DEVELOPMENT OF DUAL-LAYER HOLLOW FIBER WITH MODIFIED ELECTROLYTE FOR MICRO-TUBULAR SOLID OXIDE FUEL CELL

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In the Name of ALLAH, The Most Gracious and The Most Merciful

Specially dedicated to my beloved husband

(Ahmad Taufiq Abd Jaafar)

my children

(Muhammad Al-Fateh, Solahuddeen Al Ayyubi)

my parents

(Jamil Kasa, Che Amah Abd Kadir)

siblings

(Rosli, Siti Norjuita, Mohd Fitri, Mohd Haikal Hakim)

in-laws

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ABSTRACT

The excellent ionic conductivity at temperature ranges from 400-700 °C has made cerium gadolinium oxide (CGO) as one of promising alternative solid electrolyte materials for intermediate temperature solid oxide fuel cell (IT-SOFC) application. However, the requirement of high sintering temperature up to 1550 °C for densification of CGO electrolyte complicates the cell fabrication process as it reduces the porosity in the electrode layers, particularly in the co-sintering step of anode/electrolyte dual-layer hollow fiber (DLHF). Hence, the fabrication of the DLHF is challenging due to the different sintering behaviors of the each layer. The main objective of this study is to develop anode/electrolyte DLHFs with improved electrolyte properties with reduced co-sintering temperature for IT-SOFCs via a single-step phase inversion-based co-extrusion/co-sintering technique. The sintering properties of electrolyte flat sheet was studied by comparing two approaches, (i) using mix particle size electrolyte and (ii) addition of lithium oxide as sintering additive in the electrolyte. The DLHF with modified electrolyte was later fabricated by phase inversion based co-extrusion and co-sintered at temperature ranging from 1400 to 1500 °C. The DLHF was evaluated in term of the morphology, mechanical strength and gas-tightness as well as electrical conductivity, porosity and permeability of the anode layer. This study showed that a dense CGO flat sheet layer sintered at 1450 °C with the addition of 30% nano size CGO particles were obtained. Meanwhile, the doping of 2 mol% of lithium nitrate into CGO was found to reduce the sintering temperature to 1400 °C. When the co-sintering temperature increased, the mechanical strength, gas-tightness and electrical conductivity were increased, whereas the porosity and permeability of the anode layer were decreased. The DLHF that was co-sintered at 1450 °C showed sufficient properties and therefore, it was chosen for the construction of micro-tubular SOFC (MT-SOFC). When comparing the maximum power density of MT-SOFC namely nickel (Ni)-CGO/CGO (unmodified), Ni-CGO/30%nano-70%micron CGO (first approach) and Ni-CGO/lithium (Li)-CGO (second approach); it was found that the Ni-CGO/30%nano-70%micron CGO cell performed the best. At 500 °C, the cell produced the highest maximum power density, which was 275 Wm^{-2} as compared to Ni-CGO/Li-CGO cell (60 Wm^{-2}) and Ni-CGO/CGO cell (200 Wm^{-2}). Porous anode in Ni-CGO/30%nano-70%micron CGO DLHF provided active reaction site, while dense electrolyte layer resulted from pore filling caused by the introduction of 30% nano sized CGO particles improved the gas-tightness of the electrolyte. Meanwhile, the closed pore caused by the migration of Li ions in anode sponge–like region of Ni-CGO/Li-CGO hindered the triple phase boundary region that impaired the cell performance. This limited the inclusion of Li in DLHF design. Nevertheless, the results from this study has proven the feasibilities to accelerate the densification of electrolyte as well as presented an advanced electrolyte material for MT-SOFC.

