are widely commercialized, including expensive manufacturing cost, which limits mass-scale production, and the difficulties in efficiently collecting current from electrodes, especially from the small lumen of micro-tubes.

In the MT design, various cell components are configured in the form a multi-layer cylindrical tube and conventional fabrication routes usually consist of repetitions of coating and sintering, which makes the overall process complicated and cost-consuming [6-8]. To achieve better process economy, the ram co-extruder developed by Kendall’s group enables the extrusion of multiple pastes with matched rheology in a single-step process [9, 10], which dramatically simplifies the manufacturing route. The main drawback of this process is the difficulties in individual thickness control and the inflexibility in morphology tailoring. Some other studies have reported the development of a phase inversion-based co-extrusion technique, which allows flexible process control and adjustable morphologies [11-
13]. Moreover, this technique leads to a stronger adhesion between cell components, resulting in lower ionic resistance and over-potential loss. In terms of scale-up, a key challenge is how to collect current effectively, especially from the lumen side of individual cell, without creating further mass transfer resistance and ohmic loss. Various techniques have been reported for lumen-side current collection, such as wrapping metallic wires on one end of inner anode uncovered by electrolyte [6, 14, 15], with some additional silver or platinum paste to improve the contact. This approach has been widely applied especially for MT-SOFCs fabricated via multi-step processes. As for co-extruded micro-tubes, current collection is usually achieved by inserting nickel mesh and pin, or silver wires into the anodic lumen [16-18]. However, reproducibility and contact loss need to be considered when evaluating the overall cell performance. Some numerical calculations conducted have suggested that the contact loss, which is resulted from problematic adhesion between anode and wires, is the main contributor towards total ohmic loss (up to 70%) [18]. To sum up, a new current collection technique addressing process economy, reduced contact loss, and negligible mass transfer resistance is still of great interest.

In this chapter, the triple-layer co-extrusion process, which has been well established in previous chapters, and the nickel-based composite anodic current collector have been integrated, addressing manufacturability and current collection efficiencies. Some precious metal-ceramic composites have been investigated as current collector in addition to metallic wires and it has been reported that a certain concentration of metallic phase needs to be reached to change the insulating characteristic of the ceramic phase to the metallic conductive behaviour [2].
Moreover, the adhesion and conductivity strongly depends on the particle sizes of each component. Anodic current collector/anode/electrolyte triple-layer hollow fibers have been successfully fabricated via a phase inversion-assisted co-extrusion process, during which a thin nickel-based inner layer was uniformly coated throughout the interior anode surface for improved adhesion with superior process economy. The compositions of ceramic materials have been adjusted and investigated via dilatometry to help realize the co-sintering process. The effects of thicknesses of anodic current collector on cell performance have been systematically studied after a complete MT-SOFC was delivered, including I-V characterization and impedance analysis. Moreover, numerical calculations on ohmic loss contribution have been conducted to study the effectiveness of this new anodic current collector.

### 6.2 Experimental

#### 6.2.1 Materials

Commercially available cerium-gadolinium oxide (Ce$_{0.9}$Gd$_{0.1}$O$_{1.95}$ (CGO), surface area 35.5 m$^2$ g$^{-1}$, mean particle size (d50) 0.1-0.4 μm) and nickel oxide (NiO, surface area 3.7 m$^2$ g$^{-1}$, mean particle size (d50) 0.5-1.5 μm) were purchased from NexTech Materials Ltd and used as supplied. Polyethersulfone (PESf) purchased from Radel A-300, Ameco Performance (USA), polyethyleneglycol 30-dipolyhydroxystearate (Arlacel P135, Uniqema), and dimethyl sulfoxide (DMSO) purchased from VWR International, LLC were used as the polymer binder, dispersant and solvent of spinning suspensions, respectively.
6.2.2 Fabrication of electrolyte/anode/anodic current collector triple-layer hollow fibers

Spinning suspensions of anode, anodic current collector and electrolyte were prepared separately by mixing ceramic powders, solvent, polymer binder and additives, details of which are described elsewhere [13, 17] and in previous chapters. CGO and NiO were applied in current collector (weight ratio 1:9) and anode (weight ratio 4:6), while the electrolyte is composed of 100% CGO, as shown in Table 6.1.

Table 6.1: Compositions of the spinning suspensions for triple-layer hollow fibers.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Current collector (wt.%)</th>
<th>Anode (wt.%)</th>
<th>Electrolyte (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiO</td>
<td>63.0</td>
<td>40.8</td>
<td>/</td>
</tr>
<tr>
<td>CGO</td>
<td>7.0</td>
<td>27.2</td>
<td>55.7</td>
</tr>
<tr>
<td>Polymer binder (PESf)</td>
<td>7.0</td>
<td>6.8</td>
<td>5.57</td>
</tr>
<tr>
<td>Dispersant (Arlacel P135)</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Solvent (DMSO)</td>
<td>22.4</td>
<td>24.7</td>
<td>38.2</td>
</tr>
</tbody>
</table>

Prior to the co-extrusion, all suspension were degassed under vacuum to eliminate any air bubbles trapped inside and then transferred into individual stainless steel syringes. Triple-layer precursor fibers were fabricated via a phase inversion-based co-extrusion process, in which all suspensions, together with the internal coagulant (H₂O), were extruded simultaneously through a custom-designed quadruple-orifice spinneret. An air gap of 25 cm was adopted to guarantee sufficient time for the lumen-side phase inversion process before the precursor enters the external coagulant bath. The extrusion rates of internal coagulant and three suspensions
were precisely controlled by syringe pumps (Harvard PHD22/200 HPsi and KDS410) to achieve independent adjustment of layer thicknesses. The extrusion rates of internal coagulant, anode and electrolyte were maintained at 10, 7 and 1.5 ml min⁻¹, respectively, while the extrusion rate of anodic current collector was reduced from 5 to 1 ml min⁻¹. Precursor fibers were left in the external coagulant bath overnight to complete the solidification of polymer binder, before being cut to a length of 15 cm.

