STRUCTURAL STUDY OF CO-EXTRUDED DUAL-LAYER HOLLOW FIBRE FOR MICRO-TUBULAR SOLID OXIDE FUEL CELL

SITI HALIMAH BINTI AHMAD

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To my beloved family,

Mr. Azam Omar,
Mr. Ahmad Salleh,
Madam Aminah Rahmat,
Mr. Md. Shamsuddin Salleh,
Madam Rohaizat Baharuddin,
Muhamad Muzakkir,
Muhamad Muzamil,
Siti Nur Ain

With love and gratitude.

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ABSTRACT

This study provides information on the structure of solid oxide fuel cell (SOFC). Porous anode provides active site reaction while dense electrolyte layer prevents direct flow of gases through one electrode to another. Therefore, anode and electrolyte structural modifications were thoroughly investigated using different types of pore formers and various ceramic particle sizes, respectively. In the preliminary study, 0 to 10 wt.% corn starch and polyetherethylketone (PEEK) functioned as pore former were added into nickel oxide-yttria-stabilized zirconia (NiO-YSZ) anode suspensions. The results showed that high loading of pore former increased the porosity in anode but reduced the mechanical strength. As compared to using corn starch, addition of 2 wt.% PEEK produced anode with better porous structure by generating more connected open pores and the hollow fibre (HF) was 67 % stronger. The electrolyte of dual-layer HF was subsequently modified by varying the loading of YSZ particle sizes (i.e. micron, submicron and nano-sized) during suspension preparation. The most promising electrolyte layer with thin, dense, gas-tight and defect-free was comprised of 70 % submicron-YSZ and 30 % nano-YSZ. The HF yielded the highest mechanical strength of 85 MPa, good gas-tightness behaviour of 3.16×10^{-6} $molm^{-2}s^{-1}Pa^{-1}$ and successfully reduced the co-sintering temperature from 1450 to 1400 °C. Lastly, the anode suspension consist of 2 wt.% PEEK and electrolyte suspension composed of a mixture of particle sizes of micron, submicron and nano-sized YSZ in a ratio of 3:4:3 were co-extruded and co-sintered to produce the structural modified electrolyte/anode. Results revealed that the connected open pores at the entrance of anode inner surface resulted from the addition of pore former was significantly contributed to gas permeability of anode. However, the electrolyte was not fully densified due to less efficient electrolyte packing particles which resulted to the reduction in mechanical strength and integrity of HF.

ABSTRAK

Kajian ini menyediakan maklumat mengenai struktur sel bahan api pepejal teroksida (SOFC). Anod berliang menyediakan ruang tindak balas aktif manakala lapisan elektrolit padat menghalang aliran langsung gas dari satu elektrod kepada yang lain. Oleh itu, ubahsuai struktur anod dan elektrolit masing-masing telah disiasat menggunakan pelbagai jenis pembentuk liang dan saiz zarah seramik. Dalam kajian awal, 0 hingga 10 % jisim kanji jagung dan polieteretilketon (PEEK) yang berfungsi sebagai pembentuk liang telah ditambah ke dalam ampaian anod nikel oksida-ytria-zirkonia-terstabil (NiO-YSZ). Hasil kajian menunjukkan muatan pembentuk liang yang lebih tinggi meningkatkan lagi keliangan dalam anod tetapi mengurangkan kekuatan mekanikal. Berbanding dengan menggunakan kanji jagung, penambahan 2 % jisim PEEK menghasilkan anod dengan struktur berliang yang lebih baik dengan menjana lebih banyak liang terbuka yang bersambung dan gentian geronggangnya (HF) adalah 67 % lebih kuat. Elektrolit dwi-lapisan HF kemudiannya diubahsuai dengan mengubah muatan saiz zarah YSZ (iaitu mikron, submikron dan nano) semasa penyediaan ampaian. Lapisan elektrolit yang paling berpotensi dengan ciri-ciri nipis, tumpat, kedap gas dan tanpa kecacatan itu terdiri daripada 70 % submikron-YSZ dan 30 % nano-YSZ. HF tersebut menghasilkan kekuatan mekanikal tertinggi iaitu 85 MPa, sifat gas-ketat yang baik iaitu 3.16×10^{-6} $molm^{-2}s^{-1}Pa^{-1}$ dan berjaya mengurangkan suhu pensinteran bersama dari 1450 ke 1400 °C. Akhir sekali, ampaian anod yang mengandungi 2 % jisim. PEEK dan ampaian elektrolit dengan campuran saiz zarah mikron, submikron dan nano YSZ dalam nisbah 3:4:3 telah disemperit dan disinter bersama bagi menghasilkan elektrolit/anod dengan struktur terubahsuai. Keputusan menunjukkan bahawa liang terbuka yang berhubung di jalan masuk permukaan dalaman anod hasil daripada penambahan pembentuk liang adalah penyumbang ketara kepada kebolehtelapan gas anod. Walau bagaimanapun, elektrolit tidak tumpat sepenuhnya kerana penyendatan zarah elektrolit yang kurang cekap yang menyebabkan kepada pengurangan kekuatan mekanikal dan integriti HF.

