

EFFECT OF ARGENTUM ON DEVELOPMENT AND PROPERTIES OF  
COMPOSITE CATHODE  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$  – SDCC-Ag FOR LOW  
TEMPERATURE SOLID OXIDE FUEL CELL (LTSOFC)

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*Specially dedicated to:*

My father and mother,  
Mr. Abu Bakar Bin Ishak and Mrs. Romlah Binti Ismail,  
There's no love and sacrifices like yours,  
And nobody can replace both of you,  
And yet not even a single word can be expressed to thank all of your kindness  
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## ABSTRACT

Lowering the operating temperature of solid oxide fuel cells (SOFC) has gained much attention in research nowadays. Recently, research on cathode materials focused on composite cathode carbonate with Argentum (Ag) addition which allows outstanding performance at low operating temperature. This study focused on the effect of Ag on development and properties of composite cathode Lanthanum Strontium Cobalt Ferrite-Samarium Doped Ceria Carbonate-Argentum (LSCF-SDCC-Ag) for low temperature SOFC (LTSOFC) applications. Composite cathode powders LSCF-SDCC-Ag with Ag addition of 1-5 wt.% has been developed via high energy ball milling (HEBM) technique and sintered at 500-600°C. The characterisation of the composite cathode powders involved the XRD analysis to determine the chemical compatibility and crystallite structure of the composite cathode powders. The morphology and distribution of elements in powder were observed via FESEM and EDS respectively. Analysis to investigate the physical properties such as particle size, crystallite size, porosity and cross section of pellets were employed. Thermal properties such as TEC and TG were also identified. The resistance of composite cathode pellets were measured via two-probe electrical test at temperature 400-600°C. All the composite cathode powders with Ag addition from 1-5wt.% and sintered between 500-600°C exhibited good chemical compatibility as there were no secondary constituent was detected via XRD sensitivity. The carbonate phase managed to maintain their phase as confirmed via FTIR and TG analysis. The crystallite size and particle size was increase with increasing of Ag amount meanwhile the porosity decrease with increasing amount of Ag and sintering temperature. LSCF-SDCC-Ag 5wt.% sintered at 600°C, 2wt.% sintered at 550°C and 3wt.% sintered at 600°C recorded the nearest average TEC value with SDCC with percentage difference of 0.3%, 3.0% and 4.5% respectively, while the sintering temperature of 550°C shows consistency and nearly TEC value of composite cathode LSCF-SDCC-Ag towards electrolyte SDCC. Composite cathode LSCF-SDCC-Ag (2 wt.%) sintered at 550°C yielded the lowest resistance amongst all. Hence, it was concluded that the composite cathode LSCF-SDCC-Ag with Ag addition of 2 wt.% sintered at 550°C in which demonstrate lowest resistance ( $0.61\Omega$ ) and within acceptable average TEC value ( $9.74\pm 4.98 (10^{-6}/K)$ ) with electrolyte SDCC ( $10.20\pm 6.27(10^{-6}/K)$ ) potentially to be served as composite cathode for low temperature SOFC applications.

## ABSTRAK

Merendahkan suhu pengoperasian sel fuel oksida pepejal (SOFC) menjadi tumpuan kajian masa kini. Dewasa ini, kajian terhadap bahan katod tertumpu kepada katod komposit berkarbonat dengan penambahan Argentum (Ag) yang memberikan prestasi cemerlang pada suhu pengoperasian rendah. Kajian ini menumpu kepada kesan kehadiran Ag terhadap pembangunan dan sifat katod komposit Lanthanum Strontium Cobalt Ferrite-Samarium Doped Ceria Carbonate-Argentum (LSCF-SDCC-Ag) bagi aplikasi SOFC bersuhu rendah. Serbuk katod komposit LSCF-SDCC-Ag dengan penambahan Ag 1-5 wt.% dibangunkan dengan kaedah pengisaran bebola berhalaju tinggi (HEBM) dan disinter pada suhu 500-600°C. Pencirian serbuk katod komposit melibatkan analisis pembelauan sinar-X (XRD) bagi menentukan keserasian kimia dan struktur kristalit serbuk katod komposit. Morfologi dan serakan unsur serbuk katod komposit diperhatikan melalui mikroskop elektron pengimbas pancaran medan (FESEM) dan analisis spektroskopi serakan tenaga (EDS). Analisis sifat-sifat fizikal seperti saiz partikel, saiz kristalit, keliangan dan keratan rentas pelet telah dijalankan. Sifat-sifat termal seperti pekali pengembangan terma (TEC) dan termogravimetri (TG) juga telah ditentukan. Kerintangan pelet katod komposit telah diukur menggunakan kaedah pengujian elektrik 2-prob pada suhu pengujian 400-600°C. Semua katod komposit dengan penambahan Ag 1-5wt.% dan disinter pada suhu 500-600°C menunjukkan keserasian kimia yang baik kerana tiada kehadiran jujuk baru yang dikesan melalui sensitiviti XRD. Fasa karbonat juga mampu dikekalkan oleh katod komposit setelah dipastikan melalui analisis transformasi Fourier inframerah (FTIR) dan TG. Saiz kristalit dan saiz partikel telah bertambah dengan pertambahan Ag manakala keliangan telah berkurang disebabkan pertambahan Ag dan juga suhu pensinteran. LSCF-SDCC-Ag 5wt.% disinter pada 600°C, 2wt.%, disinter pada 550°C dan 3wt.% disinter pada 600°C mencatatkan purata nilai TEC yang paling hampir dengan SDCC iaitu peratus perbezaan TEC katod-elektrolit masing-masing sebanyak 0.3%, 3.0% dan 4.5% manakala suhu pensinteran 550°C menunjukkan purata nilai TEC yang konsisten dan hampir antara katod komposit LSCF-SDCC-Ag dengan elektrolit SDCC. Katod komposit LSCF-SDCC-Ag (2 wt.%) disinter pada 550°C menghasilkan kerintangan yang paling rendah iaitu (0.61Ω) dan mempunyai lingkungan purata nilai TEC ( $9.74 \pm 4.98 (10^{-6}/K)$ ) yang sesuai dengan elektrolit SDCC ( $10.20 \pm 6.27 (10^{-6}/K)$ ) adalah berpotensi untuk dijadikan katod komposit untuk aplikasi SOFC bersuhu rendah.

