CO – EXTRUDED TRIPLE LAYER HOLLOW FIBER SOLID OXIDE FUEL CELL USING METHANE

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DEDICATION

To whom support me till the end.

Especially my parents

Families

Friends

Wife and son

Thank you for everything

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ABSTRACT

Solid oxide fuel cell (SOFC) is one of the most promising fuel cells and it has been developed extensively in recent years. However, carbon deposition on the anode site is the main issue of this system when methane is used as the fuel. Therefore, the objective of the research is to develop a methane-fueled micro tubular solid oxide fuel cell (MT-SOFC) with excellent carbon resistant property. In the first phase of this work, triple layer hollow fiber, which consisted of anode which used nickel oxide (NiO) and yttria stabilized zirconia (YSZ), anode functional layer (AFL) also made of NiO and YSZ, and electrolyte from YSZ, was fabricated via phase inversion-based co-extrusion/co-sintering technique with varied fabrication parameters (i.e. ratio NiO/YSZ in the AFL and sintering temperature) and such triple layer design that has been previously reported is able to possess several advantages such as high power output and high thermal expansion coefficient. Further, the cell was tested using methane gas as fuel. The hollow fiber with the ratio of 2:8 of NiO to YSZ of AFL suspension shows crack-free properties. After sintering between 1400 ºC and 1500 °C, the hollow fiber recorded an increase from 110.1 to 130 MPa on three-point bending tests and 1.26×10^{-5} to 4.6×10^{-6} mol m^{-2} s^{-2} Pa^{-1} for gas tightness tests. The maximum power densities obtained at 800 °C were 0.8 W/cm^2. In the second stage of the study, the prolonged operation of the SOFC was done using methane fuel to observe the carbon deposition phenomenon. The fuel cell showed significant reduction of power density from 0.8 W/cm^2 at 800 °C to 0.2 W/cm^2 after 90 min. In the third stage of the work, ceria gadolinium oxide (CGO) was incorporated in the anode suspension to increase the resistance towards carbon poisoning. With the addition of 3wt.% of CGO at the anode layer, the performance degradation was reduced to only 50% from the initial power density after 90 min, in comparison to the cell without CGO (the reduction of 75% after 90 min), although the initial power density of the modified one was slight lower (0.4 W/cm^2) than the unmodified cell (0.8 W/cm^2). It was shown that the CGO able to reduce the degradation of the cell under methane as fuel.

ABSTRAK

Sel bahan api pepejal oksida (SOFC) adalah salah satu sel bahan api yang mempunyai harapan yang cerah dan telah dibangunkan secara meluas sejak beberapa tahun lepas. Tetapi, pemendapan karbon di kawasan anod menjadi isu utama di dalam sistem ini apabila gas metana digunakan sebagai bahan api. Oleh itu, objektif penyelidikan ini adalah untuk membangunkan SOFC bersaiz tiub mikro (MT-SOFC) berasaskan gas metana dengan mempunyai sifat kalis karbon. Untuk fasa pertama kajian ini, tiga lapisan gentian berongga dimana anod terdiri daripada nikel oksida (NiO) dan yttria distabilkan zirkonia (YSZ). Lapisan berfungsi anod (AFL) juga dihasilkan dari NiO dan YSZ dan elektrolit adalah dari YSZ, telah direka dengan menggunakan teknik fasa penyongsangan berasaskan teknik penyemperitan/pesinteran bersama dengan pelbagai parameter fabrikasi (contoh, nisbah NiO/YSZ dan suhu pesinteran) dan reka bentuk tiga lapisan ini telah dilaporkan sebelumnya mempunyai beberapa kelebihan seperti penghasilan kuasa yang tinggi dan pekali pengembangan haba yang tinggi. Kemudian, sel tersebut diuji dengan menggunakan gas metana sebagai bahan api. Gentian berongga dengan nisbah 2:8 NiO kepada YSZ pada mendapan AFL menunjukkan gentian bebas dari keretakan. Selepas disinter pada suhu diantara 1400 ºC dan 1500 ºC, gentian berongga merekodkan peningkatan dari 110 ke 130 MPa bagi ujian pembengkokan tiga titik dan 1.26 x 10^{-5} ke 4.6 x 10^{-6} mol m^{-2} s^{-2} Pa^{-1} bagi ujian gas ketat. Ketumpatan kuasa pada suhu 800 ºC adalah 0.8 W/cm^2. Pada peringkat kedua kajian ini, operasi berpanjangan SOFC telah dijalankan untuk memerhati fenomena pemendapan karbon. Sel bahan api menunjukkan pengurangan ketara di mana ketumpatan kuasa berkurangan dari 0.8 W/cm^2 pada 800 ºC kepada 0.2 W/cm^2 selepas 90 minit. Peringkat ketiga kajian pula, ceria gadolinium oksida (CGO) telah dimasukkan di dalam mendapan anod untuk meningkatkan rintangan terhadap keracunan karbon. Dengan penambahan sebanyak 3 wt% CGO di lapisan anod, pengurangan prestasi telah dikurangkan sebanyak 50% daripada ketumpatan kuasa pada permulaan selepas 90 minit, apabila dibandingkan dengan sel tanpa CGO (pengurangan sebanyak 75% selepas 90 minit) walaupun ketumpatan kuasa permulaan adalah lebih rendah (0.4 W/cm^2) berbanding dengan sel tidak diubah suai (0.8 W/cm^2). Ini menunjukkan CGO mampu untuk mengurangkan penurunan sel apabila metana digunakan sebagai bahan api.

