LANTHANUM STRONTIUM COBALT FERRITE-COPPER OXIDE AS CATHODE FOR INTERMEDIATE TEMPERATURE SOLID OXIDE FUEL CELL

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by

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		Unit
Ea	Activation energy	$^{kJ}/_{mol}$
R	Ideal gas constant	$^{kJ}/_{mol.K}$
T	Temperature	^{o}C
ASR	Area specific resistance	$\Omega\ cm^2$
R_Ω	Ohmic resistance	Ω
R_p	Polarization resistance	Ω
C	Capacitance	F
R	Resistance	Ω
P	Power	W
m	Mass	g
t	Thickness	cm
K	Rate constant	-
rpm	Rotation per minute	rpm

LIST OF ABBREVIATIONS

SFOP	Sel fuel oksida pepejal
$SOFCs$	Solid oxide fuel cells
$IT-SOFC$	Intermediate temperature solid oxide fuel cells
$LSCF$	Lanthanum, Strontium, Cobalt and Ferum
La	Lanthanum
Sr	Strontium
Co	Cobalt
Fe	Ferum
CuO	Copper oxide
PEMFC	Proton exchange membrane fuel cell
AFC	Alkaline fuel cell
PAFC	Phosphoric acid fuel cell
MCFC	Molten carbonate fuel cell
GDC	Gadolinium doped ceria
LSO	Lanthanum silicate oxide
LSGM	Lanthanum, Strontium Gallium, Magnesium
$MIEC$	Mixed ionic electronic conducting
ORR	Oxygen reduction reaction
TBP	Triple boundary phase
SDC	Samaria doped ceria
YSZ	Yttria-stabilized zirconia
CCL	Current collector layer
CPE	Constant phase element

AC	Alternate current
XRD	X-ray diffraction
SEM	Scanning electron microscopy
EDX	Energy dispersive X-ray
TGA	Thermogravimetric analysis
BET	Brunauer–Emmett–Teller
BJH	Barrett-Joyner-Halenda
EIS	Electrochemical impedance spectra

LANTANUM STRONTIUM KOBALT FERIT-OKSIDA KUPRUM SEBAGAI KATOD BAGI SEL FUEL OKSIDA PEJAL BERSUHU SEDERHANA

ABSTRAK

Sel fuel oksida pejal (SFOP) adalah peranti cekap dan mesra alam yang boleh menukarkan tenaga kimia menjadi tenaga eletrik dan haba untuk aplikasi berskala besar. Walau bagaimanapun, suhu operasi yang tinggi bagi peranti ini menghadkan pemilihan bahan yang sesuai untuk dijadikan elektrod dan elektrolit sekaligus mengurangkan keupayaan sel tersebut. Oleh itu, pembangunan bahan yang dapat memberikan prestasi elektrokimia yang unggul pada suhu ppertengahan (600-900^{o}C) adalah wajar untuk sel fuel oksida pejal (SFOP). LaSrCoFe-O_3 (LSCF) yang didopkan dengan kuprum oksida merupakan bahan katod yang sangat menarik dan mempunyai potensi yang tinggi untuk SFOP-BS kerana ciri-ciri keistimewaannya termasuk kekonduksian elektrik dan aktiviti pemangkin yang tinggi untuk tindak balas pengurangan oksigen. Kajian ini bertujuan untuk mengenapasti kesan kaedah sintesis iaitu kaedah pejal dan kaedah sol gel terhadap sifat fizikal dan kimia bagi katod komposit tersebut. Sampel disintesis pada suhu yang berbeza di antara 600 ^{o}C hingga 900 ^{o}C bagi setiap kaedah. Keputusan XRD menunjukkan suhu optima bagi sampel yang menggunakan kaedah pejal pada 800 ^{o}C dan suhu optima bagi sampel yang menggunakan kaedah sol gel pada 600 ^{o}C. Walaubagaimanapun, tiada bendasing ditemui pada kedua-dua sampel.Berdasarkan analisis EDX menunjukkan kedua-dua kaedah menghasilkan sampel yang tiada bendasing. Imej SEM menunjukkan saiz zarah LSCF-CuO meningkat apabila suhu meningkat dan ianya menunjukkan corak yang sama pada analisis BET yang juga menunjukkan kawasan permukaaan aktif berkurang apabila suhu meningkat. Kedua-dua analisis memberikan keputusan yang sama iaitu sampel kaedah sol gel menunjukkan hasil yang bagus berbanding sampel kaedah pejal. Analisis TGA menunjukkan kehilangan berat pada sampel sol gel lebih banyak berbanding sampel pejal. Kajian terhadap sampel kaedah sol gel dan sampel kaedah pejal diteruskan melalui elektrokimia analisis. Analisis EIS menunjukkan sampel disintesis secara sol gel memberikan bacaan perintang polarisasi yang rendah berbanding sampel kaedah pejal. Pengurangan suhu penalaan juga menurunkan bacaan perintang polarisasi. Tambahan pula, penambahan kuprum oksida pada katod LSCF menyebabkan pengurangan yang ketara pada perintang polarisasi berbanding katod LSCF sahaja.