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**LIST OF SYMBOLS/ABBREVIATIONS**

$e^-$	-	electron
$E_a$	-	activation energy
$H^+$	-	proton
kW	-	kilo watt
Mw	-	mega watt
$I$	-	current
V	-	volt
$\lambda$	-	wave length $CuK_\alpha$
$\sigma$	-	conductivity
$\theta$	-	Bragg's diffraction angle
$O^{2-}$	-	oxygen ion
$O_2$	-	oxygen gas
$H_2O$	-	water
$CO_2$	-	carbon dioxide
$CO_3^{2-}$	-	carbonate
P	-	power
Ni	-	nickel
Cu	-	cuprum
R	-	resistance
$R_p$	-	polarization resistance
S	-	active surface area
V	-	volt
$W_w$	-	wet weight of pellets in air
$W_d$	-	dry weight of pellet in air
$W_s$	-	sinking weight of pellets in auxiliary liquid

$\pi$	-	pi
$r$	-	Resistance
$\Omega$	-	Ohm
SOFC	-	Solid Oxide Fuel Cells
Ag	-	Silver
Pt	-	Platinum
Pd	-	Palladium
HEBM-		High Energy Ball-Milling
XRD	-	X-ray Diffraction
FESEM-		Field Emission Scanning Electron Microscopy
EDS	-	Energy Dispersive Spectroscopy
TEC	-	Thermal Expansion Coefficient
TG	-	Thermogravimetri
FTIR	-	Fourier Transform Infra-Red
PEMFC-		Polymer Electrolyte Membrane Fuel Cell
DMFC-		Direct methanol fuel cells
AFC	-	Alkaline Fuel Cell
PAFC	-	Phosphoric Acid Fuel Cell
MCFC-		Molten Carbonate Fuel Cell
UKM	-	University Kebangsaan Malaysia
UTHM-		University Tun Hussein Onn Malaysia
MIEC	-	Mixed ionic and electronic conductors
$\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$	-	Lanthanum strontium cobalt ferrite
SDC	-	Samarium-doped ceria
SDCC	-	Samarium-doped ceria carbonate
IT-LTSOFC	-	Intermediate to low temperature solid oxide fuel cell
ITSOFC	-	Intermediate temperature solid oxide fuel cell
$\text{Li}_2\text{CO}_3$	-	Lithium carbonate
$\text{Na}_2\text{CO}_3$	-	Sodium carbonate
YSZ	-	Ytria-stabilized zirconia
LSM	-	Lanthanum strontium manganate
CHP	-	Combined heat and power
TPB	-	Triple phase boundaries
GDC	-	Gadolinium-doped ceria

- ORR - Oxygen reduction reaction
- ASR - Area specific resistance
- PEG - Poly ethylene glycol

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## **CHAPTER 1**

### **INTRODUCTION**

#### **1.1 Background of study**

The generation of electricity commonly has been accomplished through the combustion of fossil fuels. This is highly inefficient process. Most fossil fuel power plant convert only about one-third of the energy stored in the fuel to electricity. Moreover, fossil power plants produce contaminating emissions that must be controlled.

Fuel cells are devices directly convert fuel to electricity. Efficiencies of sixty percent are common. Moreover, useable heat energy is available that increases the overall efficiency to about eighty percent. If hydrogen gas is the fuel used, the only emission is steam. If natural gas is the fuel used, the emissions are steam and carbon dioxide. Meanwhile, the greenhouse effect of fuel cells is always less than the traditional power plants (The American Ceramic Society, 2006).

Fuel cells have been founded by science for more than 150 years. In the early of 1839, Friedrich Schoenbein first revealed the possibility of a fuel cell that combine hydrogen with oxygen (Schoenbein, 1839). One month later, Sir William Robert Grove published the experimental observation of voltage in a concentration cell combining hydrogen with oxygen in the presence of platinum (Grove, 1839). A few years later, in 1845, Sir William Groove found the new findings which formally confirmed the technical feasibility of a fuel cell as a power generating device. Widely research have been done for the last decades in purpose of improvements and boosting the efficiency of fuel cells. As the result, fuel cells available in several type in which the classification was made according to the type of electrolyte used.

There were several types of fuel cells such as Polymer Electrolyte Membrane Fuel Cell (PEMFC), Alkaline Fuel Cell (AFC), Phosphoric Acid Fuel Cell (PAFC), Molten Carbonate Fuel Cell (MCFC) and Solid Oxide Fuel Cell (SOFC) (Williams, 2002 & Gasik, 2008).

This research was focused on SOFC. Thus due to their unique operation and performance characteristics, SOFC are well suited for distributed on-site cogeneration of heat and power. The SOFC is an important enabling technology for future sustainable energy systems. SOFC in particular can be used in wide variety of fuels. This fuel tolerance is a result of the high operating temperature, which not only accelerates the fuel reactions, but also accelerates unwanted chemical reactions that can lead to degradation of materials. Therefore, progress in SOFC relies heavily on materials development and, although significant progress has been made over the past several decades but still many technical challenges remain and need to be overcome before SOFC can be widely commercialized (Fergus *et al.*, 2009).

Malaysia as the developing and competitive country in Asia Pacific also doing the research towards fuel cells especially on SOFC. These researches are doing by the local university. There are active researches by the Fuel Cells Institute of University Kebangsaan Malaysia (UKM) towards SOFC and the project also linked with other sub-university like University Tun Hussein Onn Malaysia (UTHM) in Batu Pahat Johor. In realize about the importance of this kind of energy sources towards the country in the future, there were several institutions and others universities such as University Technology Malaysia (UTM) and Universiti Malaysia Perlis (UNIMAP) also has led the research regarding SOFC and also the other types of fuel cells.

SOFC have been widely and continuously developed by the researchers for more than 40 years. However, some aspect of the research not fully covered especially for the intermediate and low temperature SOFC which is still open for investigation (Sakito *et al.*, 2008). Currently, there are many research in improving the components of SOFC such electrolyte, anode, cathode, interconnects and also the manufacturing technology. This research was conducted with the purpose of contribution to improve the cathode of SOFC for low temperature operation as well as to ensure SOFC operate in optimum operation without with extended durability and also without any limitation such expensive performance costs, limitation of material and manufacturing processes as well (Fergus *et al.*, 2009).

## 1.2 Problem statement

SOFC system has gained increase attraction to be develop due to high-energy conversion efficiency, self-reforming ability, no need of noble metals as catalysts, use of solid state materials and compatibility with common hydrocarbon fuels (Mata *et al.*, 2007 & Wen *et al.*, 2002). Due to the accelerating in SOFC's development, the practical SOFC system with a high performance have been demonstrated (sakito *et al.*, 2008). At moment, the most successful SOFC operated at 1000°C. However, the cost of performance has not been acceptable for the commercial applications. Lowering the SOFC operation temperatures has been widely pursued to reduce the costs, extend the materials selection to suppress the degradation of SOFC components and consequently to extend the cell lifetime (Sholklapper *et al.*, 2008). Inexpensive metallic materials may be used for interconnect and manifold components at an operating temperature lower than 800°C . However, the SOFC performance decreases with decreasing the operation temperature, because of increasing the electrode polarization and the electrolyte resistance (Sakito *et al.*, 2008)

In improvising and extended the cell lifetime, great effort has been made to lower the operating temperature of SOFC in purpose to increase their applicability and competitiveness (Andersson *et al.*, 2006 & Zhu, 2001). By lowering the operation temperature, a wider range of cheaper materials can be used to construct the fuel cell components and systems. Lower temperature operation also affords more rapid start-up, improved durability, and higher robustness as well as simplified system requirements. Reduction in the SOFC operating temperature from the current 700–850°C down to 450–600°C would bring advantages of reduced materials cost, better manufacturing capability and enhanced durability (Meng *et al.*, 2011).

Hamimah (2012) reported that the operating temperature of SOFC needs to be lowered (<700°C) to stabilized their performance and make them become commercially feasible. Previous reports indicate that key improvements in cell performance can be realized by investigating and enhancing novel or as-developed cathode materials (Fu *et al.*, 2007, Murray *et al.*, 2002 & Li *et al.*, 2010). One approach to improve low temperature cathode performance involves the development of composite cathode materials. By referring to the previous research, the addition of

mixed ionic and electronic conductors (MIEC), such lanthanum strontium cobalt ferrite ( $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ ) to samarium-doped ceria (SDC) electrolytes has been proven to produce a high performance potential cathode for intermediate to low temperature solid oxide fuel cell (IT-LTSOFC) (Murray *et al.*, 2002 & Rahman *et al.*, 2013). The use of binary carbonate ( $(\text{Li}/\text{Na}_2)\text{CO}_3$ ) together with SDC as to improve the ionic conductivity has opened a new segment of research in which the LSCF-SDCC composite cathode was said to be performed well at low temperatures of 400-600°C. The combination of LSCF with SDCC has been proved to yield outstanding properties as composite cathode materials for intermediate to low temperature SOFC (IT-LTSOFC) (Bod'en *et al.*, 2007, Zhang *et al.*, 2011 & Rahman *et al.*, 2013).