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LIST OF ABBREVIATIONS

AFC	-	Alkaline fuel cell
CO_2	-	Carbon dioxide
CGO	-	Cerium gadolinium oxide
DMFC	-	Direct methanol fuel cell
H_2	-	Hydrogen
H_2O	-	Water
HF	-	Hollow fiber
$LaMnO_3$	-	Lanthanum manganite
LSCF	-	Lanthanum strontium cobalt ferrite
LSM	-	Lanthanum strontium manganite
MCFC	-	Molten carbonate fuel cell
MIEC	-	Mixed ionic electron conductor
MT	-	Microtubular
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
SEM	-	Scanning electron microscopy
SOFC	-	Solid oxide fuel cell
TEC	-	Thermal expansion coefficient
TGA	-	Thermogravimetric analysis
TPB	-	Triple-phase boundaries
XRD	-	X-ray diffraction
Y_2O_3	-	Yttria
YSZ	-	Yttria-stabilized zirconia
ZrO_2	-	Zirconia

LIST OF SYMBOLS

A	-	Area of hollow fiber
b	-	Width
B_F	-	Bending strength
cm	-	Centimeter
cP	-	Centipoise
d	-	Thickness
D_i	-	Inner diameter
D_O	-	Outer diameter
g	-	Gram
L	-	Length of hollow fiber
m	-	Meter
min	-	Minute
mol	-	Mole
N	-	Load
P	-	Gas permeability
p_a	-	Atmospheric pressure
Pa	-	Pascal
p_o	-	Initial pressure
p_t	-	Final pressures
R	-	Gas constant
s	-	Second
T	-	Temperature
t	-	Time for measurements
V	-	Voltage
V_c	-	Volume of the test cylinder
wt	-	Weight
°C	-	Degree Celsius
%	-	Percent
µm	-	Micrometer

CHAPTER 1

INTRODUCTION

1.1 Research Background

Energy is the most discussed issue in the world and its demands increase significantly with the rapid economic growth. In the past decade, global community was witnessed the surprising economic development in Asia, Europe and Middle East. The rise of living standards in large population causes the increase in world energy consumption. Energy demand largely comes from fossil fuel such as petroleum, natural gas and coal. Due to their abundance, such fuels remain the popular choice.

Until now, millions of barrels crude oil are being produced every day. In the hydrocarbon utilization, the combustion process was used as part of the energy generation. Eventhough it is a well-developed and cost-effective process, the main disadvantage is the generation of unwanted by-products such as NO_x or CO_x. These gases could contribute to greenhouse effect [1].

The technology development of renewable energy is expected will be fully established in the next decade. It is valuable if sufficient scientific and technological breakthrough are achieved. It is important to support the renewable energy technology since it can sustain the environment. The primary sources of renewable energy comes from hydroelectric, geothermal, tides, wind, biomass and solar. However, the low power output and high cost remain as the big obstacle for commercialization.

As a result, fuel cell was introduced in 1960s as an attractive power generation technology that converts from chemical energy into electricity directly. Fuel cell could render more efficient power. It is suitable in many applications especially in stationary or transportation because its ability to produce high efficiency and minimize air pollution and cost [2]. Fuel cell is able to generate electricity as long as the fuel being supplied. The electrochemistry of fuel cell relies on the combustion of fuel such as hydrogen combustion

$$H_2 + O_2 \rightarrow H_2O \qquad (1.1)$$

When the combustion process being measured at molecular scale, the hydrogen and oxygen molecules reacted by colliding each other. The hydrogen molecules are oxidized at the anode while the oxygen molecules are reduced at cathode simultaneously. The resulting reaction produces steam, electron and heat. The electron produced from oxidation of hydrogen will be captured by current collector and thus lead to electricity generation. The simple operation is shown in Figure 1.1.

