

STRUCTURAL CHARACTERISTICS OF PORE FORMER ASSISTED
CATHODE LAYER IN MICRO-TUBULAR SOLID OXIDE FUEL CELL

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To my family and friends.
And to the ones who keep me going on.

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In the name of Allah SWT. Praise to Him, The Almighty that permits the completion of this thesis.

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ABSTRACT

The cathode performance of solid oxide fuel cell (SOFC) depends substantially on its surface area, porosity and microstructure, and therefore the processing method is very important in determining cathode performance. By improving the structural characteristics of the layer, the cathode performance during fuel cell operation can be fully maximized. This study aims to improve the porosity and pore structure of the cathode deposited layer of micro-tubular SOFC (MT-SOFC) by inducing pores with pore formers. Three types of pore formers have been used to investigate the formation of induced pores in the cathode layer of SOFC, which are polyether ether ketone (PEEK), corn starch and graphite. Each pore former chosen in this study possesses different particle geometry in order to produce distinct pore geometry in the cathode layer. The cathode layer was brush painted on an anode/electrolyte dual layer support hollow fibre that had been previously sintered at 1500°C for 12 hours. The coated cathode consists of three layered coats, with functional layer as the first two layers followed by a current collector layer on the last coat. After the deposition of cathode layer, it is sintered at 1200°C for 5 hours. The study divides the characterization into three main parts; pore former geometry identification, pore former behavior in lanthanum strontium cobalt ferrite (LSCF) powder and pore former in LSCF as solid oxide layer. PEEK was able to produce pores that promote both fine microstructures for triple phase boundary generation and porous structure for efficient diffusion of gases. The increase in pore former loading has increased the porosity and decreased the grain size, but at the expense of decreasing mechanical strength of the fuel cell.

ABSTRAK

Tahap prestasi katod dalam sel bahan api pepejal teroksida (SOFC) bergantung pada luas permukaan, keliangan dan mikrostrukturnya, maka langkah-langkah pemrosesan yang digunakan amat penting dalam mengukur tahap prestasi katod. Dengan menaik taraf ciri-ciri struktur lapisan tersebut, tahap prestasi katod semasa operasi sel bahan api akan dapat dimaksimumkan sepenuhnya. Kajian ini bertujuan untuk menambah baik keliangan and struktur liang lapisan katod MT-SOFC secara penturapan liang melalui pembentuk liang. Tiga jenis pembentuk liang telah digunakan untuk menyiasat pembentukan liang di dalam lapisan katod SOFC; iaitu *poly ether ketone* (PEEK), kanji jagung dan grafit. Setiap pembentuk liang yang dipilih di dalam kajian ini mempunyai bentuk partikel yang berbeza bagi menghasilkan geometri liang yang berlainan pada lapisan katod. Lapisan katod tersebut kemudiannya diberuskan pada dwi-lapisan anod/elektrolit sokongan gentian berrongga yang telah disinter terlebih dahulu pada 1500°C selama 12 jam. Lapisan katod yang telah disalut terdiri daripada tiga lapisan, lapisan berfungsi pada dua lapisan pertama dan diikuti dengan lapisan pengumpul arus sebagai lapisan terakhir. Setelah disalut dengan lapisan katod, proses sinter kali kedua akan dilakukan pada 1200°C selama 5 jam. Pencirian dalam kajian ini terbahagi kepada tiga bahagian utama; identifikasi geometri pembentuk liang, kelakuan pembentuk liang di dalam serbuk LSCF dan pembentuk liang dalam LSCF sebagai lapisan pepejal teroksida. PEEK mampu menghasilkan liang untuk meningkatkan kehadiran mikrostruktur bagi generasi sempadan tiga fasa dan struktur liang untuk resapan gas yang efisien. Penambahan jumlah kandungan pembentuk liang telah meningkatkan keliangan dan mengurangkan saiz butiran, tetapi meningkatkan pengurangan tegangan mekanikal sel bahan api.