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
DIR	-	Direct internal reforming
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
IIR	-	Intermediate internal reforming
IT	-	Indirect temperature
K_2CO_3	-	Potassium carbonate
KOH	-	Potassium hydroxide
Li_2CO_3	-	Lithium carbonate

$LaMnO_3$	-	Lanthanum manganite
LSCF	-	Lanthanum strontium cobalt ferrite
LSM	-	Lanthanum strontium manganite
MCFC	-	Molten carbonate fuel cell
MgO	-	Magnesia
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
PEEK	-	Polyetheretherketone
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
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
USM	-	Universiti Sains Malaysia
XRD	-	X-ray diffraction
Y_2O_3	-	Yttria
YSZ	-	Yttria-stabilized zirconia
ZrO_2	-	Zirconia

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

The fuel cell is extensively discovered as clean and sustainable technology for producing electricity. This is due to the major threats that need to be tackled such as the rising of oil price, serious global warming and the soaring of human demand on energy (Traversa, 2009). Fuel cell shows promising characteristics to solve these problems as it consumes fuel at high efficiency with less impact on the environment. The technology does not generate significant amounts of pollutants such as carbon monoxide and nitrogen oxides, and yields more electricity from the same amounts of fuel especially when compared with internal combustion engines (Atkinson *et al.*, 2004).

Generally, the fuel cell is defined as an electrochemical device which converts chemical energy of fuel directly into electrical energy. It produces electricity through a chemical reaction, without undergoing combustion process. The energy conversion system is very efficient in generating electricity either for stationary or transportation applications (Barbir, 2008). In addition to that, the fuel cell is mechanically ideal as it does not require any moving parts during operation, and therefore, making them quiet and reliable sources of power.

The fuel cell is made up of an electrolyte and two conducting electrodes, called as anode (positive electrode) and cathode (negative electrode). The electrolyte allows the ion transfer (depend on the type of fuel cells; anion-conducting and

cation-conducting electrolyte) from one electrode to the other. In electrodes, the operation of fuel cells involves a combined oxidation-reduction reaction. Oxidant is reduced on the cathode side and fuel is oxidized in the anode side. Electrons that released by anode are transferred to the cathode via external load, by which the production of electricity is realized.

There are many kinds of fuel cell have been introduced. However, this study is focusing on solid oxide fuel cell (SOFC) based on solid oxide electrolyte. SOFC becomes a promising technology in the power generation field (Zuo *et al.*, 2012) because of its great flexibility of fuel from biomass to pure hydrogen (Lo Faro *et al.*, 2012). SOFC operates at high operating temperature ranging from 500 °C to 1000°C. Operation in such high operating temperature allows an internal reforming reaction (conversion of hydrogen from hydrocarbon) to occur. Therefore, fuel pre-treatment is not required for SOFC system since the reforming reactions could directly promote within anode cells due to the high operating temperature (Assabumrungrat *et al.*, 2004).

Two structural designs of the SOFC have been commercialized; planar and tubular SOFCs. The tubular design has been introduced by extrusion method in order to prevent the thermal shock problem facing by conventional planar design. Since power density is inversely proportional to the tubular cell diameter, Singhal and Kendall (2003) introduced a smaller cell diameter known as micro-tubular SOFCs (MT-SOFCs) to boost the performance. In fact, the development of this advanced cell design, i.e. MT-SOFCs promote an excellent thermal stability during rapid heat cycling, quick start-up capability, high power output density, low capital cost and portable characteristics as compared to the conventional planar and tubular SOFCs (Meng *et al.*, 2013).