LANTHANUM STRONTIUM COBALT FERRITE-COPPER OXIDE AS CATHODE FOR INTERMEDIATE TEMPERATURE SOLID OXIDE FUEL CELL

ABSTRACT

Solid oxide fuel cells (SOFCs) are the efficient yet environmentally benign devices that can convert chemical energy into electrical energy and heat for large scale applications. However, high operating temperature of this device limits the selection of proper materials to be used as electrode and electrolyte as well as sacrifices the durability. Thus, it is desirable to develop materials with superior electrochemical performance at intermediate temperature (600-900 ^{o}C) for SOFC. LSCF doped with CuO is an attractive yet promising cathode material for IT-SOFC owing to its distinguished properties including high electrical conductivity and high catalytic activity for the oxygen reduction reaction. This study was devoted to investigate the influence of the synthesis routes, which are solid state route and sol-gel route toward chemical, physical and electrochemical properties of composite LSCF-CuO. The samples were synthesised at different temperatures ranging from 600 ^{o}C to 900 ^{o}C for each route, respectively. XRD results showed high purity of as-synthesised samples while in the meantime, increase in crystallinity was observed as the calcining temperature increases, indicating bigger crystal size after calcined at 900 ^{o}C. SEM images showed that the LSCF-CuO particles tend to expand as the calcining temperature increases. Meanwhile, from the TGA results, it was clear that the LSCF-CuO has significantly loss its weight after calcined at designed temperatures (600 ^{o}C, 700 ^{o}C, 800 ^{o}C, 900 ^{o}C). LSCF-CuO showed promising electrochemical properties than

LSCF and the polarisation resistance obtained from LSCF-CuO synthesised using sol-gel method was much lower compared to that of solid state method. Moreover, it was found that reducing calcining temperature can greatly influence the electrochemical performance, which was in line with characterisation results. EIS analysis also showed that addition of copper oxide toward LSCF type cathode greatly enhanced the performance as the LSCF-CuO type cathode produced much lower polarization resistance as compared to pure LSCF type cathode.

CHAPTER ONE

INTRODUCTION

1.1 Introduction

Fuels are one of the most important aspects in daily life and can be usually used for lots of applications including as the source of electrical energy and heat. However, as the world moves on, fuels mainly produce a lots of harmful gases that will bring harm to the environment. Thus, researchers have put all their effort to reduce the harmful effect and at the same time continue to find the best way to produce a clean energy without releasing too much greenhouse gases into the atmosphere. Fuel cells are devices that are capable of converting chemical energy from fuels such as hydrogen and ethanol directly into electrical energy through environmental friendly way. Fuel cells can be divided into several types such as proton exchange membrane fuel cell (PEMFC), alkaline fuel cell (AFC), phosphoric acid fuel cell (PAFC), molten carbonate fuel cell (MCFC) and solid oxide fuel cell (SOFC) (Singh & Minh, 2014). The name of the fuel cell is determined by the types of electrolyte used as well as its operating temperature as shown in Figure 1.1.

Recently, extensive focused topic regarding hydrogen as an alternative energy of conversion and storage has been given due to the high gravimetric energy density and zero carbon emission (Bernal-Agustin & Lopez, 2008; Bockris & Veziroglu, 2007). This device is one of the promising alternatives applied as power sources for more applications including engine and power plant due to several advantages like high energy conversion efficiency and fuel flexibility (Minh, 2004; Singhal, 2002). However, the use of hydrogen as fuel has narrowed its applications due to practical engineering and economic limitation caused by its distribution problems. Therefore, to solve this problem, various studies with similar proportion to the conventional fuels have been done toward alternatives fuels that could be effective in a period of transition towards zero carbon emission (Schlapbach, 2009; Sakintuna, et al., 2007).

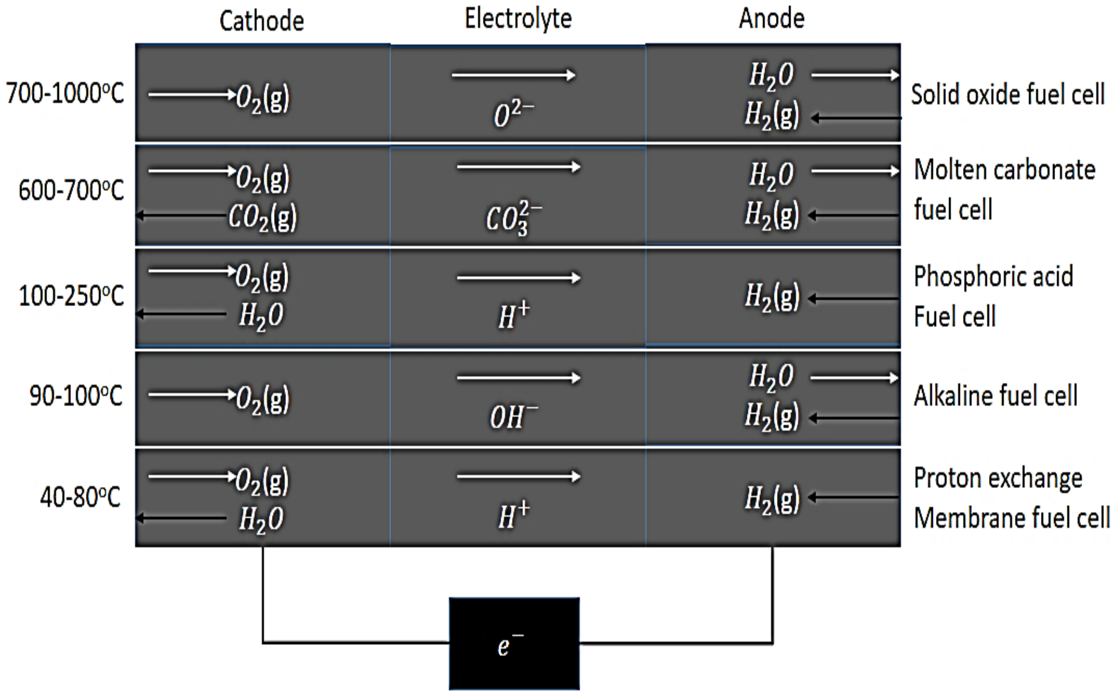

Figure 1.1: Schematic diagram of fuel cells

There are various applications of SOFCs in industry. Among these application, solid oxide fuel cell is commonly used in heat engine to produce electricity. Most commonly industrial section or even some regional areas use hydrocarbon combustion process to produce electricity since these methods is practical to be applied in many areas and seem fit due to the accessibility of material and fuel.