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LIST OF ABBREVIATIONS

SOFC	-	Solid Oxide Fuel Cell
PEEK	-	Poly Ether Ether Ketone
TGA	-	Thermogravimetric analysis
XRD	-	X-Ray Diffraction
BET	-	Brunauer–Emmett–Teller
SEM	-	Scanning Electron Microscopy
FESEM	-	Field Emission Scanning Electron Microscopy
ASTM	-	American Society for Testing and Materials
AFM	-	Atomic Force Microscopy
YSZ	-	Yttria-stabilized Zirconia
IT-SOFC	-	Intermediate Temperature Solid Oxide Fuel Cell
HT-SOFC	-	High Temperature Solid Oxide Fuel Cell
MT-SOFC	-	Micro Tubular Solid Oxide Fuel Cell
CGO	-	Cerium Gadolinium Oxide
LSCF	-	Lanthanum Strontium Cobalt Ferrite
AFC	-	Alkaline Fuel Cell
PAFC	-	Phosphoric Acid Fuel Cell
MCFC	-	Molten Carbonate Fuel Cell
PEMFC	-	Polymer Electrolyte Membrane Fuel Cell
DMFC	-	Direct Methanol Fuel Cell
MEA	-	Membrane Electrode Assembly
TEC	-	thermal expansion coefficient
CVD	-	Chemical vapour deposition
LSM	-	Lanthanum strontium manganite
MIEC	-	Mixed Ionic Electronic Conductor
APS	-	Air plasma spraying
VPS	-	Vacuum plasma spraying

PMMA	-	Poly methyl methyl acrylate
PESf	-	Poly ethyl sulfone
DMSO	-	dimethyl sulfoxide
CHP	-	Combine heat and power
TPB	-	Triple phase boundary
PEG	-	Poly ethylene glycol
PAEK	-	Polyaryletherketone

LIST OF SYMBOLS

W	-	Power produced, energy per unit time
λ	-	Wavelength of the X-ray for XRD
θ	-	Range of observed angle for XRD
P	-	Porosity of ceramic body, %
M	-	Saturated mass of the ceramic body
D	-	Dry mass of the ceramic body
S	-	Suspended mass of the ceramic body
B_F	-	Bending force of a specific fuel cell
N	-	Load at fracture in the bending test
L	-	Length of hollow fibre subjected to testing
D_0	-	Inner diameter of the fuel cell
D_1	-	Outer diameter of the fuel cell

CHAPTER 1

INTRODUCTION

1.1 Background of Study

In the effort to meet with the energy demand of the modern world, oil exploration is expanding literally to the center of the earth. Modern advanced technologies have allowed us to dig deeper, expedite crude oil extraction and extract more oil from oil reservoir. In spite of new crude oil reserves found occasionally, total depletion of non-renewable crude oil sources is inevitable. Crude oil accounts for more than half of the global energy sources. Thus, the other sources of energy have to be fully utilized and optimized in order to relieve the global energy demand from crude oil. Moreover, in the conversion of crude oil into electricity, it includes the release of gasses which may possess threat to the environment and the health of people.

In the effort to fully utilize the use of environmental friendly energy such as solar, wind, geothermal and hydroelectric energies, they requires a lot of time before being able to cope with the global energy demand, as well as the technical and economic challenges present. Subsequently, the introduction of better utilization of fossil fuel in energy generation is crucial. On the same grounds, fuel cells have been regarded as a better replacement for current energy production devices because of its high efficiency. Generally, fuel cells produce electricity through an electrochemical process without involving combustion. Fuel cell functions by converting chemical

energy directly into electricity which is able to reduce energy losses. They also produce less emission than the conventional combustion system. Continuous operation is possible for fuel cells with the condition of uninterrupted supply of fuel and oxidant. The fuel are stored externally, thus it will not be internally depleted as conventional battery. The fuel cell also involves no moving parts, making them quiet and requires less maintenance.