Previous researches also reported that the silver (Ag) as a potential candidate material to combine with LSCF was able to enhance the conductivity as to overcome the resistance at cathode during the low temperature operation (Simner *et al.*, 2007). Silver metal was an excellent candidate for the cathode in SOFC with operating temperature below than 800°C, because of its good catalytic activity, high electrical conductivity and relatively low cost (Sakito *et al.*, 2008). Besides, the use of Ag also improves cathode microstructure as the melting point of Ag is 961°C, it might aid the sintering behavior at cathode (Zhang *et al.*, 2005).

In this research, the focus was to develop composite cathode LSCF-SDCC-Ag to suit with low temperature solid oxide fuel cell application. This research also was designed to investigate the effect of Ag addition in composite cathode LSCF-SDCC materials as well as to identify its chemical, physical and electrical properties.

### 1.3 Objectives

This study embarks on the following objectives:

- 1) To develop Ag added composite cathode LSCF-SDCC-Ag for low temperature solid oxide fuel cell application.
- 2) To identify the effect of Ag addition to the chemical, physical, thermal and electrical (resistance) properties of composite cathode LSCF-SDCC-Ag.



## 1.4 Scopes of study

The scopes of this research are:

### 1) Preparation of composite cathode powders

- i) Commercial powder LSCF, SDC,  $\text{Li}_2\text{CO}_3$ ,  $\text{Na}_2\text{CO}_3$  were used to produce composite cathode LSCF-SDCC with ratio (50 wt.% : 50 wt.%)
- i) LSCF-SDCC mixed with Ag with amount of Ag addition (1, 2, 3, 4 and 5 wt.%)

Each batch of composite cathode powders was going through the preparation, characterization and testing processes as listed below:

- i) The wet milling method was employed for the preparation of the LSCF-SDCC powders.
- ii) The dry milling method has been implemented for the mixing process of LSCF-SDCC with (1-5 wt.%) Ag powders.
- iii) The composite cathode LSCF-SDCC was calcined at temperature of  $750^\circ\text{C}$ .
- iv) The composite cathode LSCF-SDCC-Ag has been fabricated into pellets and sintered at temperature of  $500^\circ\text{C}$ ,  $550^\circ\text{C}$  and  $600^\circ\text{C}$ .

### 2) Characterisation of the composite cathode powders

#### a) Chemical properties

- i) X-ray diffraction (XRD) analysis
- ii) Fourier-transform infra-red (FTIR) analysis

#### b) Physical properties

- i) Crystallite size measurement via Scherrer's equation
- ii) Field emission scanning electron microscopy (FESEM) and particle size measurement via SmartTiff software
- iii) SEM-Energy dispersion X-ray spectroscopy (SEM-EDS) and cross section of composite cathode pellets via SEM
- iv) Porosity measurement via Archimedes' method

- c) Thermal properties
  - i) Thermogravimetric analysis (TGA)
  - ii) Thermal expansion coefficient (TEC) measurement
- 3) Electrical test of composite cathode powders LSCF-SDCC-Ag
  - i) 2-point probe electrical test has been conducted to measure ohmic resistance measurement of composite cathode samples with and without Ag powder.

## 1.5 Significant of study

Conventional fossil fuels will continue to be the primary source of energy in the future for at least the next 50 years. Unfortunately, the excessive and continuous use of fossil fuel contributes to the pollution. Rather than focus on the problem, the solution had been made. Fuel cells had emerged for last decades as the new alternative energy and play the role as the green technology. Years by years until today, there were active researches had been construct to improve the energy resource especially for the fuel cells.

This study significantly for the purpose of green technology energy resources. High temperature SOFC emerge with the package of conversion efficiency, fuel flexibility, very low emissions and environmental impact among all types of power generation systems. They are in an excellent position to offer clean and efficient power generation which conventional heat engines find it difficult to compete (Huang & Goodenough, 2009).

This research was focused on the effect of Ag addition on development and properties of composite cathode LSCF-SDCC-Ag for LTSOFC applications. Significantly, this research was aimed to develop LTSOFC with lower performance costs so that it is more applicable and practically effective. Previous research reported that lower operation temperature contribute to the lower operational cost. Low temperature SOFC is still new and need a lot of improvements and developments. This study has played an important role on developing cathode materials for LTSOFC. This study was also one of the great efforts in realizing the commercialization of LTSOFC with superior properties, stabilities and durability.

## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 Introduction

Statistic facts revealed that the world energy demand is growing at a rate of 1.8% per year. This is resulting from increment of industrialization mostly from the developing countries. The highly demands also associates with the conservation of fossil fuel leads to the emissions of greenhouse gases and other pollutants. The consequences are the emissions from developing countries may account for more than half of the global carbon dioxide CO<sub>2</sub> emissions by 2030. The industrialized should therefore to take the challenge to lead the way towards the development of new energy systems. For sure this requires a comprehensive strategy on developing the new energy sources that will collapse the entire obstacle as mention above. Short and long-term objectives that need to achieve are greater energy efficiency and better integration of renewable energy sources. Parallel with this aim, as an efficient and clean technology, fuel cells can make a different and substantial contribution as the highly prospected energy sources (Stolten & Emonts, 2012).

#### 2.2 Fuel cell

A fuel cell is an electrochemical device that converts the chemical energy of a reaction, between fuel and oxygen, directly into electrical energy. The basic components that build up the fuel cells consists of an electrolyte layer in contact between anode and cathode, interconnect and sealants (Williams, 2002). In general, gaseous fuels are supplied continuously to the anode which is negative electrode, and an oxidant, usually oxygen from air is supplied continuously to the cathode which is

positive electrode. The electrochemical reactions occur at the electrodes to produce an electric current.

Fuel cells differ from secondary batteries (accumulators) and battery (primary) and it should not be confused between these three items. The battery is an energy storage device and the maximum energy it contains is determined by the amount of chemical reactant stored within the battery itself. The battery produces electrical energy when the chemical reactants are consumed or discharged. In a secondary battery, the reactants are regenerated by recharging, which involves energy supplied into the battery from an external electricity source. The fuel cell, on the other hand, is an energy conversion device that has the capability of producing electrical energy for as long as fuel and oxidant are supplied to the electrodes (Williams, 2002 & Gasik, 2005). Fuel cell started its history in 1839 when Sir William Grove found his valuable findings. That fuel cell at that time was the earliest version of a lead-acid accumulator, but it implemented platinum electrodes with sulphuric acid electrolyte. Platinum here working as both a catalyst and a current collector (Grove, 1874).