The co-sintering was conducted in static air to yield triple-layer ceramic hollow fibers using a tubular furnace (CARBOLITE). The temperature was first increased to 600 °C at a rate of 2 °C min⁻¹ and held for 2 hours, then to 1500 °C at a rate of 15 °C min⁻¹ and dwelled for 12 hours. The furnace was then cooled down to room temperature at the rate of 3 °C min⁻¹. A reduction that converts NiO into Ni is needed for hollow fibers samples prior to some post-sintering characterizations. The reduction was conducted at 550 °C in a pure hydrogen atmosphere for 2.5 hours.

6.2.3 Characterizations

Prior to the co-sintering, shrinking behaviours of all three components were studied using a dilatometer (NETZSCH, model DIL 402C). Powder mixtures that have identical ratios as spinning suspensions were compressed into cubes with a dimension of 6mm×6mm×6mm using a house-developed die. The measurements were carried out in static air and the system was heated up to 1500 °C at 5 °C min⁻¹. The morphology of the triple-layer hollow fibers was investigated using scanning electron microscopy (SEM) characterization (JEOL JSM-5610). Images with varied
magnifications were obtained using both secondary electrons imaging (SEI) mode and backscattered electrons (BSE) mode.

Mechanical property was investigated using a tensile tester (Instron Model 5544 with a load cell of 5 kN) by a three-point bending method. Reduced samples were cut into a certain length of approximately 5 cm and placed upon two sample holders which had a gap of 3 cm. The fracture force was recorded by the testing system and the bending strength was subsequently calculated via the equation below:

\[
\sigma_F = \frac{8FLD_o}{\pi(D_o^4 - D_i^4)} \quad (6.1)
\]

where \( F \) represents the measured fracture force (N), \( L \), \( D_o \) and \( D_i \) represent the length between two sample holders (m), the outer and inner diameters of the hollow fiber samples (m), respectively.

Gas-tightness was investigated via \( \text{N}_2 \) permeation tests via the same procedure as described in Chapter 3. The pressure drop of the system over time was monitored and the gas-tightness was evaluated based on \( \text{N}_2 \) permeance, which was calculated using the equation below:

\[
P = \frac{V}{RT \times A_m t} \ln \left( \frac{p_o - p_a}{p_i - p_a} \right) \quad (6.2)
\]

\[
A_m = \frac{2\pi(R_o - R_i) L}{\ln(R_o / R_i)} \quad (6.3)
\]

where \( P \) is the \( \text{N}_2 \) permeance of the test membrane (mol m\(^{-2}\) s\(^{-1}\) Pa\(^{-1}\)); \( V \) denotes the volume of the test vessel (m\(^3\)); \( T \) denotes the temperature of measurement (K); \( p_o \), \( p_i \), \( p_a \) represent the initial, final and atmospheric pressure readings (Pa), respectively; \( A_m \) is the effective area of tested fibers (m\(^2\)); \( R_o \) and \( R_i \) denote the outer and inner radiuses of electrolyte, respectively; \( L \) is the length of the fibre (m).
and \( t \) is the time for the measurement (s). It is worth noticing that the measurement of each sample was repeated 5 times.

Prior to the electrochemical performance tests, graded cathode was deposited via dip-coating. The first layer, adjacent to the electrolyte, was composed of 50 wt.% CGO and 50 wt.% LSCF, while the slurry of second layer comprised pure LSCF. After a sintering step at 1100 °C for 4 hours, a complete cell was conducted with an active cathode length of 1 cm. Silver wires of 0.2 mm diameter (99.99% purity, Advent Materials Ltd, UK) were wrapped along cathode for exterior current collection. Two additional strips of silver paste painted as ‘bridge’ to improve the contact between wires and cathode surface. As for interior current collection, silver wires were formed into springs and inserted into the lumen for a length of 5 mm at both ends, fixed with silver paste for improved adhesion. The completed single cell was fixed into two gas-tight alumina tubes (Multi-lab Ltd, UK) and sealed with ceramic sealant (Aremco, Ceramabond 552-VFG). It is worth noticing that instead of single supporting tube, three alumina tubes have been adopted as support in this chapter arranged in a triangle-shape design for better robustness of the reactor. Both wires, which functioned as anode and cathode current collectors, were connected to a potentiostat/galvanostat (Iviumstat, Netherlands) for subsequent electrochemical performance tests, as illustrated in Figure 6. 1. These measurements were conducted at 600 °C, with 20 ml min\(^{-1}\) of pure H\(_2\) fed to anode as the fuel and 30 ml min\(^{-1}\) of air fed to cathode as oxidant. Electrochemical impedance spectroscopy (EIS) analysis was undertaken under open-circuit conditions in the frequency range of 10\(^5\)-0.01 Hz with signal amplitude of 10 mV.
6.2.4 Modelling