The engine operated by the fuel usually takes the heat from burning the fuel and uses it to heat up the gases. The gases then expand into a certain volume resulting hot gas, which then flow out in a turbine device running a dynamo inside it. This causes the air pollution, which emits a lot of carbon dioxide and coal into the air in a large scale. This method can be considered as inefficient and can cause heavy pollution if it is not controlled compared to fuel cell that can be less pollutant and surprisingly economic. In addition, the application of SOFC inside the gas turbine can potentially become one of the promising applications in the future.

The scheme in Figure 1.2 indicates the application of solid oxide fuel cell inside the gas turbine generator. This scheme is capable to operate near 50% conversion of fuel to electrical energy and can provide pressurized hot gas to operate the turbine at 35% efficiency. This system can be further improved by applying a steam turbine up to 75% efficiency. However, the most common problem of SOFC is the operating cost as the hydrocarbon fuel has a much lower cost compared to the bio ethanol at the moment. So, SOFC devices are not generally chosen unless the regulations of low emission of toxic gases are imposed. In order to promote clean energy and low toxic gases emission, Nissan motor Co Ltd applied the SOFC that uses the bio-ethanol fuel to generate electricity through it. This can be a first step to reduce the carbon emission released by hydrocarbon based consumption fuel in vehicle (Nissan, 2016). Usually, the energy produced from the SOFCs is from 20-25kW and it have been proven as a clean energy and release low emission of toxic gases. These fuel cells can also be applied as clean energy on vehicles and residential areas, which will reduce the carbon emission up to 50% (Richter, et al., 2009).

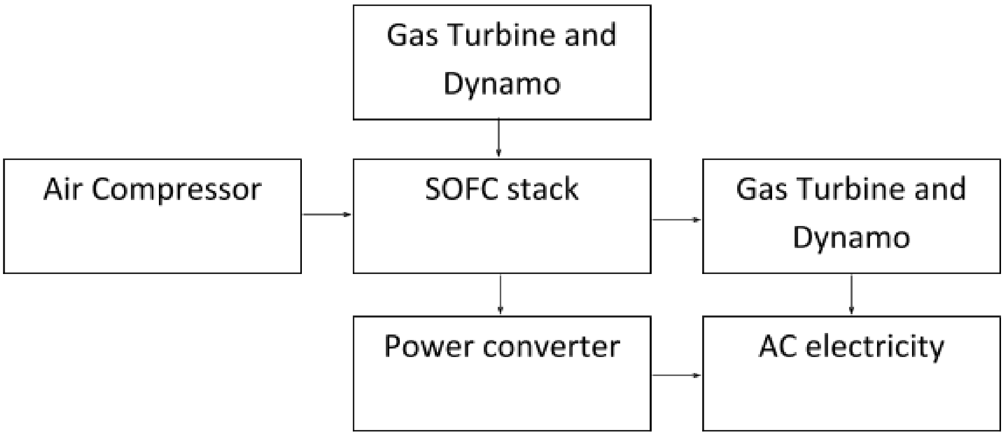

Figure 1.2: Schematic diagram of solid oxide fuel cell inside gas turbine generator

1.2 Problem Statement

There are several factors that influence the performance of the cell known as method of producing the cathode, cathode composition selection and operating condition of the cells (Colomer & Kilner, 2011). The cathode in SOFC will determine the performance of the entire cell since the oxygen reduction reaction (ORR) process which is important to determine the cells performance occurred here. In order to the cathode to perform well in cell, it is important to understand that a good cathode must have sound chemical compatibility, high conductive material, nano-particle size and ability to operate at the designed temperature (Minh & Takahashi, 1995; Singhal, 2000).

Generally, there are several ways to enhance the performance of the cathode. The popular ways currently applied are the new composition of varies metal salt with a good chemical compatibility among themselves, which also known as mixed ionic electronic conducting (MIEC) material. The most common material usually being studied in MIEC are lanthanum, strontium, cobalt, and ferum (LSCF) due to the stability of LSCF and specialty of LSCF, which has a good chemical compatibility among themselves. However, most LSCF type cathodes give a good performance at a considerable high temperature where optimal temperature for LSCF type cathode has been found to be at 900 ^{o}C, which almost reaching high temperature of SOFCs' range (Kim, et al., 2010). Application of high temperature toward cathode may results in performance degradation due to the poisoning effect (Perz, et al., 2016). Therefore, enhancement towards the MIEC type cathode needs to be done to reduce the temperature in intermediate temperature range while maintaining the performance. One way to enhance the LSCF is by applying composite cathode onto the LSCF with another noble metal due to the stability of LSCF. Copper oxide was chosen as a research subject to be composited with the LSCF due to the fact that it able to improve the electro-catalytic activity (Lu, et al., 2012; Zhao, et al., 2009). However, the ratio of LSCF-CuO and synthesizing route were still left undone to optimize the performance. Application of composite cathode can be considered a challenge due to the difficulties to match between the MIEC materials with another noble metal.

Nowadays, there are several routes that can be used to synthesize MIEC type cathode, among which are solid state route and sol-gel route that still in haze to identify which route provides better properties since several elements favor specific route only. However, the key in producing the suitable route for the designed cathode needs to be determined since there are several cathodes that could be synthesized using specific route due to their special treats. Ruiz-Preciado et al. and Bhaskar et al. stated that sample prepared by these methods has a significant value in terms of morphology and performance (Ruiz-Preciado, et al., 2015; Bhaskar, et al., 2017). The development of highly active cathode material is important as it determines the performance of the cells. Up until now, there are no reports comparing LSCF-CuO performance via conventional solid state route and conventional sol-gel route. Thus, the present study compares the effects of synthesis procedures on electrochemical properties by synthesizing LSCF-CuO by the conventional solid state reaction and sol-gel method.