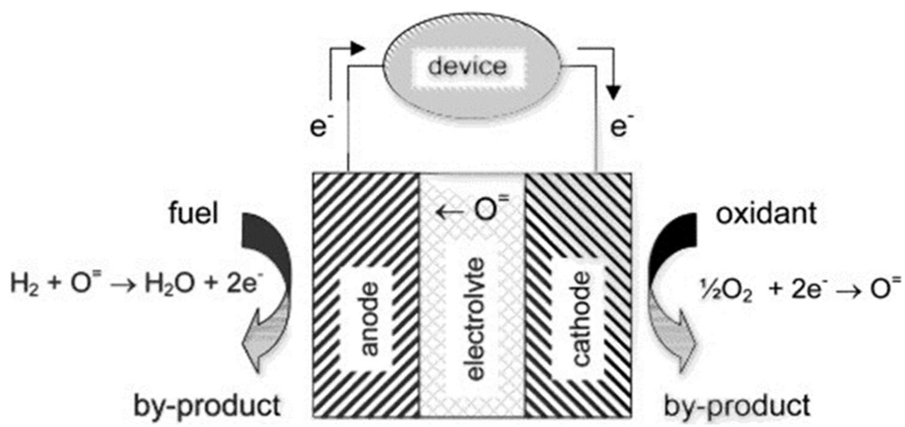

Figure 1.1 Simple operation of fuel cell [3].

There are many types of fuel cell that applied different fuel and working temperature. Usually, for small appliances require low operating temperature while the stationary power station utilizes the high temperature operations as listed in Table 1.1. Fuel cells have several advantages such as clean by-product and off-grid applications. In addition, noise free operation and transportable advantages thus allowing fuel cells to be applied in small resident, automotive, portable electronic devices, remote area electricity generator, marine and space applications [4].

Table 1.1 Fuel cell type

	Polyelectrolyte Fuel Cell	Phosphoric Acid Fuel Cell	Alkaline Fuel Cell	Molten Carbonate Fuel Cell	Solid Oxide Fuel Cell
Electrolyte	Polymer membrane	Liquid H_3PO_4	Liquid KOH	Molten Carbonate	Ceramic
Charge Carrier	H^+	H^+	OH^-	$CO3^{2-}$	O^{2-}
Operating temperature	80°C	200°C	60 – 220 °C	650 °C	600 – 1000 °C
Catalyst	Platinum	Platinum	Platinum	Nickel	Ceramic
Cell component	Carbon based	Carbon based	Carbon based	Stainless based	Ceramic
Fuel compatibility	H_2, methanol	H_2	H_2	H_2,CH_4	H_2,CH_4

Solid oxide fuel cell (SOFC) is regarded as the most efficient among other types of fuel cells. Due to operation at high temperature, it is suitable as stationary power station. SOFC has its own advantage when comes to fuel flexibility. Unlike other fuel cells, electricity could be generated from SOFC by using various fuels such as hydrogen [5], methane [6], methanol [7] or complex hydrocarbon like tar and biomass [8]. Operation at high temperature does make the catalyst site active, hence more fuel conversion can be more rapid [4].

When involving high temperature, it must be noted that the SOFC systems need a reactor to operate. The reactor needs to able reach up until 1000°C for the SOFC high temperature system to work. The high temperature system put the emphasis on the material used especially electrolyte. Different electrolyte materials highly conductive at different temperature. Therefore, it is important to match the working temperature with the material being used.

For research purposes, the single system is used to test the new material, gases or flow system. Meanwhile the stacking was used since the SOFC single system was established. There are few companies such as Siemen Westinghouse that developed the SOFC systems for being applied in various industries.

Although hydrocarbon fuels are suitable for SOFC, hydrogen fueled SOFC systems are still the main focus in SOFC research. There are many advantages of using hydrogen such as simplicity of the system and the stability issue. In such a way, the modularity by using hydrogen as fuel was far more superior as compared to the hydrocarbon system.

However, the hydrogen was usually obtained from methane conversion. Reformer usually a reactor that act hydrogen production from methane [9-11]. Therefore, the SOFC system can prevent from the catalyst site being poisoned by carbon. There are several conversion routes of methane as shown in Figure 1.2, depending on the reactant, such as steam or oxygen.