The first generation of MT-SOFC was designed in an electrolyte-supported SOFC system with yttria-stabilized zirconia (YSZ) electrolyte tubes up to 5 mm in diameter. Thick electrolyte layer was first produced to serve as “cell backbone”, that is responsible to provide mechanical strength to the entire cell for deposition of the remaining cell layers (Wei *et al.*, 2008). Other promising designs are electrode-

supported SOFC which uses thick anode or cathode as the supporting layer. Table 1 shows the difference of the three supported systems (i.e. Electrolyte, anode and cathode supporting layer). Based on this comparison, it can be seen that anode-supported MT-SOFC is more favourable because it allows the application of a thin electrolyte layer, which results to the reduction in ohmic lose and consequently, enhance cell power density (Buchkremer *et al.*, 1997; Mizutani, 2008).

Current method for fabricating the anode-supported MT-SOFC is very challenging. The SOFC comprises of cathode/electrolyte/anode multi-layer hollow fibre (HF) as shown in Figure 1.1, need to be fabricated. This fabrication of multi-layer HF involves many steps of extrusion and layer depositions (Wei *et al.*, 2008). Each step needs to undergo a sintering process and these repetition steps lead to high fabrication cost. Fortunately, the cost can be reduced by using an economical fabrication method, i.e. single-step co-extrusion and co-sintering method.

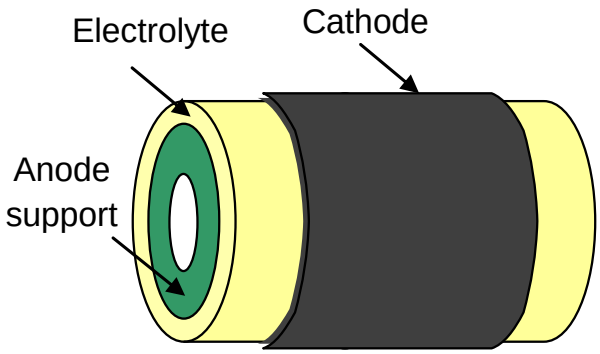
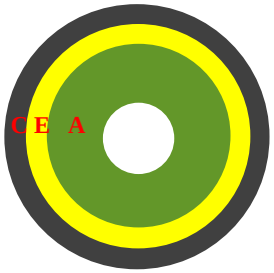
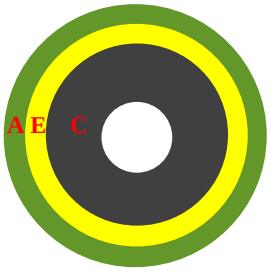


Figure 1.1: Schematic diagram of anode-supported MT-SOFC comprised of a thin electrolyte layer and two electrodes, where anode acts as support (Othman, 2011).

The single-step fabrication reduces the cost, energy, chemical and time production because it fabricates electrolyte/anode dual-layer hollow fibres (HFs) simultaneously with smaller diameter and better adhesion (Droushiotis *et al.*, 2009). The phase inversion technique was also applied during co-extrusion in order to form asymmetric structure on the prepared HF (Li, 2007). Therefore, in this study, the single-step phase inversion-based co-extrusion and co-sintering method can be employed to fabricate the electrolyte/anode dual-layer hollow fibre with desired anode and electrolyte microstructure.

Table 1.1: The advantages and disadvantages to different MT-SOFC performances.

MT-SOFC Configuration	**Electrolyte-supported SOFC**	**Electrode-Supported SOFC**	
		Anode-supported SOFC	**Cathode-supported SOFC**
Schematic images	 Thick electrolyte	 Thick anode	 Thick cathode
Advantages	• High mechanical robustness due to dense structures and good stability for RedOx (Reduced and Oxidation Atmosphere) cycles (Sammes *et al.*, 2005) • Gas-diffusible due thin electrodes layer (Sammes *et al.*, 2005)	• Low operating temperature (about 750 °C) and ohmic resistance due thin electrolyte layer (Mizutani, 2008) • High the electrical output due to low ohmic resistance (Mizutani, 2008) • Low materials cost since nickel (Ni) or nickel oxide (NiO) is relatively cheap • Easy to fabricate	• Good stability under RedOx condition and low carbon deposition due thin anode (Lee, 2003)