1.3 Research Objectives

Solid oxide fuel cells (SOFCs) have a great potential to be applied as clean energy, electronic industry and automobile. One of the challenges nowadays in processing a good type of SOFCs is the operating condition where optimal SOFCs are operating at high temperature range. Therefore, it is important to reduce the operating condition from high temperature range to intermediate temperature range while maintaining the performance. Therefore, the main objectives for this project are:

- To synthesize LSCF-CuO as cathode for IT-SOFC using solid state route and sol gel route and determine which route produce better results.
- To verify LSCF-CuO type cathode is suitable for intermediate temperature range via physical, chemical and electrochemical characterization.
- To identify the optimal parameter for the LSCF-CuO cathode in intermediate temperature range based on the morphology of the sample at different calcining temperatures.
- To examine the electrochemical performance of the LSCF-CuO half-cell using the in-house fabricated cathode by comparing the polarization resistance and activation energy of the samples.

1.4 Thesis structure

This thesis contains five main chapters arranged as the following: Chapter One (Introduction) explains the solid oxide fuel cells, study statement and objectives. Chapter Two (Literature review) reveals the information regarding the SOFCs in intermediate temperature, MIEC type material explanation, composite type cathode, methodology for solid state route and sol-gel route, reviews on cathode composition selection and electrolyte selection. Chapter Three (Methodology) briefly describes the method chosen and the analysis conducted toward the sample. Chapter Four (Result and Discussion) presents the result of varies analyses toward the sample. Lastly, Chapter Five (Conclusion and Recommendation) concludes the thesis with several recommendations that can be used for future studies.

CHAPTER TWO

LITERATURE REVIEW

2.1 Literature structure

This chapter consists of six main units. Section 2.2 explains the Intermediate Temperature Solid Oxide Fuel Cells. Section 2.3 and 2.4 show the Mixed Ionic Electronic Conducting (MIEC) material and Composite Type Cathode that amplify the uses of Fe^{3+} inside the cathode and composite cathode technique that enhances cathode performance. Section 2.5 discusses the Route producing LSCF Type cathode. Next, Section 2.6 explains the cathode processing route that includes the methodology of the sample preparation via solid state route and sol-gel route chosen in this thesis.

2.2 Intermediate Temperature Solid Oxide Fuel Cells (IT-SOFCs)

Solid oxide fuel cells (SOFCs) operate on the basis of thermally activated electrochemical reaction that requires relatively high operating temperature (Singh & Minh, 2014). A typical SOFCs single cell comprised three basic components, which are anode, cathode and electrolyte, whereas the process involved in SOFC is oxygen reduction reaction (ORR) process that requires oxygen and hydrogen as a fuel and produces water as the result as shown in Figure 2.1.

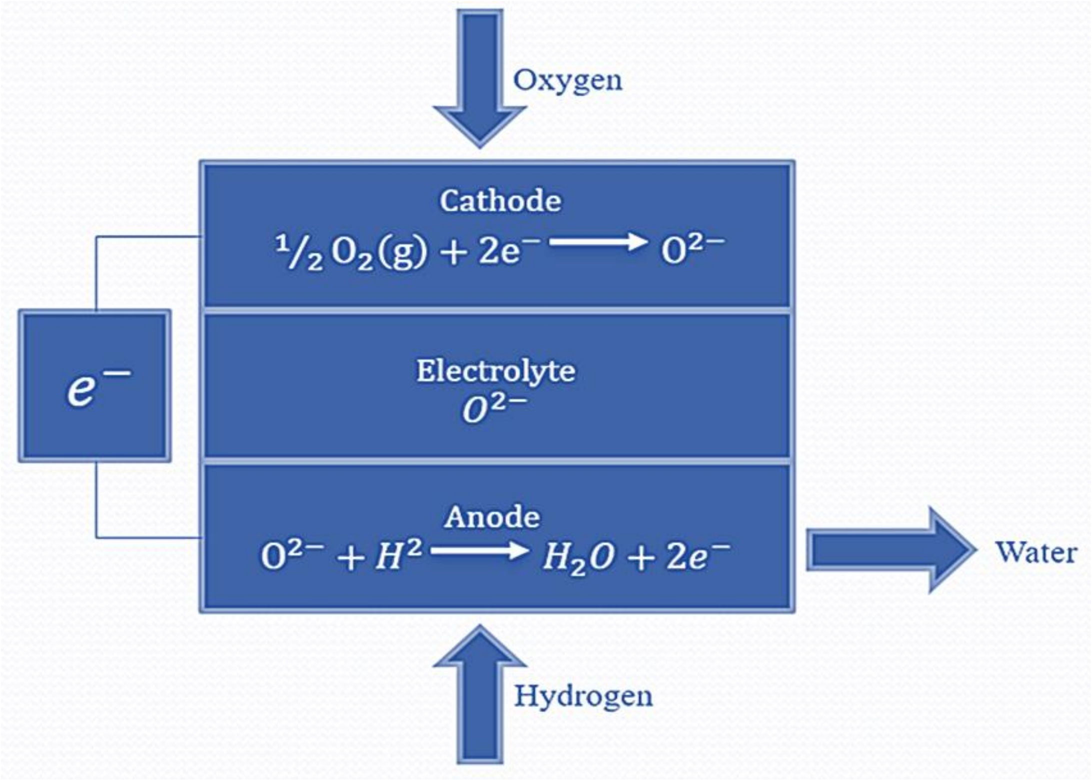

Figure 2.1: Process diagram of general solid oxide fuel cell (SOFCs)

Each of these components must fulfill specific requirements such as the stability of microstructural, similar thermal expansion, porosity and catalytic activity as stated by several journals and books (Minh & Takahashi, 1995; Singhal, 2000). As focused on the cathode section, the performance of the overall SOFCs depends on the cathode performance since the quality of cathode can affect its oxygen reduction reaction process. One of the most important aspects in maintaining the high performance of SOFCs cathode is the chemical compatibility of the components inside the cathode, which must be high to withstand high operation temperatures without reacting with each other. Some components are only applicable on low and intermediate temperatures while some are capable to withstand the high temperatures while maintaining the reactivity of cathode components. However, high operating temperature limits the choice of proper material and may eventually reduce the durability. Thus, it is important to develop the material with a good performance at the range of intermediate temperatures (600-800 ^{o}C) for SOFCs, allowing it to reduce production cost while maintaining a good performance since the decrease in balance-of-plant complexity is expected to reduce the overall cost of the fuel cell systems according to several studies (Park, et al., 2000; Atkinson, et al., 2004).