As a result of its relatively high conversion rates of chemical energy to electrical energy, solid oxide fuel cells (SOFCs) have been promoted as a promising energy generation devices (Singhal and Kendall, 2003). SOFCs can be considered as a green technology through the application of H_2 gases of which can be produced from non-hydrocarbon sources. In addition, SOFC operation does not produce exhaust gases as in normal combustion engine, instead SOFC only produces excess hydrogen gas (H_2), carbon dioxide (CO_2) and water vapour. SOFC is a multiple layer structure consisting of at least, three solid oxide layers, an electrolyte layer sandwiched between anode and cathode layers. Generally, oxygen atoms will be reduced on the porous cathode surface by electrons to form oxide ions, which are then carried through the dense electrolyte layer to a porous anode zone that has been supplied with fuel where the oxide ions can react by donating electrons to an external circuit. Figure 1.1 shows the complete fuel cell reactions at both porous cathode and anode, oxygen ion and electron pathway.

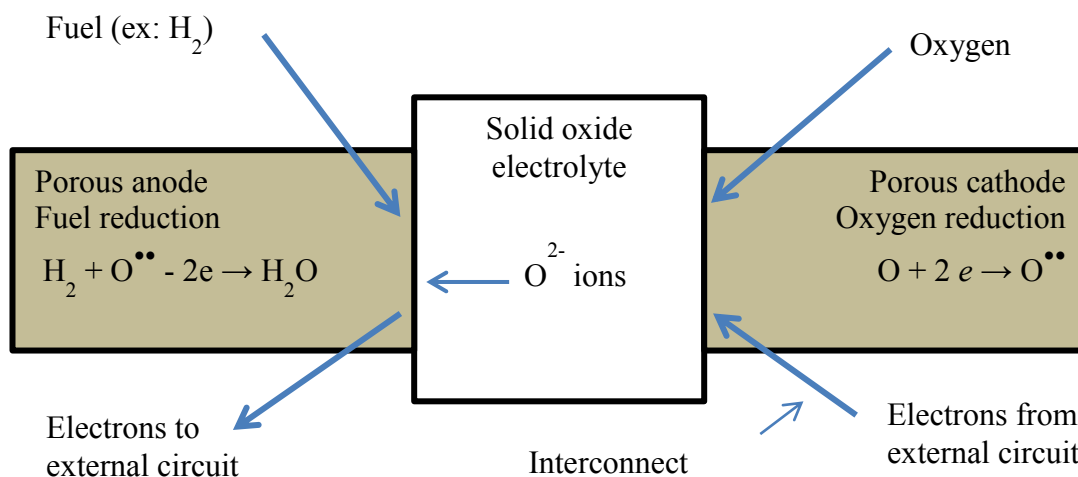


Figure 1.1 Solid oxide fuel cell reaction and ion/electron pathway (Singhal and Kendall, 2003)

There are two types of SOFC configuration that are commonly studied, namely planar and tubular SOFCs. Planar SOFCs boast in highly compact configuration which in turn generates high power density. Nevertheless, the design of this type requires high temperature sealing near the edges of the cell and only few sealants are suitable for the operational condition of SOFC (Minh and Takahashi 1995c). Additionally, slow start-up period and problems associated with formations of cracks in the thin planar structures are among the drawbacks in this configuration. Because of the geometry of the planar design, the fabrication of this type of SOFC cell is able to be mass produced via screen printing. Based on Figure 1.2, the unit cell of a planar SOFC is stacked with the interconnect in between to allow maximum conversion of energy per unit area.