Fuel cells started to begin its own path and were seen as an attractive subject for the generation of power because of the good efficiencies as compared to other technologies that were very poor. For instance, the coal-burning generator station developed by Edison in Manhattan in 1882 converted only about 2.5% of the available energy into electricity. Still in 1920s, the overall thermodynamic efficiency of reciprocating steam engines was approximately 13-14% and steam turbines efficiency just under 20%. Those kinds of poor thermal efficiencies have motivated the pioneer at that time to develop the fuel cells (Perry & Fuller, 2002). At the beginning of the 20<sup>th</sup> century, coal has played the role as the major fuel then the emphasis was put coal-derived fuels first. As the efficiency of other technologies rapidly improves, the interest in fuel cells slightly goes down. Only when the “space race” began in the late 1950s, the works on develop fuel cell begin to move on especially for the purpose of space deployment (Gasik, 2005 & Perry & Fuller, 2002).

### 2.3 Types of fuel cell

Fuel cells types exist in different variety classified depending on the combination of type of fuel and oxidant, whether fuel is processed outside (external reforming) or inside (internal reforming) the fuel cell, the type of electrolyte, the operating temperature, whether the reactants are supplied to cell by internal or external manifolds and some of the added characteristic which determine the types of the fuel cells (Williams, 2002). Theoretically, the fuels at the anode of fuel cell are the candidates of any substance capable on chemical oxidation that can be supplied continuously. So far, hydrogen gas has become the suitable candidate for most of applications. This is certainly because of its high reactivity when suitable catalysts are used, its ability to be produced from hydrocarbons for terrestrial applications and its high energy density when stored cryogenically for closed environment purpose, such as in space. Corresponding to the hydrogen fuel, the most common oxidant is gaseous oxygen, which is readily and economically available from air for terrestrial applications, and again easily stored in a closed environment (Gasik, 2008). The most of fuel cells are classified by the type of electrolyte used. The types are:

1. Polymer electrolyte membrane fuel cell (PEMFC)
2. Alkaline fuel cell (AFC)
3. Phosphoric acid fuel cell (PAFC)
4. Molten carbonate fuel cell (MCFC), and
5. Solid oxide fuel cell (SOFC)

In addition, PEMFC also use methanol as a fuel so these fuel cells are often called “direct methanol fuel cells (DMFC)”. “Direct” means that methanol in this case is not being externally reformed, but rather oxidized directly. It is simply conclude that the operating temperature and useful life and power density of a fuel cell determine the physicochemical, thermo mechanical and other properties of material used in the components consist of electrodes, electrolyte, interconnect, current collector and many more.

## 2.4 Solid oxide fuel cell (SOFC)

A fuel cell is an electrochemical device that provides efficient and clean power generation. Due to their unique operation and performance characteristics, solid oxide fuel cells (SOFC) are well suited for distributed on-site cogeneration of heat and power. The SOFC is an important enabling technologies for future sustainable energy systems and beneficial to develop. SOFC, as currently developed as its specialty compared to other fuel cells, they can be used with the wide variety of fuels and are affected less by impurities than PEMFC. This fuel tolerance is a result of the high operating temperature, which not only works on the fuel reactions, but also works on unwanted chemical reactions that can be the causes of materials degradation. Therefore, progress in SOFC based on materials development and, although significant progress have been achieved over the past several decades, but still many technical challenges remain and need to overcome before SOFC can be widely commercialized.

This research is conducted focusing on cathode materials of SOFC. However, this chapter will discuss the entire components and elements of SOFC in order to gain overall understanding on SOFC. The electrolyte of SOFC is the components that convert the chemical energy to electrical energy. Recent efforts to reduce the operating temperature of SOFC require electrolytes with higher conductivities than the most commonly used yttria-stabilized zirconia (YSZ). Recently, the research have been made to reduce the operating temperature of SOFC from 1000 °C down to intermediate temperature range of 600-800 °C and pursue to the low temperature range of below 600 °C (Huang, 2007, Bieberle-Hutter, 2008, Johnson, 2009 & Peters, 2008)

Because of their high operating temperatures, SOFC do not require platinum catalysts for the electrode like PEMFC. However, the difference between the high-temperature gas compositions at the anode and cathode requires that different materials to be used for the two electrodes, cathode and anode. For the cathode, the most commonly material used was lanthanum strontium manganate (LSM), but recently, alternative cathode materials with improve electrochemical properties and resistance to chromium poisoning are being developed such as lanthanum strontium cobalt ferrite (LSCF).

Another components that build up the SOFC are two supporting components of the fuel cell stack specifically, interconnects and sealants. Interconnects is the component which conduct the electrical current between the two electrodes through the external circuits and it also exposed to both high oxygen partial pressure (air) and low oxygen partial pressure (fuel), which needs to meet material stability. Ceramic interconnects have been used currently, but metallic interconnects provides more flexibility towards production of lower cost SOFC. Sealants is the another crucial components of SOFC. It plays the function as the separator between the two gases. The most common approach is to use a glass or glass-ceramic, which can provide a gas-tight seal, but it is influence by thermal and mechanical stresses. Another approach is to use compressive seals, which are more reliable and acceptable of differences in thermal expansion, but require application of a load during operation.

The developments of fuel cells also include the material processing for SOFC applications. One of the challenges is to developing materials that satisfy the material requirements and specifications. It is also further complicated by the need to fabricate the materials in the desired shapes and with the desired microstructures. The production of a cost-effective SOFC requires corresponding relation between materials properties and processing methods to produce materials with desired properties at an acceptable cost (Fergus *et al.*, 2009).

#### **2.4.1 Advantages of SOFC**

SOFC convert chemical energy directly into electrical energy with advantages of high efficiency, low emission and fuel flexibility (Haile, 2003). The all solid state cell composition makes the SOFC system simple in concept, design and construction which is the two-phase, gas and solid contact for the reaction occur reduces corrosion and eliminates all the problems associated with the liquid electrolyte management such in MCFC. For high operating temperature of SOFC, resulting in fast electrochemical kinetics which is low activation polarization and no need for noble metal catalysts.

It is important to notice that in SOFC, carbon monoxide is no more a contaminant, rather it becomes a fuel. More important advantage, the SOFC serves high quality waste heat, which can be utilized for cogeneration applications for additional electric power generation. The SOFC operating condition is also

compatible with the coal gasification process, which makes SOFC systems highly efficient when using coal as the primary fuel. It has been estimated that the chemical to electrical energy conversion efficiency is at least 50%-60% and estimates go as high as 70%-80%. Additionally, nitrogen oxides are not produced and the amount of carbon dioxide released per kilowatt hour is around 50% less than power resources based on combustion because of the high efficiency of the SOFC (Li & Karimi, 2007).

For SOFC operating at higher temperature, in range of 600-1000 °C, there are some added advantages. Its not only provides high quality waste heat, but also effectively activates the processes of reforming and electrochemical oxidation of hydrocarbon fuels in the presence of catalysts. This specialty is technically important for several reasons. First, it opens the opportunity for SOFC to use more hydrocarbon fuels, either in gaseous or in liquid state, which they are properly cleaned and reformed into simple fuels such as hydrogen H<sub>2</sub> and carbon dioxide CO<sub>2</sub>. This certainly contrast to low-temperature type of fuel cells such as PEMFC where CO<sub>2</sub> poisons the anode. The second is that excessive heat produced from the electrochemical oxidation of fuels can be used by the highly endothermic steam reforming reaction simultaneously occurring, which makes internal on-cell reformation possible. Co-production of heat and power, known as combined heat and power (CHP), is the third advantage of high temperature SOFC. the recovery of waste heat along with the production of electricity enables the total energy efficiency of such a system to be in the range of 85%-90%.