ABSTRAK

Kekonduksian ionik yang sangat baik pada julat suhu antara 400-700 °C telah menjadikan cerium gadolinium oksida (CGO) sebagai bahan alternatif elektrolit pepejal untuk penggunaan sel bahan api pepejal teroksida (IT-SOFC). Walau bagaimanapun, keperluan suhu pensinteran yang tinggi sehingga 1550 °C untuk pemadatan CGO telah merumitkan proses fabrikasi sel kerana mengurangkan keliangan dalam lapisan elektrod terutamanya dalam langkah pensinteran bersama anod/elektrolit gentian geronggang dwi lapisan (DLHF). Oleh itu, fabrikasi DLHF adalah mencabar berikutan perbezaan kelakuan pensinteran dalam setiap lapisan. Objektif utama kajian ini adalah untuk membangunkan anod/elektrolit DLHF dengan ciri elektrolit yang lebih baik dan mengurangkan suhu pensinteran untuk IT-SOFCs melalui teknik langkah tunggal songsangan fasa bersama penyemperitan dan pensinteran. Sifat pensinteran kepingan rata elektrolit telah dikaji dengan membandingkan dua pendekatan; (i) menggunakan elektrolit dengan saiz partikel bercampur dan (ii) penambahan litium oksida sebagai bahan tambahan pensinteran dalam elektrolit. DLHF dengan elektrolit yang diubahsuai kemudiannya dihasilkan dengan teknik songsangan fasa bersama penyemperitan dan pensinteran pada suhu antara 1400-1500 °C. DLHF ini dinilai dari segi morfologi, kekuatan mekanikal dan keketatan gas serta kekonduksian elektrik, keliangan dan kebolehtelapan lapisan anod. Didapati lapisan kepingan rata CGO padat yang disinter pada 1450 °C dengan tambahan 30% zarah CGO saiz nano dapat diperoleh. Sementara itu, pengedopan 2 mol% litium nitrat ke dalam CGO telah menurunkan suhu pensinteran kepada 1400 °C. Apabila suhu pensinteran bersama meningkat, kekuatan mekanikal, keketatan gas dan kekonduksian elektrik meningkat manakala keliangan dan kebolehtelapan lapisan anod berkurangan. DLHF yang telah disinter bersama pada suhu 1450 °C menunjukkan ciri yang mencukupi dan oleh itu, telah dipilih untuk pembinaan tiub mikro SOFC (MT-SOFC). Dengan membandingkan ketumpatan kuasa maksimum MT-SOFC iaitu nikel (Ni)-CGO/CGO (tidak diubahsuai), Ni-CGO/30%nano-70%mikron CGO (pendekatan pertama) dan Ni-CGO/litium (Li)-CGO (pendekatan kedua); didapati sel Ni-CGO/30%nano-70%mikron CGO menunjukkan prestasi terbaik. Pada 500 °C, sel tersebut menghasilkan ketumpatan kuasa maksimum yang paling tinggi iaitu 275 Wm^{-2} berbanding sel Ni-CGO/Li-CGO (60 Wm^{-2}) dan Ni-CGO/CGO (200 Wm^{-2}). Anod berliang dalam sel Ni-CGO/30%nano-70%mikron CGO menyediakan tapak tindakbalas aktif manakala lapisan elektrolit padat terhasil daripada pengisian liang dengan pengenalan 30% zarah CGO bersaiz nano telah meningkatkan keketatan gas elektrolit. Manakala liang tertutup disebabkan oleh perpindahan ion Li dalam kawasan anod bagi sel Ni-CGO/Li-CGO telah menghalang rantau sempadan tiga fasa yang menjejaskan prestasi sel. Ini telah menghadkan penglibatan Li dalam reka bentuk DLHF. Walau bagaimanapun, hasil kajian ini telah membuktikan kebolehlaksanaan untuk mempercepatkan pemadatan elektrolit dan juga mengemukakan bahan elektrolit termaju untuk MT-SOFC.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

AFC	-	Alkaline fuel cell
ASTM	-	American Society for Testing and Materials
CaO	-	Calcium oxide
CO_2	-	Carbon dioxide
CGO	-	Cerium gadolinium oxide
DMFC	-	Direct methanol fuel cell
DMSO	-	Dimethyl sulfoxide
Fe_3O_4	-	Ferum oxide
H_2	-	Hydrogen
H_2O	-	Water
HF	-	Hollow fibre
HT	-	High temperature
IT	-	Intermediate temperature
K_2CO_3	-	Potassium carbonate
KOH	-	Potassium hydroxide
Li_2O		Lithium oxide
Li_2CO_3	-	Lithium carbonate
$LaMnO_3$	-	Lanthanum manganite
LSCF	-	Lanthanum strontium cobalt ferrite
LSM	-	Lanthanum strontium manganite
MCFC	-	Molten carbonate fuel cell
MgO	-	Magnesium Oxide
MIEC	-	Mixed ionic electron conductor
MT	-	Micro-tubular
Na_2CO_3	-	Sodium carbonate
Ni	-	Nickel
NiO	-	Nickel oxide

NMP	-	N-methyl-2-pyrrolidinone
O_2	-	Oxygen
OCV	-	Open circuit voltage
PAFC	-	Phosphoric fuel cell
PEMFC	-	Proton exchange membrane fuel cell
PES	-	Polyethersulfone
PF	-	Pore former
PMMA	-	Poly methyl methacrylate beads
RedOx	-	Reduced and Oxidation Atmosphere
Sc_2O_3	-	Scandia Oxide
SEM	-	Scanning electron microscopy
SOFC	-	Solid oxide fuel cell
SSR	-	Sintering shrinkage rate
TEC	-	Thermal expansion coefficient
TGA	-	Thermo-gravimetric analysis
TPB	-	Triple-phase boundaries
XRD	-	X-ray diffraction
Y_2O_3	-	Yttria oxide
YSZ	-	Yttria-stabilized zirconia
ZrO_2	-	Zirconia oxide

LIST OF SYMBOLS

A	-	Area of hollow fibre
b	-	Width
B_F	-	Bending strength
cm	-	Centimetre
cP	-	Centipoise
D	-	Dry weight
d	-	Thickness
D_i	-	Inner diameter
D_O	-	Outer diameter
g	-	Gram
J	-	Joule
K	-	Kelvin
L	-	Length
L	-	Length of hollow fibre
m	-	Metre
min	-	Minute
mol	-	Mole
N	-	Load
nm	-	Nanometre
M	-	Saturated weight
P	-	Gas permeability
p_a	-	Atmospheric pressure
Pa	-	Pascal
p_o	-	Initial pressure
p_t	-	Final pressures
R	-	Gas constant
s	-	Second