Theoretical calculations were conducted to quantify different contributors towards total ohmic loss $\Delta \Phi_{total}^{IR}$, which is the summation of ohmic losses resulted from silver wires, CGO electrolyte, Ni-CGO anode, LSCF-CGO cathode, as well as the contact loss between electrodes and corresponding current collectors, as shown in the equations (6.4-6.7) below:

$$\Delta \Phi_{total}^{IR} = \Delta \Phi_{wires}^{IR} + \Delta \Phi_{electrolyte}^{IR} + \Delta \Phi_{anode}^{IR} + \Delta \Phi_{cathode}^{IR} + \Delta \Phi_{contact}^{IR}$$  \hspace{1cm} (6.4)

$$\Delta \Phi_{total}^{IR} = \frac{I_{cell}}{A_{wire}} \frac{L_{wire}}{\sigma_{wire}} \left[ \frac{1}{r_2} \int_{r_2}^{r_5} \frac{j(r)}{\sigma_{electrolyte}} \, dr + \frac{1}{r_5} \int_{r_5}^{r_3} \frac{j(r)}{\sigma_{anode}} \, dr + \frac{1}{r_5} \int_{r_5}^{r_3} \frac{j(r)}{\sigma_{cathode}} \, dr \right] + \Delta \Phi_{contact}^{IR}$$  \hspace{1cm} (6.5)

$$\Delta \Phi_{total}^{IR} = \frac{I_{cell}}{A_{wire}} \frac{L_{wire}}{2 \pi L} \left[ \frac{1}{\sigma_{electrolyte}} \int_{r_2}^{r_5} \frac{dr}{r} + \frac{1}{\sigma_{anode}} \int_{r_1}^{r_5} \frac{dr}{r} + \frac{1}{\sigma_{cathode}} \int_{r_1}^{r_5} \frac{dr}{r} \right] + \Delta \Phi_{contact}^{IR}$$  \hspace{1cm} (6.6)

$$\sigma_{electrolyte} = \frac{\sigma_{0,electrolyte}}{T} \exp \left( \frac{-E_{electrolyte}}{RT} \right)$$  \hspace{1cm} (6.7)
where $r_1, r_2, r_3, r_4$ denote corresponding outer and inner radiiuses of anode, electrolyte and cathode, as shown in Figure 6.2.

![Figure 6.2: Schematic diagram of various radiiuses for ohmic contributor calculation.](image)

$I, j(r), L, A$ denote current, current density, length and cross-sectional area of silver wires, respectively; $\sigma$ represents the conductivity of different cell components. It is worth noticing that the thickness ($r$) of each individual cell was considered when integrating $j(r)$ to account for the radial decrease in current density, to prevent over-prediction of ohmic losses. In addition, the axial ohmic loss through anode and current collector has been considered as negligible due to good electrical conductivity. The values of some parameters were obtained from references [18-20], including $\sigma_{\text{wire}}, \sigma_{0,\text{electrolyte}}, E_{\text{electrolyte}}, \sigma_{\text{anode}}$ and $\sigma_{\text{cathode}}$. 

197
6.3 Results and Discussion

6.3.1 Sintering behaviour

The co-sintering has been considered quite challenging due to the mismatch in sintering behaviours between different components, which may lead to crack, defect formation or even delamination. During this study, applying pure NiO as the inner current collector was attempted, but the resultant triple-layer fibers displayed problematic mechanical strength after co-sintering. This might be due to the variation in shrinkage rate, and subsequently the introduced tensile stress. As shown in Figure 6.3, the final shrinkage rate of anode mixture (NiO:CGO=3:2) is lower than either pure NiO or CGO, which is due to the hindering effect from isolated CGO and NiO particles, as discussed in a previous study [13] and also in Chapter 3. Moreover, the particle size of NiO is approximately 3-4 times larger than CGO, thus the small CGO particles could fit into the space in between NiO particles, leading to higher initial packing density. Therefore, the samples with mixed phases displayed lower shrinkage rates after the cubes were densified during measurements. When applying pure NiO as current collector, the excessive shrinkage of NiO introduced continuous tensile strength, towards which ceramic materials have relatively low endurance. By adding 10 wt.% CGO into the current collector, the shrinkage rate of the mixture was dramatically reduced to 9.6% (compared to 14.2% of NiO), as shown in the figure. This could be explained by that CGO particles have an insufficient amount to form a continuous phase, and therefore may have negligible boundary growth and densification during sintering process. Moreover, these isolated CGO particles introduce considerable hindering effect towards the
densification of NiO phase, and thus leading to the lowest shrinkage rate of mixture containing 10 wt.% CGO. In terms of the triple-layer co-sintering in this study, the anode layer, which is the major contributor towards mechanical strength, could be properly densified upon two compressive strengths from both electrolyte and current collector, making the resultant sintered fibers to have appropriate mechanical strength.

Figure 6. 3: Sintering curves of pure CGO and NiO; mixtures of anode and current collector.
6.3.2 Morphology of triple-layer hollow fibers

Figure 6.4: SEM images of the samples with different current collector extrusion rates: (a-d) overall view, cross-section, close-up images of electrolyte and current collector of sample ER1; (e) cross-section of sample ER3; (f) cross-section of sample ER5.