Another solution of recovering waste heat have been made is to combine a micro gas turbine with an SOFC stack to form a hybrid system. In order to maximize the electrical efficiency, the SOFC's micro gas turbine hybrid often operated under pressurization that would boost both the performance of the SOFC stack and the effectiveness of the micro gas turbine. Further move in order to be more efficient, a bottom cycle steam turbine can be added into the above hybrid system. This is particularly preferable for generators over 100 MW. The hybrid SOFC generator reported by Siemens' Company to achieve a net AC electrical efficiency of 53% for a 220 kW class.

When compared to molten carbonate fuel cell (MCFC) which is another type of high temperature fuel cell, the all solid component used in an SOFC system avoid the corrosion issues caused by the liquid electrolyte of the MCFC system, which



prolongs the lifetime of SOFC. In fact, with over 35000 operating hours at an acceptable degradation rate, a Siemens 100 kwe unit is the longest-running SOFC generator (Huang & Goodenough, 2009).

#### 2.4.2 Operating principles of SOFC

SOFC are constructed of five basic functional elements: electrolyte, cathode, anode and interconnect. For tubular SOFCs, there is an added element, the cell-to-cell connector. Ceramics or metals are the materials in making these components. The functionality of an electrolyte is to transfer oxygen continuously and solely in the form of oxygen ion  $O^{2-}$  from cathode to anode under a gradient of oxygen  $O_2$  chemical potentials. To enable the  $O^{2-}$  transportation across the electrolyte, the cathode of oxygen supply has to convert  $O_2$  into  $O^{2-}$ , a process commonly known as oxygen reduction. Likewise, the anode of fuel supply accepts  $O^{2-}$  delivered by the electrolyte and converts it into water  $H_2O$  and carbon dioxide  $CO_2$  by reacting with hydrocarbon fuels. Figure 2.1 below illustrates the working principle of an SOFC in tubular geometry.

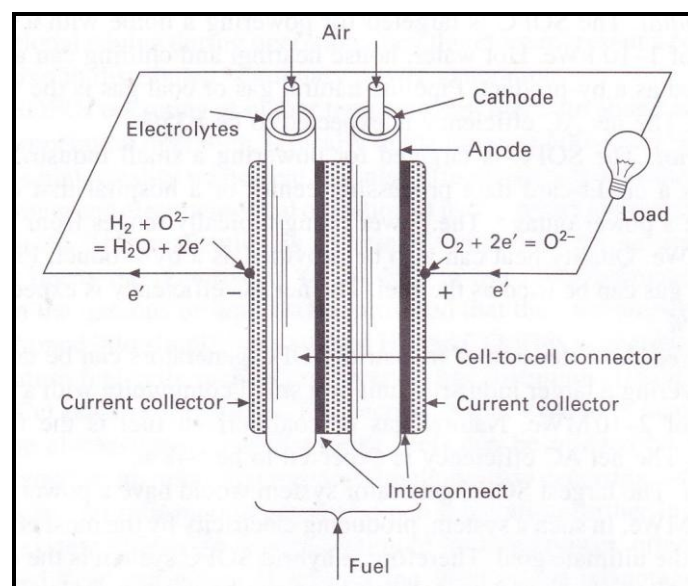


Figure 2.1: Schematic of the working principle of SOFC. Tubular SOFC are used for illustrative purposes (Huang & Goodenough, 2009)

The electrons required for the electrode reactions are released by the anode and arrive at the cathode via an external load resulting on the producing of electricity (Gasik, 2008). The overall driving force for a SOFC is the gradient of chemical

potential of oxygen existing between a cathode of high partial pressure of oxygen and an anode of low partial pressure of oxygen. The single cell of SOFC with air as the oxidant can reach maximum cell voltage up to 1.2 V, depending on temperature, system pressure and fuel composition. For practical application, this value of voltage definitely insufficient. Multiple single cells have to be connected in series and/or parallel with the support of interconnects and/or cell-to-cell connectors. The interconnects and cell-to-cell connector should be pure electronic conductors and oxide-ion insulators.

SOFC also have voltage losses by which the SOFC component exhibits an internal resistance to either electronic or ionic current flow. Entire requirement for an operational SOFC is to ensure oxygen migrant across the electrolyte in the form of oxygen ion  $O^{2-}$ , not in the form of oxygen molecule  $O_2$ . To achieve this purpose, dense barriers between air and fuel have to be created. For the one-end-closed tubular SOFC design, such barriers are easily create by allowing air and fuel to meet at the open-end where combustion occurs after the fuel is mostly utilized over the entire cylindrical surface without no physical sealing material is needed. However, for the planar SOFC design, sealing materials have to be use along the parameters of interconnects/electrodes and electrolyte/electrodes in order to avoid air from mixing with fuels, which often presents a challenge to the reliability and stability of the planar SOFC (Huang & Goodenough, 2009).

### **2.4.3 Designs of SOFC**

Modern SOFC typically consist of thin electrolyte film and a supporting substrate seems like porous or channeled dense body for gas transport. This substrate in which determine the type or design of the SOFC. From a geometric terms, the substrate can be either tubular or a planar shape.

#### **2.4.3.1 Tubular geometry**

Each types of design have their own advantages. Tubular geometry with one-end-closed feature contribute to the seal-less design which means that cost of production can be reduced. These characteristics of design are strongest advantage over planar geometry where gas seals are needed along the parameters of the stack. Tubular

geometry also can reduce the space of SOFC which make the design become more compatible. This is simply because it allows cell-to-cell connections in a stack with the using of inexpensive transition metals such as nickel (Ni) and cuprum (Cu). Figure 2.2 below shows a schematic of cell-to-cell connection in a cathode-supported tubular SOFC stack. Instead of using tubular geometry, noble metals are needed for connecting anode supported cells into stacks in an oxidizing atmosphere which lead to extra cost of SOFC production (Huang & Goodenough, 2009).

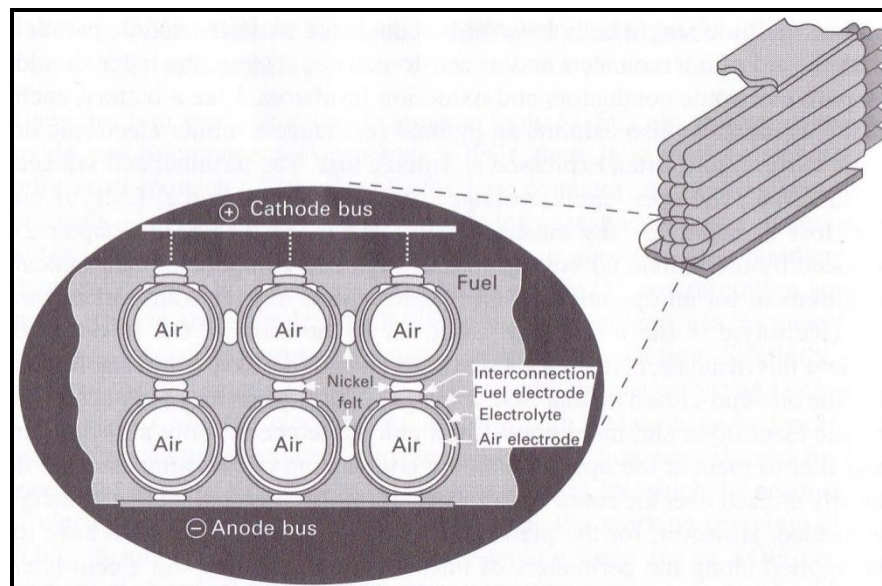


Figure 2.2: Schematic of cell-to-cell connection in a cathode-supported tubular SOFC stack (Huang & Goodenough 2009)