S	-	Suspended weight
T	-	Temperature
t	-	Time for measurements
V	-	Voltage
V_c	-	Volume of the test cylinder
W	-	Watt
wt	-	Weight
°C	-	Degree Celsius
%	-	Percent
μm	-	Micrometre

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.1 Research Background

Currently, the world is still dependent on fossil fuels as its major energy source. Nevertheless, the world today confronted with the issues of concern such as increasing energy consumption, energy security concerns, global warming and acid rain. Thus, using renewable energy and developing more efficient energy conversion devices have emerged as significant research and development (R&D) trends. Fuel cell is one of energy-conversion device that converts chemical energy directly to the electrical energy via electrochemical process. Hydrogen is the most common fuel, but hydrocarbons such as natural gas and alcohols like methanol are sometimes used. Unlike batteries, fuel cells need a constant source of fuel and oxygen/air to sustain the chemical reaction. Thus, as long as the input is supplied, fuel cells can produce electricity continuously.

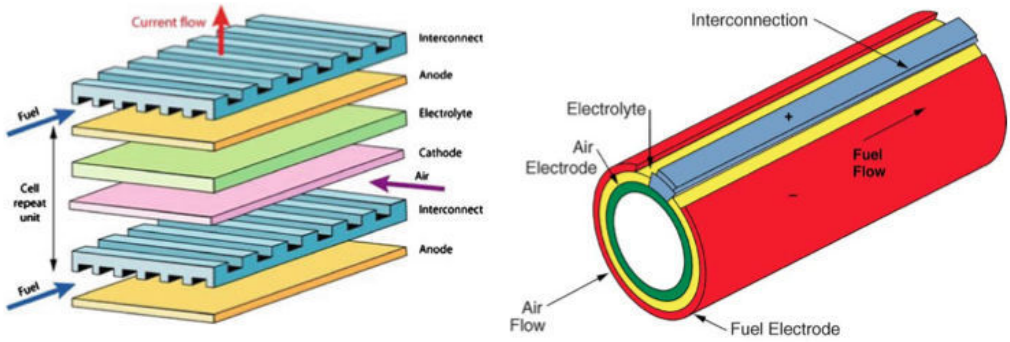
There are six common types of fuel cells as shown in Table 1.1. Primarily, their electrolyte classifies the fuel cells. This classification determines the chemical reactions that take place in the cell, the catalysts required, the temperature range in which the cell operates and the fuel required. These features typically affect the applications for which these cells are most suitable. In recent years, solid oxide fuel cells (SOFCs) have received tremendous attention due to their high-energy conversion efficiency, low emissions and excellent fuel flexibility.

Table 1.1 : Fuel Cell Types (U.S Department of Energy) [1]

Name	Electrolyte	Anode gas (fuel)	Cathode gas (oxidant)	Operating temperature	Development Status
AFC (Alkaline Fuel Cell)	Potash	Hydrogen	Oxygen	Below 80 °C	Commercial
PEMFC (Proton Exchange Membrane Fuel Cell)	Polymer Membrane	Hydrogen	Oxygen or Atmospheric Oxygen	to 120 °C	Being developed
DMFC (Direct Methanol Fuel Cell)	Polymer Membrane	Methanol	Atmospheric Oxygen	90 – 120 °C	Being developed
PAFC (Phosphoric Acid Fuel Cell)	Phosphorus	Hydrogen	Atmospheric Oxygen	200 °C	Commercial
MCFC (Molten Carbonated Fuel Cell)	Alkali-carbonates	Hydrogen Methane	Atmospheric Oxygen	650 °C	Being developed
SOFC (Solid Oxide Fuel Cell)	Ceramic Oxide	Hydrogen Methane	Atmospheric Oxygen	500 – 1000 °C	Being developed

Since 1960s, many studies conducted on solid oxide fuel cells (SOFCs) have been focusing on compact design and cell performance enhancement. Most of the developments focus on planar and tubular designs as shown in Figure 1.1. Typically, fabrication of planar SOFCs is cheaper due to its simpler techniques such as tape

casting and screen printing [2]. Furthermore, the planar SOFCs offer higher power densities production due to inherently shorter path lengths for electrons to travel from anode to cathode sides. However, the design has certain disadvantages including inherently lower thermal stability and larger areas that require high temperature for gas sealing. On the other hand, the tubular type is relatively well-established in terms of design and manufacturing technology [3]. It offers better thermo-cycling behavior and easier sealing around the circumference of the tubes [4]. However, its difficulty in designing complete interconnects axially and circumferentially because it creates longer current paths which often increase the ohmic loss. It also decreases the power densities as compared with its planar counterpart.



