

**PREPARATION AND CHARACTERIZATION OF LSCF-CUO USING
SOLID STATE METHOD AS CATHODE MATERIAL FOR
INTERMEDIATE TEMPERATURE SOLID OXIDE FUEL CELL
(IT-SOFC)**

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UNIVERSITI SAINS MALAYSIA

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by

MUHAMMAD NUR RAMADHAN B ABD RAZAK

**Thesis submitted is in partial fulfilment of the requirement for the degree
of Bachelor of Chemical Engineering**

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LIST OF SYMBOLS

Symbol	Description	Unit
<i>A</i>	Specific surface area	m ² /g
<i>F</i>	Flowrate	cm ³ /min
<i>f</i>	Frequency	Hz
<i>H</i>	Heating rate	°C/min
<i>P</i>	Power	W
<i>R_p</i>	Polarization resistance	Ω.cm ²
<i>V</i>	Total pore volume	cm ³ /g

LIST OF ABBREVIATION

Symbol	Description
AFC	Alkaline Fuel Cells
CPE	Constant Phase Element
CO	Carbon Monoxide
CO ₂	Carbon Dioxide
CuO	Copper (II) Oxide
DMFC	Direct Methanol Fuel Cell
EDTA	High Temperature Solid Oxide Fuel Cell
H ₂	Hydrogen
H ₂ O	Water
HT-SOFC	High Temperature Solid Oxide Fuel Cell
IT-SOFC	Intermediate Temperature Solid Oxide Fuel Cell
LSCF	Lanthanum Strontium Cobalt Ferum
LSM	Lanthanum Strontium Manganese
LT-SOFC	Low Temperature Solid Oxide Fuel Cell
MCFC	Molten Carbonate Fuel Cell

O ₂	Oxygen
ORR	Oxygen Reduction Reaction
PAFC	Phosphoric Acid Fuel Cell
PEMFC	Proton Exchange Membrane Fuel Cell
SOFC	Solid Oxide Fuel Cell

**PENYEDIAAN DAN PENCIRIAN LSCF- CuO MENGGUNAKAN KAEDAH
KEADAAN PEPEJAL SEBAGAI BAHAN KATOD UNTUK SEL BAHAN BAKAR
OKSIDA PEJAL BERSUHU SEDERHANA**

ABSTRAK

Sel bahan bakar oksida pejal (SOFC) adalah salah satu daripada kumpulan sel bahan bakar yang paling banyak digunakan dalam produk kejuruteraan yang berupaya menukar tenaga kimia terus kepada tenaga elektrik dan tenaga haba dengan menggunakan reaksi elektrokimia. Sel bahan bakar oksida pejal bersuhu sederhana (IT-SOFC) adalah sejenis sel yang dikendalikan pada suhu pertengahan antara 600 - 800°C memberikan prestasi elektrokimia yang lebih baik dan mengurangkan kos bahan dan operasi. LaSrCoFeO_3 (LSCF) adalah bahan katod perovskit dalam IT-SOFC yang memberikan prestasi elektrokimia yang lebih baik berbanding dengan SOFC klasik. Kajian ini menganalisa sifat kimia, fizikal dan elektrokimia komposit LSCF dengan CuO yang disintesis oleh kaedah keadaan pepejal konvensional. Serbuk yang dikalsin akan dianalisis dengan analisis difraksi sinaran (XRD), pengimbasan mikroskop elektron (SEM), analisis sinaran penyebaran tenaga (EDX), analisis termogravimetrik (TGA) dan analisis Brunauer-Emmett-Teller (BET). Data XRD menunjukkan fasa tunggal perovskit LSCF-CuO pada suhu 700°C. Imej SEM menunjukkan saiz zarah LSCF-CuO meningkat apabila suhu kalsin meningkat. Data BET menunjukkan kawasan permukaan spesifik dan jumlah liang berkurang apabila suhu kalsin meningkat. Nilai rintangan polarisasi (R_p) terendah untuk katod LSCF-CuO ialah 0.41 $\Omega \cdot \text{cm}^2$ pada suhu 800°C.