#### 2.4.3.2 Planar geometry

On the other hand, the designs of planar stacks are more compatible for anode substrate instead of cathode substrate. The planar concept is still familiar by the majority of research labs because its ability of design to achieve higher power densities (Ralph *et al.*, 2001). Anode-supported single cells have high-power-density which leads to reduce operating temperature. Major problems with this design include sealing the stacks to prevent fuel and oxidant gases mixing and the thermal mismatch between ceramic components, which has led to cracking during thermal cycling. Indirectly with this circumstance, an economic and commercially available oxidation-resistant alloy can be implemented to connect single cells into a stack. The oxidation-resistant alloys essentially provide the mechanical support for the stack

and function as interconnects and current collectors simultaneously. Figure 2.3 below shows a schematic of an anode-supported planar SOFC configuration with metal interconnect.

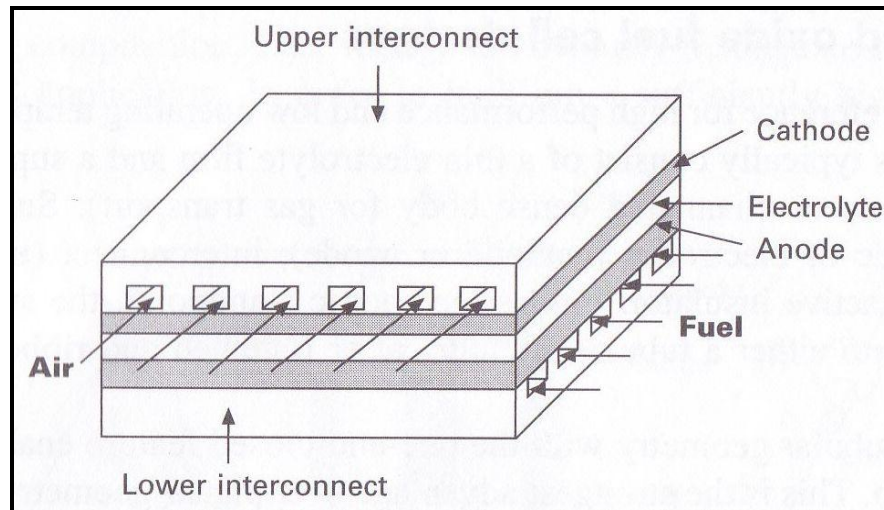


Figure 2.3: Schematic of cell configuration in an anode-supported planar SOFC stack (Huang & Goodenough, 2009)

## 2.5 Low Temperature Solid Oxide Fuel Cell (LTSOFC)

Previously, the traditional SOFC have to be operated at temperatures above  $800^{\circ}\text{C}$  in order to obtain a desirable power density. However, the performance of the electrodes decreases over long time of operation. This was due to the high temperature operation, the components of the fuel cells unavoidably react with each other, affected the stability of the SOFC system and deteriorate the cell performance (Huijismans *et al.*, 1998, Minh, 2004 & Huang *et al.*, 2011). Moreover, in terms of practical implications especially in domestic and industrial, SOFC have not been realized as it has high material cost, high temperature operation and issues of safety. In addition, high operating temperatures (above  $800^{\circ}\text{C}$ ) of SOFCs can lead to multiple materials problems which include electrode sintering, interfacial diffusion between electrolyte-electrode materials, thermal instability, brittle nature of used materials, and mechanical (or thermal) stresses due to different thermal expansion coefficients (TEC) of the cell components. Such problems have limited the development and use of SOFC to a greater development as well as commercializing the SOFC (Mahato *et al.*, 2015).

All those fact regarding the disadvantages of high temperature SOFC represents the reasons that high temperature SOFC faces the obstacle to be potentially commercialized. Hence, to overcome the disadvantages of high temperature SOFC, the effort has been done to reduce the operating temperature of SOFC to intermediate temperature (IT) (600-800°C). However, the intermediate temperature SOFC (ITSOFC) also creates another problem that the overpotential resistances of the electrodes, especially the cathode, increase rapidly with decreasing the operating temperature. Each of the SOFC components (anode, cathode, and electrolyte) requires different types of materials. As the operating temperature is reduced, the materials as well will change to suit with the temperature while maintaining the performance. Considering the type of material will affect the overall cell performance, hence the materials used also change due to the change in operational temperature.

One of the key improvements in cell performance can be realized by investigating and enhancing novel or as-developed cathode materials (Fu *et al.*, 2007 & Li *et al.*, 2010). SOFC cathode materials must have certain characteristics to help develop and maintain cell performance. Liu *et al.*, (2012) stated that (La, Sr)(Co, Fe)O<sub>3</sub> (LSCF) perovskite oxides are widely accepted as the cathode material for SOFC that operate in the intermediate temperature between 600-800°C due to their high electronic and ionic conductivities. However, it also comes to the challenge where the electrochemical performance of LSCF cathodes is not stable with time, and the performance degradation becomes one of the issues that limit LSCF applications in SOFC. There are two possible mechanisms for the degradation of LSCF cathodes, that is, the instability of LSCF materials and the change of LSCF microstructure.

Using intermediate-to low-temperature (IT-LT)SOFC) requires cathode materials that have good electronic and ionic conductivities at temperatures below 800°C. Thus, mixed ionic-electronic conductors (MIEC) such as perovskite-based materials were suggested. MIEC may help develop larger the triple phase boundaries (TPB) and increase the performance of IT-LT)SOFC (Fergus *et al.*, 2009). The selection of a suitable cathode material for an IT-LT)SOFC can also enlarge the TPB area (Viswanathan & Scibioh, 2007). The TPB between a cathode and an electrolyte helps determine the effectiveness of an electrochemical reaction. Therefore, studying

cathode component materials offering higher electronic and ionic conductivity is important. LSCF is a perovskite-based material suitable for IT-LT-SOFC applications. A composite cathode is introduced to improve cathodic polarization. Electrolyte materials such as samarium-doped ceria (SDC) and gadolinium-doped ceria (GDC) are mixed with LSCF to enhance the ionic conductivity of the cathode (Zhang *et al.*, 2005 & Huang & Chou, 2009). Composite technology allows the creation of electrodes with higher effective surface area to increase the efficiency of the exchange reactions and consequently to decrease the electrode over potentials (Seabaugh & Swartz, 2009).

Research efforts have been increasingly focusing on the development of intermediate-to-low temperature (400–600°C) SOFC (Huang *et al.*, 2012). Moreover, an innovative solid carbonate-oxide composite known as SDC carbonate (SDCC) that performed well at low temperatures of 400–600°C was discovered (Zhu, 2001 & Jarot *et al.*, 2011). The combination of LSCF with SDCC is expected to achieve outstanding properties as composite cathode materials for IT-LT-SOFC. Moreover, previous researchers also found that the addition of noble metal such as Ag, Pt and Pd towards LSCF cathode materials were said able to improve the conductivity of the LT-SOFC (Haanappel *et al.*, 2004 & Simner *et al.*, 2006)

## **2.6 Cathode for LT-SOFC**

Cathode components of fuel cell construct from porous structure materials to allow the flow of air or oxygen. Here is the region where the oxygen reduction reaction (ORR) to occur. Cathode materials with a porous structure stable at the necessary fabrication and operating conditions are desirable for improving the performance of LT-SOFC cathodes. Nowadays research has been design to lower the operation temperature of SOFC so that the fuel cell can operate at temperature below 600°C consequently a better and sustain LT-SOFC can be commercialize. Despite of having advantage from LT-SOFC, lowering the operating temperature decreases the electrode kinetics and results in large interfacial polarization resistances. This effecting most the ORR process at the cathode.