Figure 6.4 displays the SEM images of hollow fiber samples with varied current collector extrusion rates. All samples present an asymmetric structure which is composed of micro-channels and a sponge-like structure. The discernable
differences in colours from backscattered electrons (BSE) mode could help distinguish between three components and estimate the corresponding thicknesses. In order to study the effects of current collector thickness on cell performances, the initial objective was to adjust the thicknesses of inner layer by changing the extrusion rates, while maintaining the other two components, the electrolyte and the anode, at constant thicknesses. However, during actual spinning process, varying the inner layer extrusion rates leads to a change in the overall falling speed of precursor fibers. More specifically, when the extrusion rate of inner layer was reduced from 5-1 ml min⁻¹, the overall falling speed was also dramatically slowed due to the fact that the inner layer was precipitated prior to the other two components. Therefore, the subsequent accumulation of spinning suspensions of outer layers leads to both an increase in layer thicknesses and outer diameter, as summarized in Table 6.2. The thickness of current collector was slightly reduced from 99.7 µm to 79.2 µm while the extrusion rate was 5 times lower (5-1 ml min⁻¹), whereas anode, electrolyte thicknesses and outer diameter were all markedly increased, displaying an inverse proportional relationship over inner layer extrusion rate. Despite the unexpected thickness variations, the thickness ratio of current collector over anode displayed a direct proportional trend, thus the ratio was subsequently applied to evaluate the impact of current collector thicknesses on electrochemical performances, as shown in the table. In addition to hollow fiber dimensions, the adjustment of inner layer extrusion rates also affected the morphology, such as the length of micro-channels. The micro-channels of the sample with the thickest inner layer haven’t penetrated the anode/current collector interface (Figure 6. 4(f)), leaving the anode to have a full-sponge structure. Some
previous studies [21, 22] have suggested that the micro-channel length has significant effects on different physical and electrochemical properties, especially the mass transfer resistance, which could subsequently affect the overall cell performances. The close-up image (Figure 6.4(b)) of the cross-section illustrate that a relatively dense electrolyte was obtained after the co-sintering step at 1500 °C despite some micro-cracking which may be due to reason that the voids left from the burnt out of polymer binders could not be completely filled by boundary growth of particles.

Table 6.2: Dimensions, gas-tightness and mechanical strength of different hollow fibers samples.

<table>
<thead>
<tr>
<th>Extrusion rate of current collector (ml/min)</th>
<th>5</th>
<th>3</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Outer diameter (μm)</td>
<td>1571.8</td>
<td>1813.1</td>
<td>2265.9</td>
</tr>
<tr>
<td>Thickness of current collector(μm)</td>
<td>99.6</td>
<td>86.1</td>
<td>79.2</td>
</tr>
<tr>
<td>Thickness of anode(μm)</td>
<td>146.5</td>
<td>219.6</td>
<td>529.7</td>
</tr>
<tr>
<td>Thickness of Electrolyte (μm)</td>
<td>25.1</td>
<td>35.7</td>
<td>43.6</td>
</tr>
<tr>
<td>Ratio of current collector/anode (%)</td>
<td>68.0</td>
<td>39.2</td>
<td>14.9</td>
</tr>
<tr>
<td>N₂ permeance (mol m⁻² s⁻¹ Pa⁻¹)</td>
<td>7.69×10⁻⁹</td>
<td>4.10×10⁻⁹</td>
<td>8.82×10⁻⁹</td>
</tr>
<tr>
<td>Fracture force (N)</td>
<td>6.08</td>
<td>9.95</td>
<td>11.16</td>
</tr>
<tr>
<td>Bending strength (MPa)</td>
<td>146.4</td>
<td>175.3</td>
<td>126.3</td>
</tr>
</tbody>
</table>
6.3.3 Gas-tightness and mechanical strength

In addition to transporting oxygen ions from cathode to anode, electrolyte also functions to prevent direct contact between fuel gases and oxidants, which could be evaluated via gas-tightness tests. In this study, the gas-tightness was investigated via N$_2$ permeation tests. As shown in Table 6.2, samples with various current collector extrusion rates all display N$_2$ permeance at the level of 10$^{-9}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$ and decreased from 7.69×10$^{-9}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$ to 8.82×10$^{-10}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$ when the current collector extrusion rate was reduced from 5-1 ml min$^{-1}$. This is mainly due to the change in electrolyte thicknesses during the co-extrusion process and a thicker electrolyte tends to provide better gas-tightness. According to the literatures, the membrane could be considered as fully gastight if the N$_2$ permeance is at the level of 10$^{-10}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$ [23]. Therefore, all samples displayed proper gas-tightness, from which appropriate open-circuit voltage (OCV) could be obtained.

Mechanical strength is one of the essential properties for the MT-SOFCs to be built into stacks and applied in long-term operations. In this study, mechanical property was characterized by three-point bending method and the results are shown in Table 6.2. As can be seen in the table, the fracture force is increased from 6.1 to 11.2 N when the extrusion rate of current collector was reduced from 5-1 ml min$^{-1}$. This is due to the change in fiber dimensions as both anode and electrolyte, which are the major contributors towards mechanical strength, become thicker during the adjustment of extrusion rates. However, after values of fracture force are normalized by outer and inner diameters, different samples displayed a disordered trend in terms of bending strength. As suggested in previous studies [24], anode-supported hollow fibers with a bending strength of around 150 MPa could be well applied for
the construction of micro-tubular SOFCs. Therefore, further improvement in mechanical strength is required, which could be achieved by a higher sintering temperature or better control over fiber dimensions during the fabrication process.

6.3.4 Electrochemical performances and calculation of ohmic contributions

Figure 6.5 displays the effects of potential differences on current density and power density of hollow fibers with various current collector thicknesses at 600 °C, which is the preferable working temperatures for CGO-based electrolyte [25], using pure hydrogen as the fuel and air as oxidants.