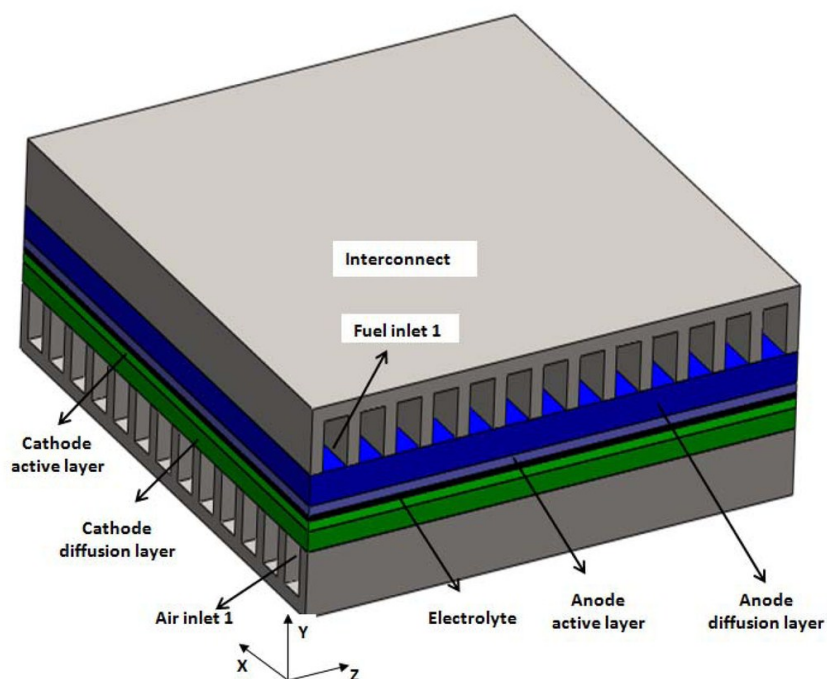


Figure 1.2 Planar SOFC unit cell (Singhal and Kendall, 2003)

On the other hand, tubular SOFC configuration has been proven to possess significant resistance to rapid thermal changes and able to operate without the need for high temperature seals. The design of this type of SOFC cell relies heavily on the diameter of the cell. Figure 1.3 below shows the cross section of an anode supported tubular geometry SOFC unit cell. Despite the advantages of the tubular configuration, this configuration suffers in the volumetric power density output of the fuel cell which is usually lower than that of in planar configuration.

By reducing the diameter of the fuel cells to the scale of 1 mm, the volumetric power density can be greatly improved. At this scale, the fuel cell is commonly referred as micro tubular SOFC (MT-SOFC). By applying this micro tubular configuration, properties such as start-up and shutdown, mechanical properties and specific surface area of the electrodes can be significantly improved. Compared to large-diameter tubular SOFC which are susceptible to layer cracking if subjected to rapid thermal cycles, the micro-tubular SOFCs shows excellent resistance even at 850 °C (Singhal and Kendall, 2003).

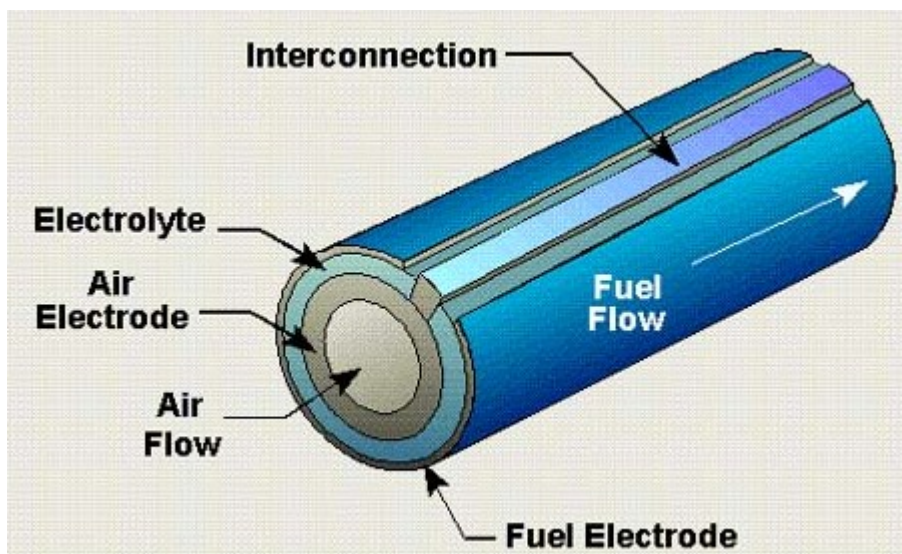


Figure 1.3 Tubular SOFC unit cell (Singhal and Kendall, 2003)