(a) Planar SOFC [5] (b) Tubular SOFC [6]

Figure 1.1 Typical SOFC Designs

Started in early 1990s, Kendall and co-workers initiated an advanced cell design namely micro-tubular SOFCs [2]. This invention was driven from the effort to improve the performance of tubular SOFCs by reducing the cell size, from centimeter to the micron scale. It is remarkable that various potential benefits appear when the diameter gets smaller. The micro-tubular SOFC offers a greater tolerance to thermal cycling, quicker start-up capability, higher volumetric output density and portable characteristics compared to the conventional planar and tubular SOFCs [7]. These characters have promoted the research in micro-tubular SOFCs. Figure 1.2 (A) shows the analyze result from 'Scopus' search which reveals the increase in the number of articles published on micro-tubular SOFC over the last one decade (2006–2016). Besides, the reported electric current output from the micro-tubular SOFCs

has also increased greatly over the recent years. Figure 1.2 (B) shows the country-wise distribution of micro-tubular SOFC researchers, the data that was also drawn from 'Scopus'. It is noticeable that the attraction in micro-tubular SOFC research is worldwide with increasing number of researchers from different countries.

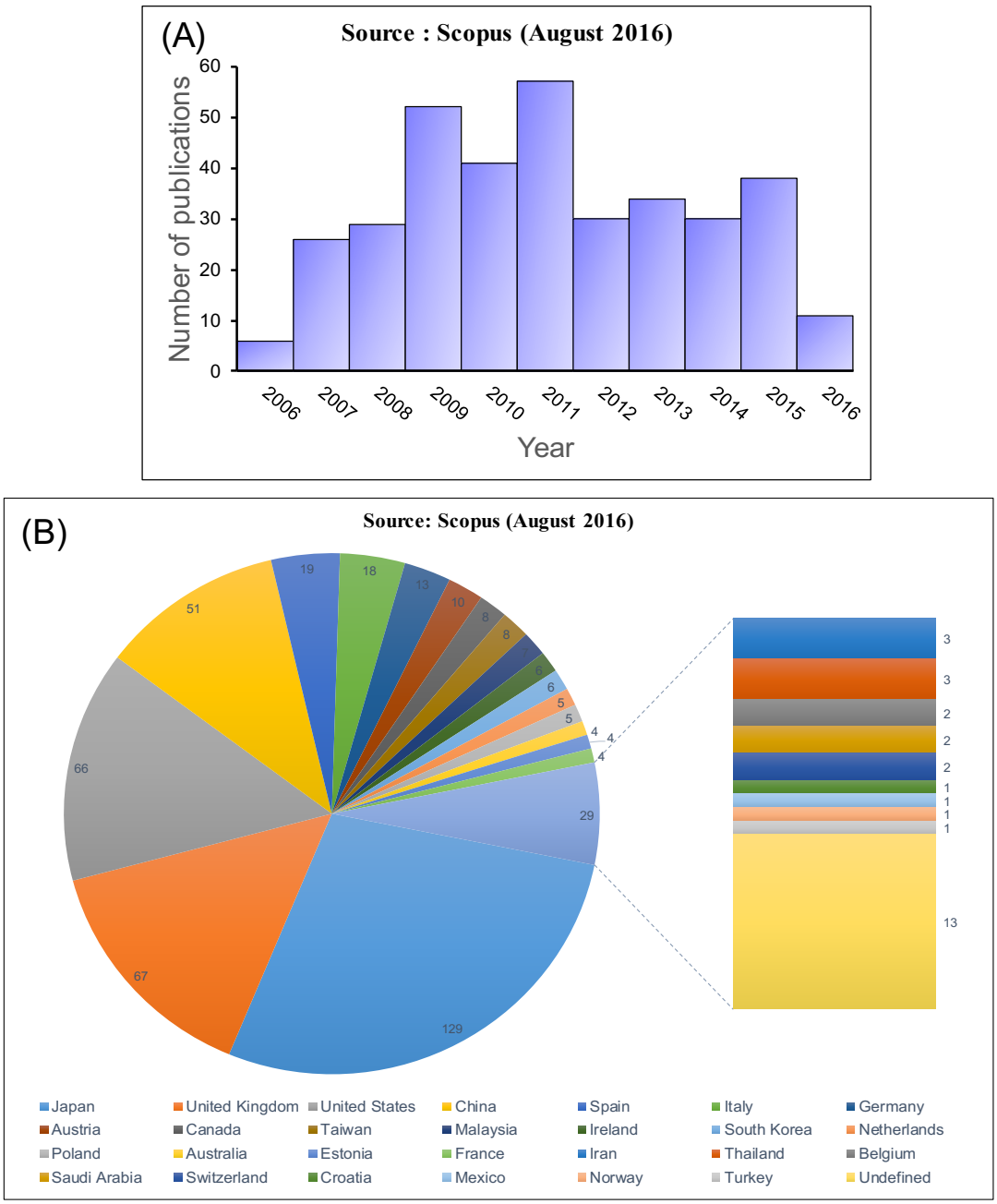


Figure 1.2 (A) The number of articles on micro-tubular SOFCs. The data is based on the number of articles mentioning micro-tubular SOFCs in the citation database Scopus in August 2016. (B) The country-wise distribution in micro-tubular SOFC research. The data is based on the number of articles mentioning micro-tubular SOFC in the citation database Scopus in August 2016.