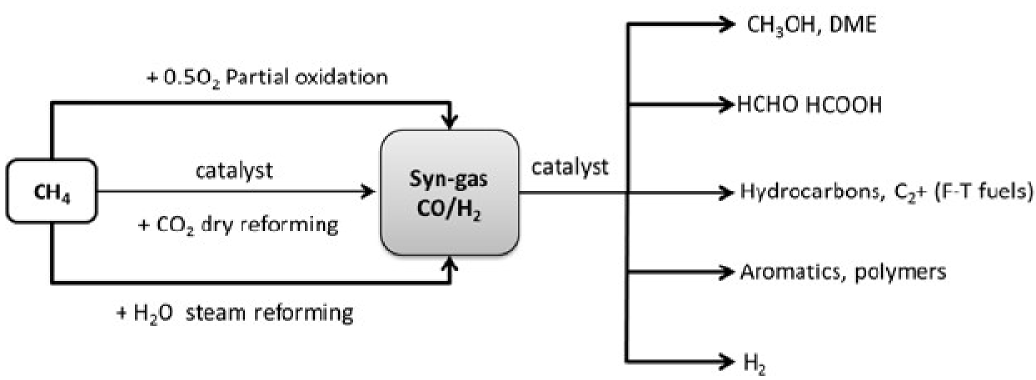

Figure 1.2 Methane conversion route [12].

As conclusion, the methane route to the hydrogen is quite complicated. Therefore, a hefty price must be paid to obtain pure hydrogen. Besides that, the production of carbon monoxide in the industry will increase due to the demand on the hydrogen also increased in the renewable energy industry.

1.2 Problem Statement

The research on the solid oxide fuel cell (SOFC) is extensively being studied. Currently, there are two different geometry of SOFC which are planar and tubular geometry [13]. In this study, the micro tubular SOFC was used due to several advantages such as high-power output, high thermal resistance and compact size. There are several methods to produce hollow fiber such as ram extrusion [14]. However, the ram extrusion process requires multiple step of sintering and layering of the hollow fiber. To solve the multi-step issue, the phase inversion technique was applied in this study. This technique able to extrude multiple suspension simultaneously which then produce triple layer hollow fiber with only single step [15]. The fabrication of triple layer hollow fiber is to reduce the resistance of the hollow fiber by taking advantage of the additional anode functional layer (AFL) could reduce the contact resistance between anode and electrolyte, hence increasing the power density [16]. The triple layer fabrication of hollow fiber was done by the Li and co-workers [17] in London. They had successfully demonstrated the fabrication and application of triple layer hollow fiber.

As mentioned earlier, the SOFC can operated until 900^{o}C, thanks to the usage of ceramic material that able to handle high temperature environment [18]. This allows the SOFC system to apply hydrocarbon as fuel. Previously, the hydrogen gas was widely used as the fuel source. However, the hydrogen needs to be produced causing the fuel to be costly. To make the SOFC system cost efficient, the use of methane as fuel is one of the solutions.

As the methane fuel being researched, there was a concern regarding the effect of using the carbon-based fuel. The carbon fuel tends to poison the cell due to the cracking reaction that produced carbon as the by-product [19-26]. The methane cracking causing the anode site to be deposited by the carbon by-product. After prolonged operation, the deposition become severe and causing the performance to be decreased.

The problem of carbon deposition in the SOFC requires solution before the methane is viable as fuel for SOFC. One of the ideas is the incorporation of ceria gadolinium oxide (CGO) as part of anode suspension. The behind reason why CGO was added at the anode layer suspension was to enable the carbon to convert into carbon gases [27, 28]. The CGO was found to be effective as the carbon oxidizing material that able to reduce the carbon deposition. The ceria alone is a good carbon oxidizing catalyst. However, the ceria easily deactivated when being sintered at high temperature. By doping the ceria with gadolinium, the deactivation issue was dismissed.

Until now, there are less research on the CGO as catalyst for carbon oxidizing catalyst in SOFC. In addition, the method of CGO addition into anode layer being complicated such as in-situ impregnation via sol-gel method. This requires another heating processes to incorporate the CGO into anode layer. Through the extensive research, the preparation of suspension for the phase inversion shows promising technique to incorporate the CGO as part of the suspension preparation.

This research will benefit the methane fuel in SOFC reaction, especially the micro-tubular configuration. Since there is less study on the micro tubular towards methane as fuel, this study aims to tackle the carbon deposition that had been suffer by the cell.