The electrochemical reactions at the electrodes in SOFC operation produce heat as a byproduct. These heats are associated with the ohmic losses, anode-cathode overpotentials and from other sources. Rather than eliminating these losses, heat management system was applied to maintain the operating temperature of the SOFC system. High temperature exhaust heats of SOFC are advantageous for the control and utilization of exhaust gases, which are among the main advantage of SOFC over the other types of fuel cells. Because both electricity and heat are desirable and useful products of SOFC operation, the best applications are to utilize both, for example residential combined heat and power, auxiliary power supplies on vehicles, and stationary power generation from coal which needs heat for gasification. A residential SOFC system can use this heat to produce hot water, as currently achieved with simple heat exchangers. In a vehicle the heat can be used to keep the driver warm. A stationary power system can use the hot gas output from the SOFC to gasify coal, or to drive a heat engine or a gas turbine motor.

The electrolyte of a SOFC is a solid oxide material layer that conducts oxygen ions at elevated temperatures, between 600-1000°C. This layer theoretically should be solid and impermeable to gasses, in order to avoid loss of fuel cell

potential through open gaseous connection between fuel and oxidant. The electronic conductivity of the electrolyte layer should be minimal to reduce power losses due to short circuiting. Other properties that an electrolyte should possess include great thermal and chemical stability at elevated temperatures under both oxidising and reducing environments (Subbarao, 1980).

The main function of the anode layer of SOFC is to stimulate the electrochemical oxidation reaction of hydrogen gas as fuel. For an anode supported cell, the anode also acts as a structural support for the entire cell. Therefore, the mechanical and thermal characteristics such as mechanical strength, ductility, thermal expansion of the anode must be evaluated extensively. The general 3 requirements of an anode includes significant material stability (chemical and thermal) during cell fabrication and cell operation, high electronic conductivity under cell operating conditions, sufficient mechanical strength and flexibility, suitable thermal expansion, ease of fabrication and also low cost (Jiang and Chen, 2014). Furthermore, ionic conductivity would be very favourable to the reaction of fuel on the anode surface.

Almost similar to the anode characteristics, cathode for SOFC has to possess certain characteristics including high in both electrical conductivity and catalytic activity for oxygen reduction and also compatible with the electrolyte layer. Compatibility in this term can otherwise be defined by thermal expansion match and chemical non-reactivity between cathode and electrolyte layer. The cathode performance depends substantially on its surface area, porosity and microstructure (Hamedani *et al.*, 2008), and therefore the processing method used is very important in determining cathode performance. By optimizing the structural characteristics of the layer, certain key aspects can be individually encountered. For example, the interfacial polarization resistance has been shown to decrease when the microstructure of the cathode were graded (Nie *et al.*, 2010). By using a graded microstructure, a more efficient distribution of layer microstructure fit for its functions can be achieved. Graded microstructure is defined as possessing multi-layered cathodes with each layer is designated for a specific function. First, the usage of corn starch as the pore former has allowed the formation of open porous

microstructure at the outermost layer of the cathode to assist gas transport. On the other hand, by using graphite as the pore former, the induced pores were uniformly distributed fine microstructure with microscopic pores with larger surface area at the inner layer of the cathode to significantly increase the generation of triple phase boundary (TPB) region at the interface of cathode/electrode (Nie *et al.*, 2011).

The performance of the cathode layer has been linked with the ability to facilitate gaseous reduction at the relative facility where chemical ions and electrons are transported in and out of the reactive zones (Kenney and Karan, 2007). Thus, it is evident that the cathode layer have to possess efficient transport properties or structural characteristics for example low particle size, high porosity and optimized composition (Barbucci *et al.*, 2005). Hence, the control in porosity is essential in enhancing the performance of the cathodes in SOFC.