Generally, the design of SOFC can be configured into two geometries; self-supporting and supported concept [8]. As depicted in Figure 1.3, self-supporting refers to the electrolyte with thickness around 80-250 μm forms as structural element of the design while for the supported concept, the electrolyte is deposited as a thin layer <50 μm on porous electrode either cathode or anode.

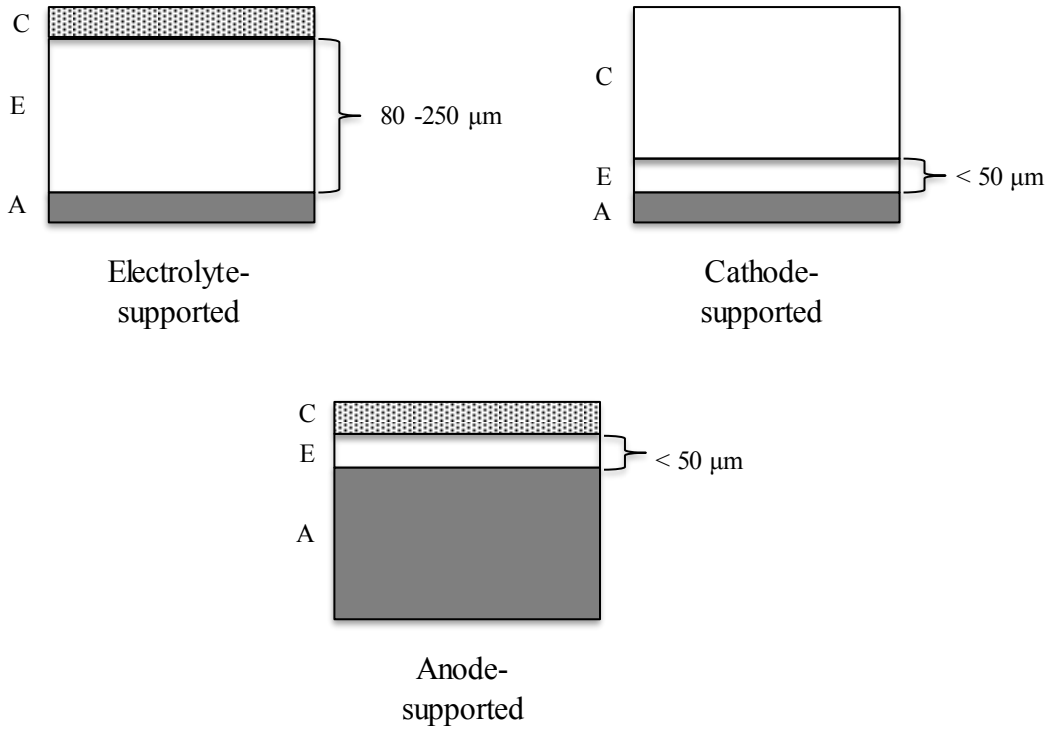


Figure 1.3 Geometries of SOFC [9]

The micro-tubular SOFCs can be constructed into the anode supported, the cathode supported or the electrolyte supported configurations depending on the component providing the mechanical strength to the micro-tubularcells. The use of anode-supported design allows for a thinner electrolyte layer, which reduces electrolytic resistance losses and yields better conductance at lower temperatures compared to an electrolyte supported [10]. This configuration is generally recognized to increase the performance, but additional caution is needed to avoid the formation of microcracks and to ensure the electrolyte layer is entirely gas tight. Nevertheless, it should be addressed that majority of recent works on micro-tubular SOFCs uses the anode-supported design.

Recently, there is a trend to move to lower temperature operation, which is intermediate (500-700 °C) or low (<500 °C) operating temperature. High operating temperature system possesses several disadvantages on commercialization for instance, long-term stability of the cell components, materials as well as high manufacturing cost. Moreover, high operating temperature limits the range of material selection. In comparison to lower temperature operation, it affords more rapid start-up, improved durability, and higher robustness as well as simplified system requirements and wider choice of selecting materials.

Consequently, the electrolytes with high oxygen-ion conductivity at low temperatures have received tremendous attractions. Cerium gadolinium oxide (CGO) is an attractive electrolyte alternative to yttria stabilized zirconia (YSZ), owing to its superior oxygen ion conductivity at low temperatures [11]. Like zirconia, ceria-based electrolytes have a cubic, fluorite-type crystal structure. This structure affords the large oxygen ions with high mobility. However, at low oxygen partial pressures and at higher temperatures ceria is partially reduced and the material becomes an electronic conductor, which can cause short circuit [12]. Although the stability of ceria in low oxygen partial pressures is inferior to that of zirconia, the chemical stability of ceria with cathode materials is superior to that of zirconia. CGO has been shown to be stable with a wide variety of electrodes, including lantahnum strontium manganate (LSM), lanthanum strontium cobalt (LSC), lanthanum strontium ferrite (LSF), lantahnum strontium cobalt ferrite (LSCF) and lantahnum nickel ferrite (LNF) [13].