![Figure 6.5: Open-circuit voltage (OCV) and power density as a function of current density of samples with different current collector thicknesses.](image)
The obtained open-circuit voltage (OCV) was increased from 0.78 to 0.85 V when the extrusion rate of current collector was reduced from 5-1 ml min$^{-1}$ as thicker electrolytes lead to better gas-tightness properties. However, these OCV values are lower than the Nernst voltage mainly due to the current leakage, which is resulted from the slight electrical conductivity of CGO, and the non-ideal gas-tightness resulted from micro-cracking during co-sintering process. One possible approach to tackle this problem is adding a buffer layer in between anode and electrolyte to formed the so-called bi-layer electrolyte, as reported in previous studies [26, 27]. As for the maximum power density, sample ER5 illustrates much lower performances compared with the other two samples, which could be due to the full-sponge anode as discussed in Section 3.2 and suggests that proper lengths of micro-channels function has a vital role in suppressing the concentration polarization. The full-sponge anode structure of sample ER5 introduces tremendous resistance towards gas diffusion, thus leading to lower power density compared with other samples. As shown in the figure, fiber sample (ER1) with the thinnest anodic current collector (approximately 15% of anode thickness) displays the highest power density of 1.07 W cm$^{-2}$ at 600 °C, which compares quite well with other studies on MT-SOFCs working at intermediate temperature range [12, 28-30].

Impedance analysis was conducted during performance tests to investigate the effects of current collector thickness on electrochemical performances, as shown in Figure 6. 6. The obtained ohmic loss for samples ER1, ER3 and ER5 are 0.53, 0.55 and 0.62 Ω, respectively. This slight increase is in accordance with electrolyte thicknesses and open-circuit voltage changes. In the case of polarization, sample ER5 presents a much higher loss (0.4Ω) compared with other two samples, which
could be due to the considerable concentration polarization and agrees well with SEM morphology and I-V characterization results.

**Figure 6.6:** Effects of current collector thickness on SEI analysis of samples under open-circuit condition.

The further determination of impedance contributions could be modelled via various methods, such as Complex Nonlinear Least Squares (CNLS) method and Determination of Relaxation Times (DRT) method, as reported in literatures [31, 32].

In this chapter, the major objective is to prove the effectiveness of the new anodic current collector design in achieving more uniform current collection and reducing contact loss. Therefore, a simplified method has been adopted to calculate various ohmic contributions, as described in previous studies [18, 33]. It is generally accepted that the total ohmic loss is mainly composed of electrolyte ohmic loss, electrode ohmic loss, contact loss and resistance from current collector. In SOFC
literatures, contact loss is usually considered as negligible, especially for planar geometric design. However, in terms of MT-SOFC, according to Droushiotis’s work [18] on anode-supported design using silver wires/wool as lumen-side current collector, the contact loss composes up to 70% of the total ohmic loss. Therefore, development of a new current collection technique with reduced contact loss could be an effective approach to improve the overall performance. The parameters for theoretical calculation are shown in Table 6. 3 and the results are shown in Table 6. 4. It could be concluded that inserting the nickel-based anodic current collector effectively lowers the percentage of contact loss down to around 6-10 %. The contributions from both electrodes (anode and cathode) ohmic loss are all less than 0.01%, thus could be considered as negligible, which is also in good agreement with previous results [18]. In this chapter, current collector resistance (silver wires) becomes the major component and it could be further reduced by adopting thicker and shorter wires. In addition, electrolyte ohmic loss, which is the second largest contributor, could be decreased by more controllable spinning and improved co-sintering step. To sum up, sample with the thinnest current collector (ER1) displays the best electrochemical performances. However, further studies will be conducted for a more controllable fabrication process to provide a more convincible value for the preferable current collector thicknesses.
### Table 6.3: Data used in the calculation of ohmic loss contributors.

<table>
<thead>
<tr>
<th>Parameters set or determined in this study</th>
<th>Parameters obtained from references</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parameter</td>
<td>Value</td>
</tr>
<tr>
<td>$A_{wire} [m^2]$</td>
<td>$3.14 \times 10^{-8}$</td>
</tr>
<tr>
<td>$L_{wire} [m]$</td>
<td>Anode: 0.6</td>
</tr>
<tr>
<td></td>
<td>Cathode: 0.2</td>
</tr>
<tr>
<td>$r_1$, $r_2$, $r_3$, $r_4$ (ER1)</td>
<td>$0.56 \times 10^{-3}$, $1.09 \times 10^{-3}$,</td>
</tr>
<tr>
<td></td>
<td>$1.14 \times 10^{-3}$, $1.17 \times 10^{-3}$,</td>
</tr>
<tr>
<td></td>
<td>$\sigma_{anode}$</td>
</tr>
<tr>
<td>$r_1$, $r_2$, $r_3$, $r_4$ (ER3)</td>
<td>$0.65 \times 10^{-3}$, $0.87 \times 10^{-3}$,</td>
</tr>
<tr>
<td></td>
<td>$0.90 \times 10^{-3}$, $0.94 \times 10^{-3}$,</td>
</tr>
<tr>
<td></td>
<td>$0.79 \times 10^{-3}$, $0.82 \times 10^{-3}$,</td>
</tr>
</tbody>
</table>

1) The calculation of wire loss has been conducted separately for the parts in and out of furnace;