**PREPARATION AND CHARACTERIZATION OF LSCF-CUO USING SOLID
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ABSTRACT

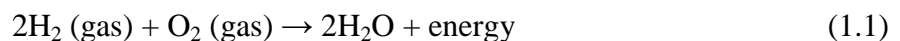
Solid oxide fuel cells (SOFC) is one of the most widely used groups of fuel cell in engineering products which converts the chemical energy directly to electrical energy and thermal energy by using electrochemical reactions. IT-SOFC is a type of fuel cell which is operated at intermediate temperature between 600 – 800°C give a better electrochemical performance and reduce the material and operating cost. LaSrCoFeO₃ (LSCF) is a perovskite cathode material commonly used in intermediate temperature solid oxide fuel cell (IT-SOFC) which give the better electrochemical performance as compared with the classical SOFC. This research investigated the chemical, physical and electrochemical characteristic of LSCF composite with CuO which synthesized by conventional solid-state method. The calcined powders were analyzed by X-ray diffraction analysis (XRD), scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX), thermogravimetric analysis (TGA) and Brunauer- Emmett- Teller analysis (BET). XRD data showed the single-phase perovskite LSCF-CuO at temperature 700°C. SEM images showed the LSCF-CuO particle size increased as the calcination temperature increased. The BET showed the specific surface area and total pores volume decreased as the calcination temperature increased. The lowest polarization resistance (R_p) value for LSCF-CuO cathode was 0.41 $\Omega\cdot\text{cm}^2$ at temperature 800°C.

CHAPTER ONE

INTRODUCTION

1.1 Introduction

Fuel cells are type of electrical devices that converts chemical energy such as hydrogen and methanol directly into electrical energy or power with environmental friendly way (Varga, 2007, Shah, 2007, Garcia et al., 2013). The reaction occurs in the fuel cell as shown below:



Chemical reaction above shows that the hydrogen from the fuel reacts with the oxygen to produce water and heat energy. This could give advantages for transportation such as high efficiency and less noise operation (Cook, 2002, Shah, 2007). There are several type of fuel cells such as proton exchange membrane fuel cells (PEMFC), direct methanol fuel cells (DMFC), alkaline fuel cells (AFC), phosphoric acid fuel cells (PAFC), molten carbonate fuel cells (MCFC) and solid oxide fuel cells (SOFC) (Chandran and Arjunan, 2015) as shown in Table 1.1.

The fuel cells can operate at high efficiency (55 – 65 % efficiency) which is much better than power generator which operates up to 40 - 45 %. Furthermore, fuel cell can replace the natural gas as there is no combustion process and the hydrogen contents in fuel cell is much higher than natural gas (Irvine and Conno, 2013, Shah, 2007). This also can reduce the emission of carbon dioxide content and greenhouse effect to the environment. Figure. 1.1 shows the various type of fuels with hydrogen contents.

Table 1.1: Type of fuel cells (Chandran and Arjunan, 2015)

	<i>PAFC</i>	<i>MCFC</i>	<i>SOFC</i>	<i>PEMFC</i>
Electrolyte	Phosphoric Acid	Molten Carbonate Salt	Ceramic	Polymer
Operating Temperature	375°F (190°C)	1200°F (650°C)	1830°F (1000°C)	175°F (80°C)
Fuels	Hydrogen (H ₂) Reformat	H ₂ /CO Reformat	H ₂ /CO/CH ₄ Reformat	H ₂ Reformat
Reforming	External	External/Internal	External/Internal	External
Oxidant	O ₂ /Air	CO ₂ /O ₂ /Air	O ₂ /Air	O ₂ /Air
Electrical Efficiency (HHV)	40-50 %	50-60 %	45-55 %	40-50 %

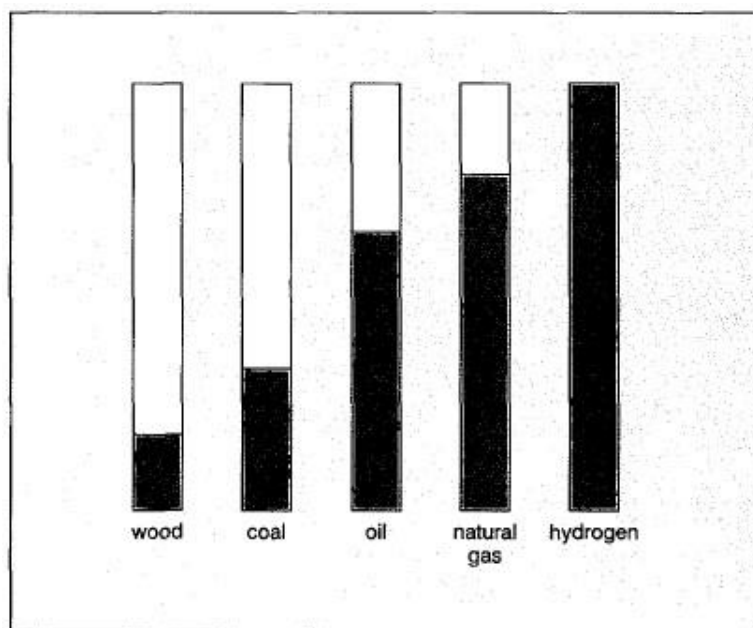


Figure.1.1: Various type of fuels with hydrogen contents (Cook, 2002).