Indeed, the general requirements for an electrolyte are high ionic conductivity, low electronic conductivity, and stable in both oxidizing and reducing environments with good mechanical properties [12–15]. Thus, the electrolyte structure must be dense because it acts as membrane that separates the air and fuel compartments and must be an oxygen ion conductor. Henceforth, electrolyte is the heart of the fuel cell whereby it determines the performance of the cell. Literature studies shows that two electrolyte systems specifically YSZ and CGO have been widely explored for SOFCs [13][15]. Each electrolyte system offers advantages

along with a number of drawbacks. Table 1.2 shows the general comparison between YSZ and CGO systems.

Table 1.2 : Comparison between YSZ and CGO systems

Electrolyte system	**YSZ**	**CGO**
Operating Temp	High Temp (800 – 1000 °C)	Intermediate Temp (500-700 °C)
Material Cost	Relatively less expensive	Relatively expensive
TEC	10.5×10^{-6} K^{-1}	12.5×10^{-6} K^{-1}
Conductivity	Ionic conductivity	Mixed ionic electronic conductivity at high temperature and low oxygen partial pressure
Mechanical strength	Sufficient mechanical strength	Ceria electrolytes are unstable mechanically at temperatures above 700 °C
Reaction with electrodes material	Chemical reaction with the cathode material	Unreactive towards potential electrode materials
Advantages	Provide high quality exhaust heat for cogeneration, and when pressurized, can be integrated with a gas turbine to further increase the overall efficiency of the power system.	Improved durability, wider choice for interconnecting material selection, and lower costs can be achieved by reducing the operating temperature below 700 °C

As shown in Table 1.2, YSZ fulfills the electrical requirements at high temperatures (800 - 1000 °C) and has good high temperature mechanical properties. However, one of its drawbacks is its reactivity with perovskite oxide electrodes such as LSM. At high temperatures, they react and forming pyrochlore, $La_2Zr_2O_7$, the perovskite $SrZrO_3$ or both [12]. Unless, the YSZ layer is protected with CGO layer [15]. Alternatively, CGO has received great attention as an electrolyte material and

it has the highest conductivity at lower temperature and lower polarization resistance [34]. Besides, doped ceria is more stable and relatively unreactive towards potential electrode materials.

Besides the progress in SOFC designs, development in the fabrication process is critically important to ensure the success of the cell. Previously, the fabrication of micro-tubularSOFC, which consists of three main components (i.e. anode, electrolyte and cathode), can only be achieved through multiple steps [17]. There are two common techniques that have been employed to fabricate the support of the cell which are plastic mass ram extrusion and dry-jet wet extrusion. For the ram extrusion technique, the support materials are mixed with binder and solvent to form a viscous paste. The paste is then extruded through a custom-made die using a ram extruder to obtain the support tubes. The support tubes are dried and cut to the desired length prior being subjected to the sintering process. The fabricated support tubes are usually of a symmetrical structure with large wall thicknesses, which results in a large resistance for the diffusion of fuel into the anode (in the case of anode-supported design).

In contrast, the dry-jet wet extrusion technique offers greater control over the morphology of hollow fiber (common terminology for the tubes prepared using this technique). The dry-jet wet extrusion is similar to the ram extrusion process. The main difference is that the spinning suspension or dope for the dry-jet wet extrusion is in suspension form and the ram extrusion is in paste or plastic mass form. Another major difference is the solidification process of the tube (or hollow fiber). In dry-jet wet extrusion, the solidification of the hollow fiber occurs via phase inversion process initiated by the solvent/non-solvent exchange. While in ram extrusion process, the tube is dried straight away after the extrusion prior to being subjected to the sintering process.

However, both techniques are only used to fabricate a single-layer of support, and thus, still require a multi-step in order to develop a complete fuel cell. By using dry-jet wet or ram extrusions, a support layer for example anode tube is first prepared and pre-sintered to provide mechanical strength to the fuel cell. The

electrolyte layer is then deposited and sintered prior to the final coating of cathode layer. Each step involves at least one high temperature heat treatment, making the cell fabrication time-consuming and costly with unstable control over cell quality.

For a more economical fabrication of micro-tubular SOFC with reliability and flexibility in quality control, an advanced dry-jet wet extrusion technique, i.e. a phase inversion-based co-extrusion process, is recently employed to fabricate a dual-layer hollow fiber, which consists of electrolyte and anode for intermediate temperature SOFC (IT-SOFC)[18]. Co-extrusion technique in developing an electrolyte/anode dual-layer hollow fiber for micro-tubular SOFC pioneered by Li and co-workers [19] and the cell from the prepared hollow fiber showed a very outstanding power output, approximately 2.32 Wcm^{-2}, which is almost double than the one prepared from conventional multi-step technique [20][21]. In comparison with conventional extrusion processes, the co-extrusion is more attractive due to the following reasons: (i) saving the production cost and time as it combines a number of processes into one; (ii) decreasing the risk of inducing defect; (iii) producing a great adhesion between layers.