In order to lower the polarization resistance of the cathode, a favorable electronic and ionic conductivity as well as a high catalytic activity for oxygen

reduction must be maintained. Cathode for LTSOFC must be produced using materials that have higher electronic and ionic conductivity to migrate the oxygen ( $O_2$ ) through the triple phase boundary (TPB). TPB is the region where provide the area in which electrode (cathode), air and electrolyte meet each other for electrochemical reaction to occur. In terms of the microstructure, TPB have a great effect on the electrochemical performance of cathode materials.

In having the higher electrochemical performance of cathode for LTSOFC, problems persist in the areas of chemical stability and thermal expansion match with other cell components also need to solve. A trade-off between electrochemical performance and thermal expansion is necessary to identify an optimum cathode performance. Furthermore, long-term stability is a significant factor to be considered for practical LTSOFC system to sustain. Hence, cathode of LTSOFC one of the important components apart from the whole complete system. Cathode for LTSOFC still in process of development and optimization so that it can be commercialize relatively with low cost.

### 2.6.1 Properties for cathode

In short, in a SOFC system, the fuel is oxidized at an electrochemical interface (electrode called anode), accepting electrons and donating these electrons at a second electrochemical interface (electrode called cathode, separated from the anode) to an oxidant, (oxygen) which is reduced by accepting these electrons (Doeff, 2012). Cathode for SOFC must have certain characteristics in order to play the role as oxygen reduction base in SOFC systems. In general, it must have these characteristics (Singhal, 2000, Wincewiz & Cooper, 2005 & Sun *et al.*, 2010):

- High electronic conductivity (preferably over  $100 \text{ Scm}^{-1}$  under oxidizing atmosphere)
- Higher ionic conductivity (approximately  $10^{-1} \text{ Scm}^{-1}$ )
- Chemically compatible with neighboring cell component (usually the electrolyte)
- Thermal expansion coefficient (TEC) compatibility with electrolyte and others SOFC's components.
- Stable during oxidation process

- Catalyze the dissociation of oxygen
- Can be made thin and porous (thin enough to avoid mass transfer losses, but thick enough to provide area and distribute current)
- Adhesion to electrolyte surface
- Suitable porosity range
- Large triple phase boundary (TPB)
- High catalytic activity for oxygen reduction reaction (ORR) to occur
- Relatively simple fabrication
- Uses relatively inexpensive materials (low cost)

The choice of cathode materials is largely dependent on the electrolyte materials used with care taken to match thermal expansion coefficients and avoid undesirable interface reactions. The materials for cathode can be categorized into two categories, (1) electronic conductivity materials and (2) mixed ionic-electronic conductivity materials. Since the operating temperature of SOFC has been lowered to low operation temperature, the mixed ionic-electronic conductivity materials has gain much attention and preferably used by the researchers. This was due to low operating temperature; the previous and familiar materials used such lanthanum strontium manganite (LSM) has low ionic conductivity and limit the TPB in cathode consequently reduce the overall cathode performance. Therefore, the mixed ionic-electronic conductivity (MIEC) material was introduced such lanthanum strontium cobalt ferrite (LSCF) purposing in enlarge the TPB area and enhance the performance of the SOFC (Fergus *et al.*, 2009 & Sun *et al.*, 2010).

There were three path of ORR in cathode, that is, the electrode surface path, the bulk path, and the electrolyte surface path as shown in Figure 2.4. All these three paths applied for cathode materials which have electronic conductance (e.g. LSM) MIEC conductance (e.g. LSCF) and composite cathode conductance (e.g. LSCF-SDC). The reaction in cathode can occurred at these three paths simultaneously and the rate of reaction that occur depend on temperature, half oxygen pressure and materials microstructure (Sun *et al.*, 2010). Hence it is very important to enlarge the TPB in optimizing the reaction to occurred in cathode region for low temperature operation. This can be achieved by the implementation and use of MIEC cathode as



well as composite cathode which have meet the characteristic of SOFC's cathode materials.

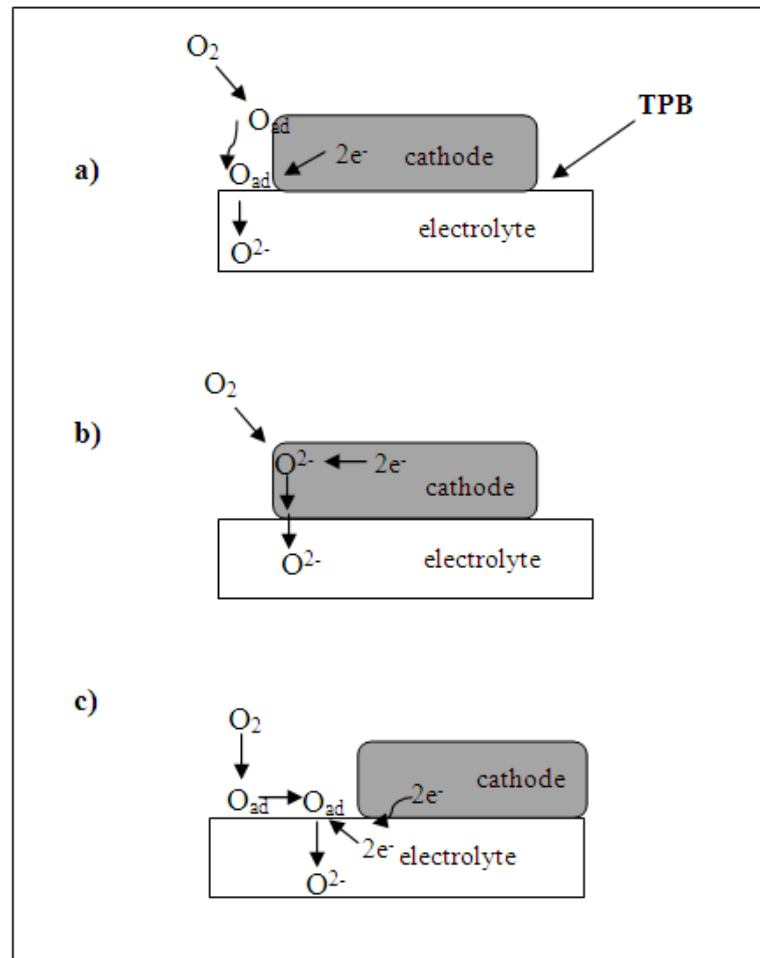


Figure 2.4: Schematic diagram of the (a) electrode surface path, (b) the bulk path, and (c) the electrolyte surface path (where  $O_2$  – oxygen gas  $O_{ad}$  – adsorption oxygen  $O^{2-}$  - oxygen ion) (Sun *et al.*, 2010)

### 2.6.2 Lanthanum Strontium Cobalt Ferrite ( $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ ) (LSCF)

LSCF is categorized as perovskite materials and suitable candidate to be used in application of IT-LTSOFC. Perovskite materials have been widely used as cathode materials in SOFC (Skinner, 2001). A perovskite-type oxide has the general formula  $ABO_3$ , in which A and B are cations with a total charge of +6. The lower valence A cations (such as, La, Sr, Ca, and Pb, etc.) are larger and coordinated to twelve oxygen anions while the B cations (such as, Ti, Cr, Ni, Fe, Co, and Zr, etc.) occupy the much smaller space and are coordinated to six oxygen anions. Full or partial substitution of A or B cations with cations of different valence is possible. When the overall valence

of the A-site and B-site cations adds up to less than six, the missing charge is made up by introducing vacancies at the oxygen lattice sites. Figure 2.5 shows the typical structure of the cubic perovskite  $ABO_3$ . (Sun *et al.*, 2010).