1.2 Application of fuel cell

Nowadays, fuel cell has been applied in various industry scale. One of the example is the application of fuel cell in stationary power sources. The stationary power sources market is keep expanding since there is a great portable power generator such as hospital and residential area. Higher frameworks will give a great distributed essential power at the multi megawatt scale (Shao, 2016).

Besides, fuel cell also has been economized for specific applications, such as power storage supplier for electronic device. Furthermore, cell phones and computers also amongst useful application of flexible fuel cells systems with a power run from 10 to 100 W. Nevertheless, in view of security inspections for indoor use in which both low temperatures and low emissions such as carbon monoxide is the main concern, electrical gadgets for outdoor use such as wheelchairs and electric bike are more comfortable for convenient applications of SOFC (Shao, 2016).

1.3 Problem statements

SOFC component is divided by three parts which is anode, cathode and electrolyte. Each of the parts has their own priority and functions. The main priority of the cathode is the site where reduction of oxygen to form oxide ions occurs. Commonly, the cathode material used for IT-SOFC is LSCF perovskite material. The researchers found that the LSCF perovskite cathode material has a good electrochemical stability which is operated from 600 to 800°C. Besides, various researches had been conducted to compare the electrochemical performance of LSCF with other cathode materials. The best way to enhance the performance of perovskite cathode is by composing the cathode with another noble metal such as CuO. The CuO metal commonly had been studied by

among researchers in terms of chemical, physical and electrochemical properties. There are various ways to synthesize LSCF cathode material ranging from solid to liquid phase state. However, up to now there are no study had been done of synthesizing LSCF-CuO composite perovskite cathode material by using conventional solid-state method. Therefore, this research aim is to synthesize LSCF-CuO using conventional solid state to identify the effects of solid state routes towards physical, chemical and electrochemical properties.

1.4 Research objectives

The main objectives for this research is:

1. To investigate effects of the different preparation route towards physical and chemical properties of LSCF- CuO.
2. To resolve the electrochemical behaviour of optimized LSCF-CuO.

CHAPTER TWO

LITERATURE REVIEW

2.1 Solid oxide fuel cell (SOFC)

SOFC is one of the most widely used groups of fuel cell in engineering products. It converts the chemical energy from fuels such as hydrogen and methanol directly to electrical energy and thermal energy by using electrochemical reactions (Garcia et al., 2013, Shao et al., 2012, Bove and Ubertain, 2008, Irvine and Conno, 2013). A common SOFC single cell comprises of three essential segments which are anode, cathode and a solid electrolyte (Garcia et al., 2013, Bove and Ubertain, 2008, Shao, 2016). Basically, at anode, hydrogen fuel undergoes oxidation process by releasing electrons to external circuit while at cathode, oxygen gas undergoes reduction process by accepting electrons from external circuit and produce electricity. (Minh, 2004, Irvine and Conno, 2013). The electrode reactions are shown below:

Half reaction at cathode:



Half reaction at anode:



Overall reaction:



The advantages of SOFC such as high efficiency and very low levels of NO_x and SO_x emissions (Singhal, 2000, Irvine and Conno, 2013) make them dominant in various application including vehicles combustion engine and coal power generator (Singhal and Kendall, 2003, Garcia et al., 2013). Besides, SOFC also contributes high efficiency which about 50% compare with hydrocarbon fuels such as natural gas, liquefied petroleum gas and biogas (Chandran and Arjunan, 2015). These hydrocarbon fuels require high cost to generate electricity and they also are non-renewable energy which require a long time to regenerate it back. Furthermore, unlike other sources, SOFC does not has moving parts or any liquid electrolytes thus it requires low maintenance and highly consistent generates electricity (Chandran and Arjunan, 2015).

2.2 Intermediate solid oxide fuel cell (IT-SOFC)

SOFC is categorized by three type cells, lower temperature solid oxide fuel cell (LT-SOFC), intermediate temperature solid oxide fuel cell (IT-SOFC) and high temperature solid oxide fuel cell (HT-SOFC). IT-SOFC is a type of cell which is operated at temperature between 500 – 800°C (Garcia et al., 2013, Vázquez et al., 2015a, Vázquez et al., 2015b) compared to traditional SOFC which is at 850 – 1000°C (Shao, 2016).