1.3 Research Objectives

The general aim of this study is to develop a carbon-resistance methane-fueled micro-tubular SOFC that fabricated via phase inversion-based co-extrusion/co-sintering technique. In order to achieve the general aim, several specific objectives need to be carried out in this study:

1. To fabricate and characterize crack-free triple layer hollow fiber (TLHF) consisting of anode in the inner layer, AFL in the middle layer and electrolyte in the outer layer

2. To test and compare the performance of the TLHF-based MT-SOFC with methane fuels at different temperatures

3. To study the stability of TLHF-based MT-SOFC under the methane fuel and analyse the carbon formation as a function of time

4. To incorporate ceria gadolinium oxide (CGO) during the dope suspension preparation in order to decrease the carbon deposition and study the carbon resistance property of the cell.

1.4 Scope of The Study

1. In this research, the triple layer hollow fiber was fabricated via phase inversion-based co-extrusion/co-sintering method.

2. During suspension preparation process, the parameter that had been adjusted was the ratio of NiO/YSZ from 4:6 to 2:8 for AFL suspension.

3. A number of ceramic materials were used in this research. Nickel oxide (NiO) and yttria stabilized zirconia (YSZ) for anode and AFL, YSZ for electrolyte and lanthanum strontium manganite (LSM) for cathode were the main components in hollow fiber.

4. The hollow fiber was co-sintered from 1400ºC up to 1500ºC in high temperature tubular furnace.

5. The characterization involved in this research are X-ray diffraction, three-point bending test, gas tightness test, scanning electron microscopy.

6. The fuel cell test was done with methane fuel at 700 to 800°C. The flowrate for fuel was at 20 mlmin^{-1}. The current-voltage (IV) curve and impedance behavior of fuel cell were acquired by using potentio-galvanostat.

7. The MT-SOFC was tested for 90 minutes using methane fuel to measure the stability of the cell. The performance reduction was recorded as proof of the anode site had been poisoned rapidly

8. The electrochemical performance was measured via open circuit voltage (OCV), power density and impedance analysis.

9. The carbon analysis helps to determine the quality of the carbon that deposited on the anode site. In addition, it also helps to understand the mechanism of carbon growth.

10. The fabrication of carbon resistant was done after the stability test. The CGO was added among the material for the suspension preparation. As much as 1 to 3 of weight percent as part of anode suspension component. After that, it was undergone performance testing at temperature ranging from 700 to 800°C.

11. The resulting performance test was measured by observing the degradation level. This compared to the previously hollow fiber without the addition of CGO.

1.5 Significance of The Study

The SOFC systems with methane as fuel are constantly being poisoned by carbon if hydrocarbons are used as fuels. The poisoning at the anode shows the reduction of performance for long period of time. Despite that, the poisoning can be removed by several ways. In addition, the methane as fuel was an alternative to the hydrogen gas as the hydrogen gas is more expensive than methane. The hydrogen content in the atmosphere was very small, hence it needs to be produced. Therefore, adding another process will increase the cost significantly. Meanwhile, the readily available methane promises a better value despite it prone to carbon deposition. Despite that, the need to overcome carbon deposition is a must to ensure the methane can functioned as a fuel for a long period of operation.

The triple layer hollow fiber is utilized in this study due to the AFL gives several advantages on the SOFC systems. Therefore, this study provides comprehensive explanation on the development of the highly carbon resistance triple layer hollow fiber for SOFC. It is known that the CGO based catalyst tends to prevent the carbon deposits. With the sufficient amount of ceria impregnated at anode site, the performance would likely to stable for long term operation.

Besides, the study also employs a promising method, i.e. phase inversion-based co-extrusion, to control the macrostructure of the hollow fiber. By manipulating the co-extrusion parameters, it could alter the solvent/non-solvent exchange process and thus, contributes to the change in morphology of the hollow fiber.

1.6 Thesis Organization

This thesis consists of 7 chapters addressing the different issue from the fabrication of triple layer hollow fiber, the performance of micro-tubular SOFC, the stability under the methane fuel and the incorporation of CGO at the anode layer.

Chapter 1 briefly explain the concept and the issue regarding energy. Chapter 2 define the fuel cell from history of fuel cell until the fabrication technique. This chapter also explain the fuel for fuel cell including hydrocarbon. On top of that, this section includes the carbon deposition problem and also the carbon prevention technique. In chapter 3, all the methods, machine, chemicals and characterization were explained in details.

Chapter 4 discuss on the fabrication of triple layer hollow fiber. in addition, the performance evaluation also being done. Chapter 5 discussed on the stability of the triple layer hollow fiber after prolonged performance testing. Chapter 6 discussed on the modification of anode layer by incorporating CGO during the suspension preparation. Chapter 7 concludes the achievement in fabricating carbon resistance TLHF for SOFC and some suggestions for future study.

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