In order to obtain a good material for cathode, the synthesis method and sintering temperature are the critical aspects in determining the morphology and microstructure of the cathode. According to Singhal & Kendall (Singhal & Kendall, 2003), cathode must have a porosity of 20% to 40% for a proper conduction of oxygen molecules to the reaction sites at the electrolyte interface. This point has been supported by Mai et al. (Mai, et al., 2005) where a the coarse structure improves the gas permeability, ionic and electronic conductivity while a fine microstructure leads to a high surface area and may therefore produce a great number of active sites. In addition, the electrochemical properties are one of the major factors in determining the performance of the cells. The electrochemical performance of the cathode is usually closely related to its ionic conductivity, triple phase boundary area and electro-catalytic activity for oxygen reduction reaction (ORR) as mentioned by Colomer et al. in their study (Colomer & Kilner, 2011; Colomer, et al., 2002). Therefore, it is crucial to develop cathode with high ionic conductivity, outstanding electro-catalytic activity and large triple boundary phase (TBP) area.

Recently, there has been a lot of studies regarding the development in the field of solid oxide fuel cells focusing on several distinct advantages and disadvantages over the cells. SOFCs are usually easy to be practiced and do not require such a noble material like platinum to operate at high performance due the flexibility and multi fuel capability of the cell design. One of the disadvantages of the SOFCs is their high operating temperature (1000-1400 ^{o}C), which causes both physical and chemical degradation of the construction material leading to the narrow choice of using the material that can be used during the fabrication process. Thus, it is desirable to develop SOFCs operating at intermediate temperature of around 600-800 ^{o}C. However, decreasing the operating temperature will not only reduce the ion conductivity, but also the kinetics of the electrode, which will cause the polarization resistance to be increased (Leng, et al., 2008). The contribution of cathode polarization resistance to the total resistance becomes more obvious then the anode polarization resistance and ohmic resistance arising from other cell components. Therefore, the development of novel and high performance cathode in the intermediate temperature range is essential (Uchida, et al., 2002).

2.3 Mixed Ionic Electronic Conducting (MIEC) material

Several types of perovskite cathode are able to exhibit high electro-catalytic activity and low interfacial resistance for oxygen reduction in the intermediate temperature range. These material is known as mixed ionic electronic conducting (MIEC) material that consists of various metal salts with a good chemical compatibility among themselves. In SOFCs, there is a factor that indicates performance of the cells whether it is good or bad, which is the oxygen reduction reaction process. This process needs a better chemical compatibility of the cathode to be performed, or else it will result in the degradation of cell performance (Simner, et al., 2003; Petitjean, et al., 2005). Therefore, one step to improve the oxygen reduction reaction process is by applying MIEC material (Virkar, et al., 2000). The use of this approach is to increase the active area for the ORR process since pure electronic conductors in this reaction are limited to the triple boundary phase (TBP) where electrolyte, electrode and gas phase are met. Then, the ORR takes place and oxygen ion enters electrolyte material. Therefore, substantial ionic conductivity of the MIEC material opens the pathway for oxygen ion migration through the MIEC itself, therefore spreading the possible reaction zone (Fleig, 2002).

There are lots of conventional cathode compositions mainly used for testing project in a small scale lab such as copper, iron and nickel. In the search of the suitable components that can be used for the development of the cathode, it has been found that among of the propose compositions, Fe based perovskite oxide was seen to give a promising result after considering lots of factors including reactant source access, cost of developing thermal expansion and redox behavior of the iron. According to Zhao et al. (Zhao, et al., 2012), a perovskite type material including LSCF possess excellent catalytic activity and high oxygen permeability to improve the oxygen reduction reaction (ORR) in the intermediate temperature range. It is often used with ceria based material or doped with other elements including coper oxide to improve its performance in terms of stability, conductivity and surface area. Besides, LSCF is widely used as a cathode due to its excellent ionic and electronic conductivities capable of expanding the active sites from the triple boundary phase to the entire cathode surface (Singh & Minh, 2005).

However, Simmer et al. mentioned that one of major drawbacks using the LSCF as cathode is the existence of cobalt that improves the conductivity but in the same time forming a high resistive materials with the cell electrolyte during the cathode sintering process at high temperatures (above 1000 ^{o}C). This phenomenon was then found to cause performance degradation of the cells (Simner, et al., 2006). These observations have been explained by Kim et al. (Kim, et al., 2010) where a conventional sintering at a temperature above 1000 ^{o}C cannot be used in metal supported SOFCs as the processing temperature is limited to the oxidation of the metal substrate. Therefore, LSCF type cathode is most likely suitable for applications on intermediate temperature range.

The performance of LSCF at intermediate temperature is strongly depends on the microstructure of the cathode (Backhaus & Monika, 2008). Researchers found that applying several types of interlayer on the electrolyte was capable of suppressing the reactivity between the cathode and electrolyte, which is important to reduce the polarization resistance in the cells. In terms of assessment towards the LSCF ratio, researchers have found the optimized ratio for the LSCF cathode. In the beginning, $La_{1-x}Sr_{x}$ was introduced based on the mixed-metal perovskite-type oxide, which was expected to have lots of useful properties as the chemical compatibility between La and Sr is high and widely used as membrane for oxygen permeation at certain temperatures and absorbent for producing oxygen-enrich carbon dioxide stream (Yang, et al., 2002; Guntuka, et al., 2008). The addition of Cobalt and Ferum onto the $La_{1-x}Sr_x$ to improve the performance in terms of conductivity has been done with the results showing that increasing electrical conductivity as a consequence of superior bulk ion diffusion can result in increased oxygen vacancies in the oxide and cause oxygen ionic conductivity and oxygen adsorption to be increased (Guntuka, et al., 2008).