1.2 Statement of Problem

Conventionally, SOFC operates at high temperature of 800 – 1000 °C which is known as high temperature SOFC (HT-SOFC). HT-SOFC is known to suffer from expensive material requirements, high energy demands and prone to the inter-diffusion of elements. Thus, current research trends are focusing more to lower the operation temperature of SOFC to the range of 500-700 °C which is commonly denotes as intermediate temperature SOFC (IT-SOFC). Due to its lower operation temperature, IT-SOFC has faster start up and shut down time and better material durability because to reduced kinetics of material inter-diffusion. Nevertheless, at lower operation temperature of SOFC, ionic resistance at the electrolyte layer increases to a point where the cell can no longer be electrolyte supported and the ionic conductivity of yttrium stabilized zirconia (YSZ) as the electrolyte material is too low.

For IT-SOFC, with the operating temperature in between 500°C to 700°C, cerium gadolinium oxide (CGO) has shown excellent performance, due to its great ionic conductivity property in reducing atmosphere (Zhu *et al.*, 1998) and is suitable as a substitution of YSZ as the base material for the anode layer and the electrolyte material combined with nickel. Lanthanum strontium carbon ferrite (LSCF) has proven to be a suitable material for the cathode layer with CGO based electrolyte (Droushiotis *et al.*, 2012). While most efforts in SOFC research were poured into the anode and electrolyte layers, less attention is given towards the cathode layer, particularly in thin layer configuration. Cathode fabrication method for SOFC currently offers minimal structural control over the layer geometry. Generally, the cathode layer must have certain characteristics which are (i) high in electrical conductivity, (ii) high in catalytic activity for oxygen reduction and (iii) possess sufficient porosity. These characteristics points to the optimization of the gaseous reaction at the electrode during fuel cell operation.

For the first two characteristics, the type of material used in the fabrication of the porous layer plays a significant role. On the other hand, the third characteristic can be related to the method used in the cathode deposition. For a sufficient porosity formulation in the solid oxide layer, the available methods to simulate the desired condition include particle size, manipulating sintering profile and pore former addition. The optimum porosity values for an efficient cathode was outlined to be 30% based on previous studies (Kenney and Karan, 2007; Kivi *et al.*, 2008). While particle size and sintering profile manipulation are studied rigorously, less attention is given to the third alternative in the attempt to create relative porosity in the cathode layer. To increase the porosity of the cathode layer, a simple pore forming agent is added into the layer preparation slurry, which is conveniently removed at the necessary sintering treatment of the cathode layer. On the contrary, the other method requires increased amount of cost, energy and time associated with using different particle sizes and manipulating the sintering curve.

This study is focused on the pore former addition into the precursor slurry for the cathode layer. In the attempt of increasing the relative porosity in the cathode layer by the addition of pore former, it is important to consider that the increase in

porosity of the layer will also increase the electrical resistance of the cathode. Theoretically, in a solid metal layer, the electron pathway is straight and less resistive. On the other hand, in a highly porous solid metal layer, the electron pathway is obstructed by the pores. The electrons have to take a longer route and thus produce resistance in the circuit. The pore former addition have to be controlled in order to produce sufficient porosity in the layer for efficient gaseous reaction to occur while maintaining low the resistance in the circuit.

There is a demand for a more systematic approach for the optimization of the cathode layer fabrication as a deposited ceramics layer on a tubular substrate. The study will be able to provide a comprehensive analysis on the pore former addition in the precursor slurry of the cathode layer. This study focuses on the fabrication method of the cathode layer for intermediate temperature SOFC (IT-SOFC) in the micro tubular SOFC design by utilizing CGO as the electrolyte material. The cathode layer will be coated onto anode/electrolyte dual layer support hollow fibre which has been sintered preceding the deposition of cathode. For this study, three types of pore former were chosen; poly ether ether ketone (PEEK), corn starch and graphite. Graphite was chosen because of its ability to generate high length of triple point boundary due to the fine microstructures of graphite particles. Corn starch was chosen because it was proven to improve layer porosity even compared to other starch derivatives. PEEK was chosen because its geometry resemblances both graphite's and corn starch's geometry at the same time. Previous studies usually employ method to either focus on the generation of the active sites or induced increased porosity in the layer. In this study, by using pore former method, the cathode layer is improved by inducing increased porosity for gas diffusion and increased reaction sites in the cathode layer simultaneously.