1.2 Problem Statement

To date, IT-SOFC is more promising compared to HT-SOFC ones due to their better long-term durability and cost effectiveness. It has been reported that CGO possesses 4 to 5 times higher conductivity at lower operating temperatures [22–28], and thus, make it more suitable to be used as the electrolyte for IT-SOFC. However, sintering temperatures as high as 1550 °C are typically needed to densify CGO electrolyte [29] which increasing cost and difficulty in the cell fabrication process. Moreover, sintering of the layers at too high temperatures to obtain full densification of the electrolyte layer would cause an interfacial interdiffusion between the electrolyte and electrodes material which eventually generate a highly resistive interface that can diminish the ionic conductivity [30]. It should be note that high sintering temperature might reduce the porosity in the electrodes layers as well [31] particularly in the co-sintering step [18] of dual-layer hollow fiber (HF).

Keeping in mind that the anode component; usually nickel oxide (NiO), are normally sintered at 1400 °C, steps would be taken to lower the sintering temperature of electrolyte material so that it can be co-sintered together with the anode at lower temperature. Thus, modification of the electrolyte sintering properties is needed to establish an appropriate sintering profile that allows the production defect-free micro-tubular SOFC hollow fiber precursor with the desired microstructure and low energy consumption.

Currently, it has been reported that introducing metal oxides as the sintering additive can effectively reduce the sintering temperature of CGO up to 900-1200 °C [32–34] by liquid phase sintering mechanism. On the other hand, successful attempts of CGO sintered at 1250 - 1400 °C has been reported by introducing nano size particle of CGO as the starting powder [35–40]. As the small particles size exhibiting as high driving force [41], it is hypothesized that nano size powders enhance the densification at lower temperature. Nevertheless, the previous works only reported on CGO button cells prepared by pressing method. To the best of author's knowledge, study on the effect of sintering additive and nano size particles on electrolytes densification prepared by phase inversion technique, has yet been reported. The feasibility of these approaches on phase inversion based co-extrusion/co-sintering technique is still unclear.

Realising the huge potential that is offered by phase inversion based co-extrusion/co-sintering technique, it is relevant to implement these two approaches in reducing the sintering temperature of CGO and understanding how it affects the microstructure, densification temperature, mechanical strength, gas tightness properties as well as the micro-tubular SOFC performance. This study is expected will produce a good quality micro-tubular SOFC with shorter fabrication time and thus the outcome is very novel and beneficial to the researchers in this area.

1.3 Objectives and Scopes

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

a) To design the experiment in modifying the sintering properties of CGO electrolyte flat sheet via two approaches i.e; mix particle size CGO and sintering additive.
b) To fabricate an anode/electrolyte of both modified dual-layer hollow fiber solid oxide fuel cell by using a promising phase inversion-based co-extrusion/co-sintering technique.
c) To study the properties of both modified dual-layer hollow fiber in terms of its morphology, conductivity, electrolyte tightness, anode permeability and mechanical strength.
d) To conduct the current-voltage performance of both modified dual-layer hollow fiber as a complete SOFC.

In order to achieve the objectives, four scopes have been identified in this research. The scopes are:

a) Modifying the sintering properties of electrolyte via two approaches.
b) Fabricating anode/electrolyte of both modified dual-layer hollow fiber via co-extrusion/co-sintering technique.
c) Characterizing the physical and chemical properties of both modified dual-layer hollow fiber in terms of its morphology, crystal structure, mechanical strength, gas-tightness properties and gas permeability.
d) Performing micro-tubular SOFC test by potentiostat/galvanostat at temperature 500 ^{o}C.

1.4 Significance of Study

This study is expected to provide a better understanding on the fundamental principle for the fabrication of dual-layer hollow fiber for micro-tubular SOFC, which consists of the modifications of electrolyte layer by considering the morphological, mechanical strength and gas tightness of the precursors. It is acknowledged that nano size particles and sintering additive has been used in various fabrication techniques to reduce the sintering temperature of CGO, however little attention has been given on their application in phase-inversion technique. Therefore, attempts are made to investigate the potential of nano size CGO and Li_2O as sintering additive in this technique. By identifying the ideal characteristics of the nano size loadings and behaviors of the sintering additive, high performance micro-tubular SOFCs can be fabricated.

Up to now, no study has been conducted to implement these two approaches in preparing dual-layer hollow fiber via phase-inversion technique. This study could be beneficial to the researchers in this area regarding to the knowledge generation on fabricating modified dual-layer hollow fiber using a single-step technique. In addition, with the utilization of low sintered electrolyte, an improved quality of SOFCs component can be produced. This study has proven the possibility to accelerate the densification by incorporating nano size CGO and sintering additives as well as presented an advanced new material to reduce the sintering temperature of CGO. Thus, it would lead to the development of low cost micro-tubular solid oxide fuel cell, in order to make fuel cell technology able to compete economically with traditional energy technologies.