### Table 6.4: Theoretical calculation results of different types of ohmic loss contributors.

<table>
<thead>
<tr>
<th>Extrusion rate of current collector (ml min$^{-1}$)</th>
<th>Ratio of current collector/anode (%)</th>
<th>$\eta_{ohm}$ (Ω)</th>
<th>$R_{electrolyte}$ (Ω)</th>
<th>$R_{wire}$ (Ω)</th>
<th>Axial loss of $R_{anode}+R_{cc}$ (Ω)</th>
<th>$R_{Contact}$ (Ω)</th>
<th>Percentage of $R_{Contact}/\eta_{ohm}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>68.0</td>
<td>0.530</td>
<td>0.204</td>
<td>0.287</td>
<td>0.010</td>
<td>0.028</td>
<td>5.4</td>
</tr>
<tr>
<td>3</td>
<td>39.2</td>
<td>0.550</td>
<td>0.221</td>
<td>0.287</td>
<td>0.009</td>
<td>0.034</td>
<td>6.1</td>
</tr>
<tr>
<td>1</td>
<td>14.9</td>
<td>0.623</td>
<td>0.269</td>
<td>0.287</td>
<td>0.005</td>
<td>0.061</td>
<td>9.8</td>
</tr>
</tbody>
</table>

1) Axial loss of anode and current collector was calculated by simulating the two layers as two parallel resistance;
6.4 Conclusions

In this chapter, anodic current collector/anode/electrolyte triple-layer hollow fibers have been successfully fabricated via a phase-inversion assisted co-extrusion/co-sintering technique. 10 wt.% of CGO powder has been added into the inner layer suspensions to adjust the shrinkage behaviours and lead to appropriate mechanical strength for the co-sintered hollow fibers. An asymmetric structure has been obtained including micro-channels and a sponge-like structure. The importance of micro-channels in facilitating fuel transportation and reducing concentration polarization has been illustrated as the sample with the longest micro-channels (ER1) displayed doubled maximum power density (1.07 W cm\(^{-2}\)) compared with the sample having the shortest micro-channels. A new anodic current collection approach for anode-supported MT-SOFCs has been delivered by employing a nickel-based inner layer, which functions to enable more uniform current collection and dramatically reduce the ratio of contact loss in total ohmic loss from 70 % down to 6-10 %. This micro-tubular design, which addresses low cost, adequate manufacturability and good efficiencies, is suitable to be applied in large-scale stack design in the future.

References


Co-extrusion of Triple-layer Hollow Fibers with Anodic Current Collector for MT-SOFC


[33] L. Kleiminger, T. Li, K. Li, and G. H. Kelsall, "CO\textsubscript{2} splitting into CO and O\textsubscript{2} in micro-tubular solid oxide electrolysers," \textit{RSC Adv.}, vol. 4, pp. 50003-50016, 2014.
CHAPTER 7

Conclusions and Recommendations for Future Work

7.1 General conclusions

This thesis mainly focuses on the establishment of a phase inversion-assisted co-extrusion technique and the development of a novel nickel-composite anodic current collection technique that addresses process economy, high efficiency and manufacturability. Triple-layer ceramic hollow fibers with various structural designs have been fabricated and applied for micro-tubular solid oxide fuel cells (MT-SOFCs). It has been demonstrated in this study that the phase inversion-assisted co-extrusion/co-sintering could realize superior process control by adjusting a number of factors during the fabrication process, including the choice of solvent, the compositions of the suspensions, spinning parameters of the co-extrusion and temperature profiles of the co-sintering. In order to understand the effects of the fabrication parameters on the properties of the obtained triple-layer hollow fibers, systematic characterizations have been conducted, such as macrostructure, shrinking behaviour, porosity, mechanical strength, gas permeability, electrolyte gas-tightness, electrical conductivity and cell performance test. The obtained results obtained have been used to fine-tune the fabrication efforts. In the end, a triple-layer
design with a novel current collector has been delivered, which is suitable for mass-scale production.

7.1.1 Fabrication of anode/AFL/electrolyte triple-layer hollow fibers

The feasibility of applying phase inversion-assisted co-extrusion/co-sintering technique for MT-SOFC application has been established by successfully fabricating anode/AFL/electrolyte triple-layer ceramic hollow fibers. By adjusting the extrusion rate of AFL during co-extrusion, different AFL thicknesses could be obtained with great adhesion between different components. Two typical morphologies in anode layer, namely micro-channels and sponge-like structure were introduced in the precursors and well preserved after the subsequent co-sintering step. Introducing an AFL between the anode and electrolyte improves the gas-tightness of electrolyte and mechanical strength. In addition, appropriate electrical conductivity has been preserved, which suggests that a continuous Ni phase was constructed within such hollow fibres. Although finger-like voids from the outer surface were observed, which is unfavourable to the gas-tightness of electrolyte, modifications could be applied during the fabrication to eliminate such voids, such as increasing the viscosity of spinning suspensions, using a larger air gap or increasing the flow rate of internal coagulant. It is worth noticing that the overall performance of SOFC is resulted from several factors, such as thickness and micro-structure of each layer or cell component. As discussed before, the anode layer becomes thinner and average porosity is reduced with the increasing thickness of AFL, while the electrolyte layer becomes thinner but less gas-tight. All these parameters need to be considered
before a proper evaluation of overall performance can be delivered. Therefore, this is one of the major reasons that effects of fabrication parameters were focused in this chapter, such as AFL extrusion rate, on micro-structures and physical properties of resultant hollow fibres in this study.