The brush painting technique was chosen as the deposition technique rather than other deposition method available such as dip coating and plasma spraying. The brush painting technique boosts in its simple chemical requirement and uses simple laboratory equipment rather than the other methods where they require special setup in order to deposit the cathode layer. Moreover, brush painting method was proven as

an efficient cathode deposition method with significant adhesion between the cathode and the electrolyte layer (Droushiotis *et al.*, 2012).

1.3 Objective of Study

The general objective of the study is to provide a comprehensive analysis of the structural characteristics by the addition of pore former in the cathode depositing slurry towards the microstructure of the cathode as a deposited layer. Hence, the specific objectives of the study can be separated to the following:

1. To evaluate the pore morphology in LSCF cathodes with PEEK, graphite and corn starch as the pore formers
2. To evaluate the effect of pore former loadings on the characteristics of the LSCF cathode layer.

1.4 Scope of Study

This study involves the application of PEEK as the pore former to induce desired porosity in the cathode layer of IT-SOFC. Firstly, the cathode layer is deposited by using LSCF with the addition of pore formers onto the co-sintered anode/electrolyte dual layer hollow fibre support by using brush painting technique. This part involves the preparation of the dual layer hollow fibre support from the green body by sintering at 1500°C for 12 hours and the deposition of the cathode layer. The temperature was chosen at 1500 °C in order to produce a dense electrolyte layer for an efficient gas barrier layer. Brush painting method was chosen as the deposition method because this method was economical and able to deposit a cathode layer with significant adhesion to the electrolyte layer. Moreover, the brush painting technique

only requires a simple setup to execute the deposition. Field emission scanning microscopy (FESEM) was used to evaluate the dense electrolyte layer and the adhesion between the cathode and the electrolyte layer.

Next, the pore formation mechanism from the pore formers was analyzed by using thermal analysis and X-ray diffraction. In this part, the pore formation mechanisms of the pore formers were evaluated to investigate the burn off temperature of the pore formers and the efficiency of the pore former burn off. The formation of secondary phase or impurities was also examined. The sintered LSCF powders with pore formers were evaluated by using thermal gravimetric analysis (TGA) and x-ray diffraction (XRD). Additionally, the surface area of the LSCF particles was evaluated by using Single Point Brunauer, Emmett and Teller (BET) Nitrogen Adsorption method.

The pore former loading was varied at 0%, 5%, 10%, 15% and 20% of PEEK, graphite and corn starch in the cathode layer deposition slurry. The pore formers were limited to PEEK, graphite and corn starch as these pore formers obeys the important requirements of a suitable pore formers and possess the significant shape that can improve the characteristics of the cathode layer. The loading of the pore former were varied from 0%, 5%, 10%, 15% to 20% in order to evaluate the effects of each pore former loading on the characteristics of the cathode layer. FESEM was used to evaluate the morphology change in the cathode layer by using different type of pore formers at different loadings.

The characteristics of the cathode layer with the induced pores from the pore formers was then evaluated. This part involves the evaluation of the characteristics of the deposited cathode layer with the induced pores from different types of pore formers at different loadings. The layer characteristics were evaluated by using Standard ASTM C373-14 for porosity measurements, atomic force microscopy (AFM) and bending strength.

1.5 Significance of Study

It is essential in the cathode layer to require an ample porosity for the gaseous reaction to take place and to provide sufficient triple phase boundary region for the reduction reaction of gaseous in the layer. This study can provide a comprehensive reference in the aspects of morphological study of pore former addition in the cathode layer. Conventionally, cathode layer was known to be rate limiting in the electrochemical reaction in the SOFC operation because of the relatively lower reactivity of the cathode material compared to the anode. Pore former addition method has been explored to be able to improve the characteristics of the cathode layer by either increasing the porosity of the cathode layer to assist in the gas diffusion or by increasing the gas reaction sites in the cathode layer. In such instance, this study bids to improve the characteristics of the cathode layer by increasing both capacities of gas transport property and reaction sites simultaneously. This study is the first to tackle both structural improvements in the cathode layer of anode supported SOFC.

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