1.5 Thesis Organisation

This thesis consists of 8 Chapters and its organization is shown in Figure 1.4. Chapter 1 briefly introduces the research background of fuel cells particularly the micro tubular solid oxide fuel cell, the objectives and scopes of the study and overview of the thesis. Chapter 2 describes the literature review on conventional and

recent introduced phase inversion-based extrusion techniques, their characteristics and performances. It also provides a review on recent approaches to reduce the densification temperature of CGO. Other than that, the future direction is presented as well. Chapter 3 presents a detailed methodology of this research work in order to achieve the targeted objectives.

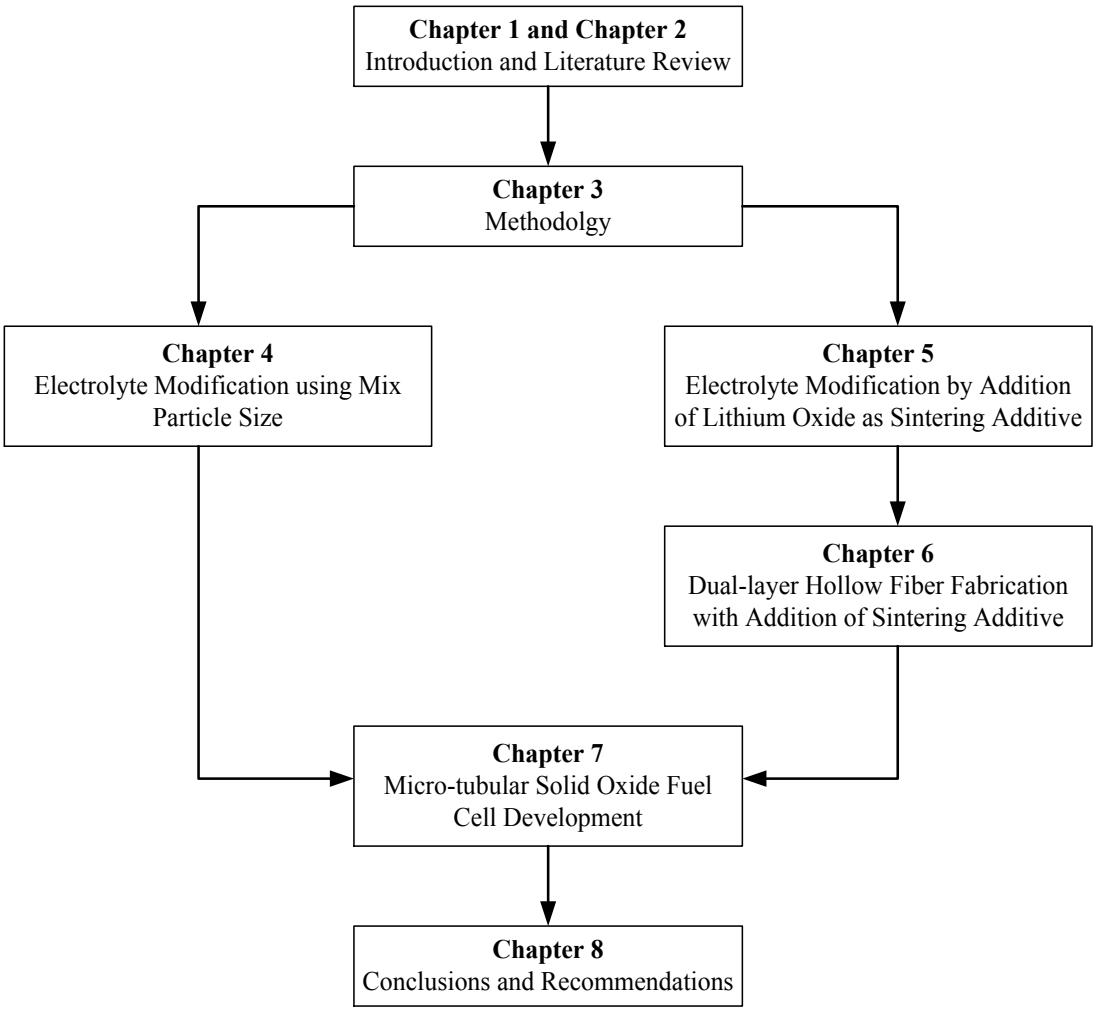


Figure 1.4 Overall Thesis Structure

Chapter 4 reports the potential of the first approach which is introducing mix particle size of CGO to reduce the densification temperature. The first part focuses on the particles behavior particularly the shrinkage rate of the mix particle size CGO. The second part clarifies the effect of nano size loading to the characteristics of the dope suspension and flat sheet. While the last part reports the development of dual-layer hollow fibers using the modified electrolyte. This includes the study on the

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