7.1.2 Effects of AFL thicknesses on electrochemical performances

A series of triple-layer hollow fibers with different AFL thicknesses have been fabricated via the phase inversion-assisted co-extrusion/co-sintering technique, which dramatically simplifies the preparation process with great control over structures of each layer. By adjusting the rheology of spinning suspensions, a more precise control over thicknesses has been achieved during co-extrusion so the effects of AFL thickness on different properties, electrochemical performances in particular, could be studied more systematically. SEM images display a typical asymmetric structure, including micro-channels and sponge-like structure. Inserting an AFL effectively improves both the cell robustness and gas-tightness of the electrolyte layer, which is accordance with the previous chapter. In terms of cell performances, there exists a trade-off effect with increased AFL thickness. Enlarged TPB means increased active reaction sites and subsequently inhibited activation polarization. On the other hand, the full-sponge structure of AFL suggests that increased thickness could comprise mass transport property and increase the concentration polarization. The performance results illustrate that AFL between 17 and 33 μm (6-11.5% of total anode thickness) contributes to improved cell performance, and a maximum power density of 1.21 W cm⁻² is obtained at 600 °C using pure H₂ as the fuel.
7.1.3 Fabrication of dual-structured anode/nickel-mesh hollow fibers

Efficient current collection, from the lumen side of micro-tubes in particular, has always been a concern in the development of MT-SOFCs and is one of the major bottlenecks that prevent this design from mass-scale production. In this study, a new anodic current collector design has been developed by fabricating dual-structured Ni-mesh/anode hollow fibers via the phase inversion-assisted co-extrusion/wet-spinning process. By applying solvent as internal coagulant and eliminating air gap, conical micro-channels originating from the outer surface have penetrated the whole cross-section. The nickel inner layer displayed a deliberate mesh-structure with uniformly distributed entrances. This mesh-structure with long micro-channels can effectively reduce the fuel transport resistance, as the conical micro-channels inside anode provide more evenly distributed and easier pathways for H$_2$ diffusion. By adjusting the extrusion rates, precise control over the nickel-mesh thickness can be achieved with superior adhesion between the two components. Increasing the thickness of current collector leads to an increased average porosity and electrical conductivity, but compromising the mechanical strength, which could be critical concern when constructing a complete single cell. The excessive shrinkage of NiO during co-sintering and the agglomeration of Ni during long-term operation suggest that other ceramic materials might well be introduced to form a composite current collection, which has compatible shrinkage behaviour and proper durability.
7.1.4 Fabrication of triple-layer hollow fibers with high-efficiency nickel-composite current collector

In this study, the fabrication of anodic current collector/anode/electrolyte triple-layer hollow fibers via a phase inversion-assisted process is evolved from the proof-of-concept research in the previous chapter, in which a dual-layer anodic current collector/anode design was developed. A certain amount (10 wt.%) of CGO powder has been added into the inner layer suspensions to adjust the shrinkage behaviours and lead to appropriate mechanical strength for the co-sintered hollow fibers. An asymmetric structure has been obtained including micro-channels and a sponge-like structure. The importance of micro-channels in facilitating fuel transportation and reducing concentration polarization has been illustrated as the sample with the longest micro-channels (ER1) displayed doubled maximum power density (1.07 W/cm²) compared with the sample having the shortest micro-channels. The new anodic current collection approach for anode-supported MT-SOFCs has been delivered by employing a nickel-based inner layer, which functions to enable more uniform current collection and dramatically reduce the ratio of contact loss in total ohmic loss from 70% down to around 6-10%. To sum up, this current collector design, which addresses cost-effectiveness, manufacturability and high-efficiency, is suitable for large-scale stack design.
7.2 Recommendations for Future Work

7.2.1 New multi-layer designs

In this thesis, triple-layer hollow fibers with various designs have been fabricated and tested. The results have suggested the insertion of AFL could effectively improve the cell performances by providing more reaction sites, while the adoption of nickel-based anodic current collector could achieve more uniform current collection by reducing the contact loss. In the future, an improved quadruple-layer spinneret will be designed to integrate the advantages from both AFL and current collector. The incorporation of more components may bring considerable difficulties in matching the rheology as the interactions between layers during spinning have been proved affect the morphology markedly. Therefore, careful manipulation over compositions of suspensions is required.

As for intermediate-temperature SOFC, it has been reported that MT-SOFCs using CGO as electrolyte have relatively low open-circuit voltage (OCV), usually around 0.8 V, compared with other electrolyte materials, such as YSZ, LGSM or SDC. This is mainly due to the minor current leakage at elevated temperatures when Ce$^{4+}$ is reduced to Ce$^{3+}$ in reducing atmosphere. One approach to tackle this problem is inserting a 'buffer layer' in between the anode and CGO electrolyte. Some previous studies have proved that SOFC with such bi-layer electrolyte could display OCV close to the Nernst voltage [1, 2]. However, the conventional multi-step fabrication introduces considerable boundary effect and subsequently increased ohmic loss. It has been shown that co-extrusion technique has the advantages of superior adhesion between components and proper process control. Therefore, co-extrusion
of bi-layer electrolyte could combine the advantages of improved OCV and reduced ohmic loss.