Therefore, the most suitable ratio for the LSCF type cathode is 6 mole of Lanthanum, 4 mole of Strontium, 2 mole of Cobalt and 8 mole of Ferum (Gao, et al., 2017). One of the attractive studies regarding the use of LSCF type cathode is composite cathode. The addition of noble metal towards the cathode is essential to improve the performance in terms of microstructure, electrical and electrochemical properties. The primary factor before introducing composite cathode is the chemical compatibility towards the LSCF. Noble metal, predominant electronic conductors and mixed ionic conductors (MIECs) have been studied by various researchers for their potential applications in intermediate temperature of SOFCs (Jacques-Bedard, et al., 2006; Kim, et al., 2006). The electro-catalytic activity of electrode is used to determine the ORR rate in SOFCs. Currently, conventional LSCF is calcined at high temperature (about 1000 ^{o}C) to obtain a good adhesion to electrolyte at intermediate temperature range. However, as the temperature increases, the grain sizes were also increased while the electro-catalytic activity decreased (Gong, et al., 2009).

2.4 Composite Type Cathode

Another way to improve the SOFC is by applying noble metal on the cathode, which also known as composite cathode technique. Applying composite cathode can be considered a challenge due to the difficulties to match between the MIEC materials with another noble metal. Therefore, it is hard to find an optimal operating condition since each material has its own limits.

The main factor in applying composite cathode is to improve the electro-catalytic activity. In order to increase the electro-catalytic activity as well as reducing the calcining temperature, Lu et al. (Lu, et al., 2012) added copper oxide (CuO) into the LSCF. However, the ratio of LSCF-CuO and synthesizing route were still left undone to optimize the performance. Generally, the application of CuO composite towards various types of cathode has a capability as a good catalyst for chemical reaction and effective sintering aid of ceramics as reported by several researchers in their studies (Lu, et al., 2012; Ran, et al., 2006; Zhao, et al., 2009; Reitz, et al., 2000).

Copper oxide infiltration is an efficient and a cost-effective way to enhance the catalytic stability of LSCF cathode. It is important to understand the mechanism leading to the observed improvement of ORR reaction efficiency as well as enhanced operational stability. Usually, copper is located either on the surface of cathode or diffused into its lattice. Hence, the catalytic property of cathode is affected by two possible processes, which are ORR reaction that would be affected at the interface between CuO and cathode where CuO acts as a catalyst and the diffusion of copper oxide into the LSCF lattice.

2.5 Route producing LSCF Type cathode

Fe-based nanomaterial has an increasing number of studies due to the demand and versatility of its applications. The critical reason of using Ferum during fabrication of nanomaterial cathode is due to the good value of electrical conductivity and reduction in the poisoning effect on the performance of cathode. Application of Ferum as a nanomaterial can be considered convenient since it has a good chemical compatibility towards various chemical components, making it a versatile and improved material towards cathode with various elements that have been widely studied over time. Route for producing Fe-based nanomaterial is solid to wet and solid to gas phase while undergoing several advancements to reduce the cost of fabrication as well as scarification for the performances.

The performance of Fe-based nanomaterial basically comprised structure, electrical conductivity, thermal effect, electrochemical conductivity and degradation factors. These factors must be considered to ensure that the cells can perform well in the industry later on. Thus, it is desirable to optimize environmentally benign and highly efficient energy devices like fuel cell (Singhal & Kendall, 2003). Normal SOFC devices operate at slightly high temperatures reaching 1000 ^{o}C. However, several technical and processing criteria eventually rise up the manufacturing cost for operating at this temperature range. Therefore, researchers tried to lower the operating temperature to slightly below than 1000 ^{o}C, which is known as intermediate temperature ranging from 600-900 ^{o}C. However, to enable this application to be applied in today’s application, new material with much lower temperature performance in terms of conductivity, chemical and mechanical compatibility needs to be developed and identified. Various composites and electrolytes need to be optimized while maximizing the performance of SOFC with minimal cost and less pollutant (Adler, 2004). These problems have been frequently studied and optimized to improve the efficiency of IT-SOFC for fully utilized as an energy source in the near future. Many of these issues and problems can be possibly alleviated by introducing a new approach. Thus, a wide variety of issues associated with the development of new product together with new solutions for the above problems can be dismissed.

2.5.2 Development of LSCF based cathode for IT-SOFCs

There are various types of Fe-based nanomaterial developed for the past 17 years that can be categorized as composite, pure or electrolyte to investigate the performance of the cathode towards IT-SOFCs. This part discusses the development of LSCF type cathode and performance by year to observe the pattern of the study towards the nanomaterial cathode at intermediate temperature. Hwang et al. (Hwang, et al., 2005) and Skinner (Skinner, 2001) investigated the composite of LSCF with SDC and platinum. Solid state route was applied showing that the addition of SDC was able to improve the oxygen ion diffusion path while the addition of platinum was able to enhance the oxygen absorption at intermediate temperature solid oxide fuel cells.