Disadvantages	• High ohmic losses resulting from thick electrolyte layer (Mizutani, 2008)	• Low mechanical reliability due to porous structures and low RedOx stability (Sammes *et al.*, 2005)	• Lack of study and research based on cathode-supported • Induce chemical reaction between cathode and electrolyte at high sintering temperature (Sarikaya *et al.*, 2012) • High polarisation resistance (Sarikaya *et al.*, 2012)

1.2 Problem Statements

The electrolyte/anode dual-layer HF can be fabricated via single-step phase inversion based-co-extrusion method and, followed by co-sintering process. A number of researches have been reported on the feasibility of using this fabrication method to produce well-adhered electrolyte/anode dual-layer HF in economic ways (Droushiotis *et al.*, 2009; Droushiotis *et al.*, 2010; Othman *et al.*, 2010b; Othman *et al.*, 2011b). Nevertheless, the most challenging issues that require to be tackled is during co-sintering. Co-sintering for HF comprises of two different materials at high temperatures (1450 $^{\circ}$C) to obtain full densification of the electrolyte layer might reduce the porosity in anode layer and it utilizes high energy consumption. Dense electrolyte layer has been compulsory since electrolyte acts as a barrier between electrodes, preventing the direct flow of fuel and oxidant whereas, anode should be porous to facilitate fuel and products.

Therefore, the conventional techniques of adding pore formers and different ceramic particle sizes may be good alternatives to create pores in anode and enhance the particle packing of the electrolyte layer respectively. It was shown that the addition of degradable pore-forming agent such as graphite (Lee, 2003), starch (Haslam *et al.*, 2005), poly methyl methacrylate beads (PMMA) (Suzuki *et al.*, 2009) into the anode suspension had successfully induced the macro-size pore in anode substrate after sintering. While, the addition of different particle sizes (especially nano-sized) is believed to improve the particle packing (Liu *et al.*, 2006) thus increase the densification of electrolyte layer during sintering.

Nevertheless, aforementioned techniques of using pore forming agent and different ceramic particle sizes have never been reported for fabricating electrolyte/anode dual-layer HF using the phase inversion-based co-extrusion and co-sintering method. Hence, this study significantly reports on the effect of pore formers in generating anode with highly porous structure and the influence of particle sizes in producing electrolyte with dense and gas-tight property. As the results of excellent electrolyte densification for dual-layer HF at low co-sintering temperature, it may also preserve the porosity in anode layer and minimizes the energy consumption.

1.3 Objectives of Study

The primary purpose of this work is to fabricate yttria-stabilized zirconia (YSZ) - based dual-layer hollow fibre consists of porous anode and dense electrolyte layer for high temperature MT-SOFC. The specific targets are as follows:

i. To investigate the fabrication of porous anode using corn starch and polyetheretherketone (PEEK) as pore former via phase inversion-based casting method.

ii. To examine the densification of thin electrolyte layer using different loading of ceramic particle size via phase inversion-based co-extrusion and co-sintering method.

iii. To analyze the properties of prepared anode and electrolyte in terms of their microstructure, crystal structure, mechanical strength, gas-tight and porosity.

1.4 Scopes of Study

In order to achieve the objectives of this research, the following scopes are outlined:

i. Analyzing the sintering shrinkage behaviour of 30-70 wt% nickel oxide (NiO) loading in anode composition and also the YSZ electrolyte so that well-matched between layers are achieved during co-sintering process.

ii. Investigating the addition of polyetheretherketone (PEEK) and corn starch as pore former with different loadings from 0-10 wt% into anode suspension as an effort to produce anode with adequate porosity and mechanical strength.

Phase inversion based-casting method and sintering are applied to produce the flat sheets thick anodes.

iii. Characterizing the anode flat sheet before and after sintering in terms of microstructure, crystal structure, porosity, mechanical durability and thermal stability.

iv. Examining the effect of different loading of YSZ particle sizes (i.e. Micron, submicron and nano-sized) in electrolyte suspension. HFs are formed through the phase inversion-based co-extrusion method using a triple orifice spinneret and followed by co-sintering at different temperature (1300, 1350, 1400 and 1450 °C).

v. Examining the properties of the precursor and sintered dual-layer HF using scanning electron microscopy (SEM), gas tightness test and 3-point bending test.

iv. Comparing the properties of dual-layer HF before and after the anode, and electrolyte modifications. A modified dual-layer HF with a combination of the best pore former loading in anode and different loading of particle sizes in electrolyte was made via phase inversion-based co-extrusion and co-sintering method.

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