7.2.2 Hydrocarbon-fuelled MT-SOFC

As discussed before, one the great benefits of SOFC is the flexibility in the choice of fuels due to elevated operating temperatures, which enables internal reforming to convert hydrocarbon into hydrogen and carbon monoxide at the presence of steam [3]. The most common fuel, especially for domestic combined heat and power (CHP) systems, is natural gas consisting primarily of methane. It has the advantages of low-cost, clean, abundant in reserves and readily available, with a well-established supply infrastructure all around the world. Internal reforming could be classified into two major categories, namely the direct reforming and indirect reforming. The former depends on nickel anode as catalyst, which is well known for its propensity to promote hydrocarbon pyrolysis, while the indirect reforming requires the presence of separately deposited catalysts. The major advantage of indirect reforming is improved control in terms of thermodynamic. It is also more convenient to develop catalysts less likely to promote carbon formation but has comparable catalytic activity than nickel anode. A number of studies have been undertaken and reported that the coking (carbon formation) on either the surface of reforming catalyst or on the anode, is a vital problem to be tackled, since over time this can lead to blocking of active sites and consequently reduced cell performances and poor durability [4-7]. In extreme cases, formation of carbon filaments or agglomerates can increase resistance to gas transport in the fuel inlet manifold or even physical blockages. In
this study, the hollow fibers with an asymmetric structure could function as reforming chamber composed of hundreds of micro-reactors. Deposition of catalysts (Cu or Zn-based catalysts) in such micro-channels could be achieved via vacuum assisted filtration, wash coating or sol-gel method, as reported elsewhere [8]. We foresee that in this way, fuels can be fully internally reformed together with water gas shift into H₂ and CO₂ with inhibited tendency towards coke-formation.

7.2.3 Multi-channel design

Multi-channel design, also known as monolithic structure, is widely applied in automotive and stationary emission control devices and large numbers of chemical industry as catalyst support [9]. It has an outstanding benefit of high surface area and low pressure-drop, which makes it suitable to be applied for electrodes of SOFCs. Some proof-of-concept studies have been conducted, during which hollow fibers with three and seven-channel design have been fabricated, as shown in Figure 7.1. Another interesting advantage has also been observed that the fracture force, measured via three-point bending method, is 3-5 times higher compared with conventional single-channel design. This property is extremely preferable when constructing single cells into a SOFC bundle, which has considerable requirement in thermal cycling and long-term stability. It is also worth noticing that the multi-channel design could considerably reduce the thickness of sponge-like structure to a minimum of 20-30 µm. As suggested in literature, the actual electrochemically active anode thickness at high current loading is only around 10 µm from electrolyte, while the remaining part of anode functions more to provide sufficient conductivity to
transport electrons. Therefore, the thin sponge region and better-distributed gas-diffusion pathways can provide more effective TPB.

![Figure 7.1: SEM images of cross-section and sponge-like region of an example multi-channel hollow fiber.](image)

**Figure 7.1**: SEM images of cross-section and sponge-like region of an example multi-channel hollow fiber.

### 7.2.4 MT-SOFC stack design

Single micro-tubular SOFC fuelled by \( \text{H}_2 \) developed in this study can be first assembled into a parallel unit as shown in Figure 7. 2. This can be achieved by applying additional cathode material as a “glue” to form a complete cathodic interconnect of the parallel unit before sintering. As for the anodic interconnect, a metallic “cup” acting as interconnects and sealant can be dip-coated on both ends of a parallel unit for connecting the current collectors as well as for sealing the gaps between each single cell. The stacks in parallel or series can be further assembled
by appropriate connection of cathode and anode interconnects of each individual parallel unit using external conductors as shown in Figure 7. 2. In the resultant SOFC stacks, fuels are introduced to the lumen/interior current collecting side of each single cell, while oxidant is directed towards the exterior cathode layer. So spacers between parallel units need to be used for continuous flow of oxidant to each individual cathode. For the stack in parallel, this spacer should be conductive, while for the stack in series, the spacer should be an insulator.

**Figure 7. 2: Schematic diagram of MT-SOFC stack design.**

In addition to the characterization techniques used for single cells, some other measures need to be designed to characterize MT-SOFC stacks systematically. This includes the resistance of cathode towards air transport, temperature distribution within the stack, long-term stability, redox cycling and fuel utilization rate. The electrochemical performances of the parallel unit and stacks need to be
Chapter 7

Conclusions and Recommendations for Future Work

cmpared with single cells under the same operating parameters, the objective being to determine the “controlling step” and hence allow optimization of the manufacturing process of single cells and assembly of SOFC stacks.

References


List of Publications

Publications


Conference Oral Presentation


Conference Poster Presentation


### Appendix: Permissions for third party copyright works

<table>
<thead>
<tr>
<th>Page Number</th>
<th>Type of work: text, figure, etc.</th>
<th>Source work</th>
<th>Copyright holder &amp; year</th>
<th>Work out of copyright</th>
<th>Permission to re-use</th>
<th>Permission requested</th>
<th>permission refused</th>
<th>Orphan work</th>
<th>Requested license No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Page 42</td>
<td>figure</td>
<td>Materials Science and Engineering A (2003), vol. 362, 228-239</td>
<td>© 2003 Elsevier</td>
<td></td>
<td>✓</td>
<td></td>
<td></td>
<td></td>
<td>3620280326681</td>
</tr>
<tr>
<td>Page</td>
<td>Type</td>
<td>Title</td>
<td>Year</td>
<td>Publisher</td>
<td>CrossRef</td>
<td>DOI</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-----</td>
<td>------</td>
<td>----------------------------------------------------------------------</td>
<td>------</td>
<td>-----------</td>
<td>----------</td>
<td>-------------</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>63</td>
<td>figure</td>
<td><em>Renewable and Sustainable Energy Reviews</em> (2002), vol. 6, 433-455</td>
<td>2002</td>
<td>Elsevier</td>
<td>✓</td>
<td>3620301420506</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

230