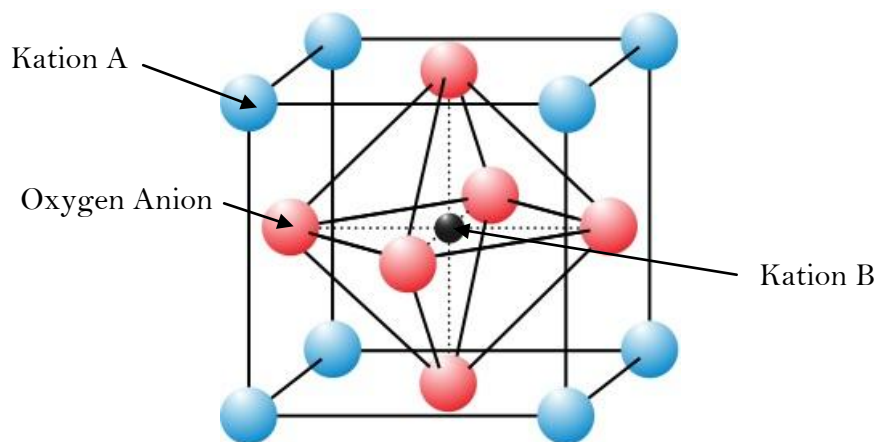


Figure 2.5: Unit cell of the  $ABO_3$  perovskite structure (Sun *et al.*, 2010)

Most cathode materials rely on doping of both the A and B sites to improve electrical conductivity and electrocatalytic performance. The ideal structure of perovskite is cubic lattice as shown in Figure 2.5. However, most of oxide perovskite compound crystallize with polymorph structure (rhombohedral, hexagonal or orthorhombic) in which there was a distortion at its perovskite structure (Tai *et al.*, 1995). Sun *et al.*, (2010) also stated that many perovskite structures are distorted and do not have cubic symmetry. Common distortions such as cation displacements within the octahedra and tilting of the octahedra are related to the properties of the A and B substituted atoms.

$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$  (LSCF6428) will give cubic crystallite perovskite structure when calcined at low temperature in range of 600-800°C. When calcined at high temperature (1000°C), the cubic structure changes to rhombohedral. The amount of Sr in LSCF6428 also affecting the crystallite structure. LSCF in which containing  $0.2 \leq Sr \leq 0.4$  tends to have rhombohedral structure meanwhile the low range of Sr containing;  $0.15 \leq Sr \leq 0.2$  will gives cubic structure (Waller *et al.*, 1996). Moreover Waller *et al.*, (1996) also found that the calcinations was the factor affecting the structure of the LSCF perovskite. Based on previous researchers, LSCF was identified as the excellent candidate for cathode materials in IT-LTSOFC applications (Wincewicz & Cooper, 2005 & Ghouse *et al.*, 2010).

There were a lots of XRD studies of these materials have been termed in situ, in which situ means that the XRD patterns were collected at high temperature or in a controlled gas atmosphere. Such in situ XRD studies of LSCF have provided valuable information regarding its thermal and chemical expansion coefficients and phase stability (Hashimoto *et al.*, 2011). Finding in study conducted by Da Côte, Da Conceicao & Souza (2013), indicates that LSCF also had rhombohedral structure (space group R3c). The rhombohedral symmetry was also observed by Tai (1995) for  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{1-y}\text{Fe}_y\text{O}_3$  samples with  $0 \leq y \leq 0.7$  in which indicates that the crystallite size increases with increasing calcination temperature while the micro-strain decreases.

## 2.7 LSCF composite cathode for LTSOFC

For the past few decades, solid oxide fuel cells (SOFC) have emerged as one of the new alternative energy resources. It offers high efficiency power generation, clean energy conversion with low emissions and low noise. Because of its high operating temperatures (800-1000°C), high temperature SOFC (HTSOFC) has facing some problems such as difficulties on construction, material and process selection, thermal expansion mismatch, lower durability and less opportunities to mass product. As the solution, research is conducting to lower the operating temperature of SOFCs aiming to improve their life expectancy and reliability (Jarot *et al.*, 2011). However, the reduction of operating temperature gives the consequences of inefficiency to the cathode elements as the cathode polarization resistance increase which cause substantial performance decline (Fan *et al.*, 2011).

Rahman *et al.*, (2012) reported that designing a high performance electrode with a low polarization resistance such as using a composite cathode potentially able to solve the problems. Recently, the addition of electrolyte material to the cathode material has increased the triple phase (air/electrode/electrolyte) regions where the electrochemical reactions occur. Mixed ionic and electronic conductors such as  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$  (LSCF) is one of the candidates that has been applied with this approach since LSCF has been recognized as one of the promising cathode for SOFCs (Rahman *et al.*, 2012).

Based on previous research, electrolyte materials such as samarium-doped ceria (SDC) and gadolinium-doped ceria (GDC) are mixed with LSCF to enhance the ionic conductivity of the cathode (Zhang *et al.*, 2005 & Murray *et al.*, 2002). The higher ionic conductivities of SDC and GDC have made them suitable to be combined with LSCF as they are ionic conductor materials. Moreover, LSCF and cerium electrolyte does not react with each other since they have the same TEC and the problems of thermal mismatch can be avoided. This combination actually will enlarge the area of electrochemical activity and enhance the electrical conductivity of SOFC (Baharuddin *et al.*, 2013).

### **2.7.1 Electrochemical properties and performance of LSCF composite cathode**

For the past decade, there are many research has been conducted worldwide regarding the development of composite cathode in order to determine the most suitable materials as the cathodes for SOFCs systems. The initial idea to fabricate composite cathode was to obtain more interface region for high ionic conduction pathway. The research work on ceria-based composite in last decade mainly focused on extensive fuel cell performance test based on various ceria-based composite ceramics, such as samarium-doped ceria (SDC) and gadolinium doped ceria (GDC) incorporated with different salts and hydrates, such as chlorides, fluorites and carbonates. Based on these extensive results, it has been approved that ceria-carbonate composite obtained the best performance, which thus became the research highlight of several last decade. This section emphasizes the implementation as well as influence of SDC and GDC ceria electrolyte towards LSCF composite cathode.

#### **2.7.1.1 Influence of SDC ceria-electrolyte**

Table 2.1 lists the electrochemical properties and performances of LSCF-SDC composite cathodes that have been developed. Zhang *et al.*, (2005) mixed LSCF powder with 30 wt.% SDC and 30 wt.% of Ag by grinding method. The implementation of composite cathode concept able to overcome the polarization of the cathode-electrolyte and from their experiment, the addition of SDC reducing the

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