The study was then continued by Kim-Heon et al. (Kim-Heon, et al., 2006) by applying the LSCF on the GDC interlayer with YSZ electrolyte. The sample was synthesized using Pechini method followed by the addition of SDC on YSZ to prevent unwanted products, which were $SrZrO_3$ and $LaZrO_3$. This sample is a good choice for intermediate temperature solid oxide fuel cells as the power density produced as high as with low polarization resistance at 800 ^{o}C and 1100 ^{o}C sintering temperature. Identical result has been reported by Fu et al. (Fu, et al., 2007) where the LSCF was composited with the SDC and tested towards SDC electrolyte and he claimed that

LSCF-SDC composite cathode with SDC electrolyte was better than LSCF with SDC interlayer on YSZ electrolyte since the addition of lower oxide ionic conductor (YSZ) to the SDC film led to a lower conductivity of the whole system. After that, many studies documented that LSCF-YSZ composite cathode on YSZ electrolyte is better than LSCF-SDC composite cathode with SDC electrolyte. Study made by Chen et al. (Chen, et al., 2008) showed a good results. The sample was able to produce a fine porous structure with fine grain size. The result of adding YSZ was able to enhance the electro catalytic activity of the cells. Guo et al. (Guo, et al., 2008) proposed a new composite cathode of LSCF-LSGM with LSGM electrolyte. The sample was able to produce a fine microstructure with decreased polarization resistance of new composite cathode with the conventional single phase LSCF cathode. Thus, it is clear that the addition of LSGM can buffer the thermal expansion coefficient of the cell while in the meantime increasing its oxygen reduction reaction.

However, Hildenbrand et al. (Hildenbrand, et al., 2010) proposed further improvement could be done as the dense LSCF and YDC were inserted as interlayer into 8YSZ electrolyte using screen printed method. It appeared that this method was capable to reduce the electrolyte resistance by factor of 1.25 and the polarization resistance by a factor of 3 compared to the conventional LSCF cells (Gazzarri & Keslar, 2007). It was also demonstrated that YDC and dense LSCF appeared to have a good chemical composition as good adhesion appears on the electrolyte. Lu et al. research regarding the addition of copper oxide towards LSCF/GDC at intermediate temperature (Lu, et al., 2012). It could be conclude that CuO able to change the morphology of the cathode with addition of SDC electrolyte. Hua et al. that continued to produce composite of LSCF-GDCS and compare the microwave sintered methods with conventional sintered method (Hua & Chou, 2015). It was found that the composition of 80% LSCF with 20% GDCS emitted the best result among the compositions present and microwave sintered was much better than conventional sintered method as it produced more fine porous and grain structure. Sample consisting LSCF synthesized using solid state route has been tested by Cao et al (Cao & Jiang, 2016) with GDC and LSO electrolyte. The result for LSCF with LSO was almost similar to the finding obtained by Mitsu et al. (Mitsu, et al., 2017) studying similar composition.

Apart from the polarization resistance factor, power density factor also needs to be considered to determine the most suitable composition for intermediate temperature solid oxide fuel cells. Simmer et al. (Simmer, et al., 2006) studied the effects of adding silver on LSCF in YSZ electrolyte via mechanofusion dry processing. It appeared that the addition of silver was able to improve the particle surface area. However, it also has a major disadvantage where the performance degraded as the silver was not chemically compatible with the YSZ electrolyte.

Power density showed a promising result where the sample tested at 700 ^{o}C. Swierczek (Swierczek, 2010) applied a composite of LSCF-SCFN with CGO electrolyte and 8YSZ-Ni anode via sol-gel modified method. The author claimed that that addition of SCFN was able to improve oxygen ion transport in the cells as reported by Molenda et al. and it was found that the best ratio for the LSCF and SCFN was 60% and 40%, respectively (Molenda, et al., 2007). The surface illustrated fine pores and grain in the surface of the sample. Choi et al. (Choi, et al., 2012) fabricated a porous structure of LSCF using aerosol deposition approach. It seemed that the additional of PVDF was able to enhance the porosity of the cathode and increase the grain structure of the sample. It was obvious that as the polymer content increases, more pores were produced. This resulted in the oxygen reduction reaction that occurred more rapidly in the cells producing higher power density.

Research pattern shown that research toward LSCF type cathode is popular to be composited with various type of electrolyte and another noble metal. Table 2.1 showed the list of several researcher toward LSCF type cathode production with various route and composite.

Table 2.1 List of several researcher toward LSCF cathode production

Author	**Year**	**Topic**	**Route**
Hwang et al.	2001	LSCF with SDC	Solid state
Skinner et al.	2001	LSCF with SDC	Solid state
Kim et al.	2006	LSCF composite YSZ	Sol gel
Fu et al.	2007	LSCF composite SDC	Sol gel
Chen et al.	2008	LSCF composite YSZ	Sol gel(Modified)
Gou et al.	2008	LSCF with LSGM	Solid state
Hildenbrand et al.	2010	LSCF with YDC and YSZ	Sol gel
Lu et al.	**2012**	**LSCF composite SDC/CuO**	**Sol gel**
Hua & Chou	2015	LSCF with GDC	Sol gel
Cao & Jiang	2016	LSCF with GDC/LSO	Solid state

Based on table 2.1, there are no researcher that has been research regarding the difference between solid state method and sol gel method in term of characterization and performance. As the year progress through, Lu et al. have done research regarding the addition of copper oxide towards LSCF and SDC (Lu, et al., 2012). Apart from that, the addition of CuO on LSCF was able to enhance the power density as well as reduce the needs for sintering temperature of the LSCF sample. However, there are no in depth explanation has been given regarding the effect of addition of copper oxide

Other factors such as different synthesizing approach, use of different propellants and application of double layer on cathode surface also need to be understand in order to determine whether or not the sample is suitable for intermediate temperature solid oxide fuel cells. It is important to understand other factors to improve the performance of Fe-based nanomaterial. Various studies were conducted on new composite cathode or newly type electrolyte to investigate its suitability and performance in IT-SOFCs. Santillan et al. (Santillán, et al., 2009) synthesized LSCF with CGO substrate via electrophoretic deposition method using different types of additive. It showed that acetyl acetone with iodine was the most appropriate way for LSCF deposition due to the improvement of porosity produced by that sample. Menzler & Haanappel (Menzler & Haanappel, 2010), and Leonide et al. (Leonide, et al., 2008) further investigated the functioning layer on the LSCF anode. Report showed that thin functioning layer was more suitable to be used due to less helium leak and negligible area specific resistance.

The study was then continued with thin double layer cathode film synthesized via electrostatic spray deposition method by Marinha et al. (Marinha, et al., 2011) with the results presenting the production of fine microstructure. It was certainly because the double layer has improved the active sites by making them larger, thus improving the surface area as mentioned by Peter et al. (Peter, et al., 2008). Moreover, it showed slight improvement from the previous study made by Nobert et al. (Menzler & Haanappel, 2010) where the sample was able to reduce the area specific resistance. This result indicated significant improvement as the thin layer doubled at the sample. Next, Conceição et al. (Conceição, et al., 2010) investigated the effects of different propellants toward the porosity of the LSCF sample. The LSCF undergone conventional sol-gel method and it was found out that glycine is the best propellant that could be used to produce LSCF via sol-gel as a result of high porosity on the sample surface.

A LSCF sample synthesized with citrate hydrothermal method was done by Garcia et al (Garcia, et al., 2013) to inspect the pores and grain structure. It was discovered that LSCF synthesized with this route was only applicable in intermediate temperature and high temperature solid oxide fuel cells since unwanted secondary phases product appear below 900 ^{o}C as reported by previous researcher (Ghosh, et al., 2005). However, a fine grain with good pores appeared on the sample indicating that more tests are needed in the future to optimize the use of citrate hydrothermal method in LSCF production.

The study continued by Magnone & Park (Magnone & Park, 2014) regarding the LSCF by replacing cobalt with titanium and the oxygen uptake capacity was measured between those two samples. Both samples showed a good crystallinity structure but in terms of chemical compatibility, cobalt showed a better chemical compatibility than the titanium since pores produced in LSCF was more than those of LSTF. There were no in depth examinations conducted and it was concluded that LSCF is much superior than LSTF in terms of oxygen uptake capacity value. Meanwhile, the effects of poisoning criteria have been examined by Ni & Skinner (Ni & Skinner, 2016) for LSCF type cathode. It was found that the addition of Ferum was able to suppress the chromium and molybdenum poisoning on the LSCF sample.

The study was then followed by that of Perz et al. (Perz, et al., 2016) where the long time degradation effects due to poisoning effect were studied. Similar LSCF sample was tested and it was found that the optimal temperature was less than 900 ^{o}C, which in the range of intermediate temperature of solid oxide fuel cells to produce a homogeneous and fine structure. It is also crucial to avoid silicon formation above 900 ^{o}C, which led to the performance degradation as reported by several researchers (Bae & Steele, 1998; Liu, et al., 2015; Viitanena, et al., 2002). As a conclusion, it is clear that the degradation of the cells is not caused by the LSCF, but the additional effects that may be correlated to gas diffusion or oxygen surface adsorption.

2.6 Cathode Processing Route

Solid state method involves the use of high temperatures to synthesise the nanomaterial. It is important to ensure that the cathode materials are purified from any contaminant and capable of producing desired particle size powder. This method introduces milling process to reduce the particle size in the cathode. Furthermore, as the particle size decreases, the cathode is able to be as compact as possible, which is good to reduce the degradation value. Although it is a small amount in this scale, but this is one of the factors that influence the electrochemical performance of solid oxide fuel cells in a large scale.

There are various ways to synthesise nanoparticle cathode via solid state route. The conventional solid state method uses water to dissolve the raw material comprising various types of salt containing nitrate (Shin, et al., 2015). The idea is to dissolve all the raw material to form a homogenous mixture and to make the separation of salt nitrate to become easier. This method does not require milling because raw materials are considered already dissolved and started to mix with each other. Then, the mixture is evaporated to remove excess water and nitrate, which is then calcined at designated temperature. Another conventional solid state method consists of mixing and milling during the early stage (Guo, et al., 2008; Cho, et al., 2012). The raw material are mixed together in ethanol and milled for a certain period. The purpose of using ethanol is to keep the raw material from sticking to the milling surface. The ethanol can be easily removed at the boiling temperature of 80 ^{o}C. Nevertheless, this process requires attention as the ethanol is easily vaporised during milling stage. The mixture is dried in the oven to remove excess ethanol and nitrate. Then, it is pressed into pellet and sintered at designed temperature. There are some modified versions of solid state route that require both vaporising and milling processes (Chiu, et al., 2017). The solid state reaction (SSR) method starts by pre-heating all raw materials individually to remove nitrate. After the raw material started to form a solid oxide, it is mixed together according to the ratio and undergoes milling process to reduce the particle size. The idea of using solid oxide as a starting material before mixing process is to ensure that all nitrate are removed before the synthesising process begin. The mixture is then sintered to remove the excess ethanol and the resulted powder is grind and sieved to prevent bulk solid from mixing with the final powder. Solid state route contains much simpler and cheaper process compared to sol-gel route. Overall, the solid state route requires mixing process to reduce the particle size of the mixture so that the product will have a fine microstructure and good grain as a result.

Sol-gel method comprises sol or solution, which is a combination of two phases known as are liquid and solid phases forming a gel type structure. It is usually used for material ether nano or micro size for fabrication purpose. It converts monomers into sol-gel state that acts as a precursor for an integrated network. In common case or undergoing sol-gel method, the density of the composition is supposed to be low as most of the liquid will be exiled from the composition to produce gel type structure. In SOFC, drying process or direct heat in furnace is followed by significant amount of densification. In order to determine the porosity distribution, the rate of solvent exiled is studied. Next, a thermal treatment is necessary to enhance the mechanical properties of the sol-gel. Usually, it only requires low temperature but long heating time to remove air particles or any significant impurities inside the sol-gel. It is also important