The advantages of IT-SOFC includes reducing the cost of material preparations, cell fabrication and operation and reduces sintering of the porous electrode (Shao,2016). Furthermore, reduction of operating temperature to intermediate temperature can reduce degradation of fuel cell (Ismail et al., 2016, Vargas et al., 2012). However, reduction of operating temperature can reduce both electrolyte conductivity and kinetics (Vargas et al., 2012, Vázquez et al., 2015a, Vázquez et al., 2015b). Therefore, IT-SOFC needs to be studied in detail for selecting the suitable material to give a better performance of fuel cell.

2.3 Component in SOFC

SOFC single cell is consists of three main components, two porous electrode which is cathode and anode and electrolyte (Garcia et al., 2013, Shao, 2016, Bove and Ubertin, 2008). For better operation of SOFCs, those components should have chemical, mechanical and thermal stability under operative condition. Besides, fabrication conditions or method utilization are very important issues for the performance of SOFC (Koteswararao P et al., 2017). Figure. 2.1 shows the schematic of SOFC consists of anode, electrolyte and cathode.

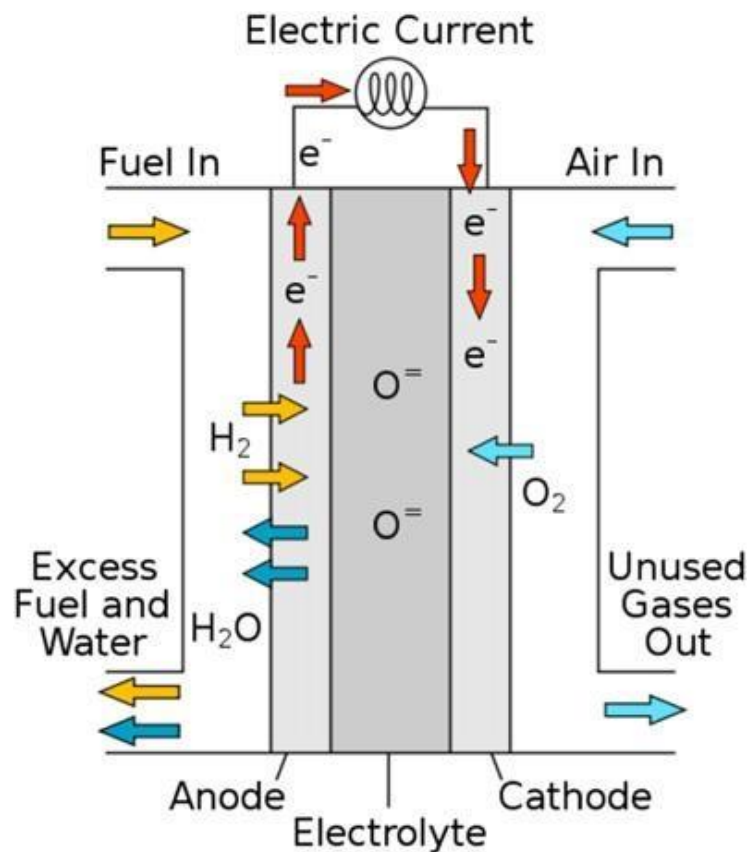


Figure.2.1: SOFC operation principle (Barelli et al., 2013).

Electrolyte is a region that separates the two porous cathode and anode. Generally, it is an oxygen ionic conductor (Fergus et al., 2016) and necessary in the fuel as they connect the cathode and anode for ionic transfer and prevent the mixing of electrode gas (Shao, 2016). It forms oxide ion carrier from cathode region to anode region which separates the oxidation and reduction reaction (Wincewicz and Cooper, 2005). The design requirements of electrolyte based on previous studies are chemically stable at high temperature, electronically insulating and uses inexpensive materials (Singhal, 2000, Maguire et al., 2000).

Anode is an electrode where it promotes the electrochemical oxidation such as hydrogen and ethanol (Fergus et al., 2016). It will give the trail for transport of the gas together with electrons and oxygen ions from electrolyte. In general, the anode materials for IT-SOFC are divided into many varieties, together with Ni-based cermet anodes, nickel-free metal-based anodes, and oxide-based anodes (Shao, 2016). The design requirements of anode based on the previous studies are highly electrolytic activity, stable in reducing environment and use inexpensive materials (Maguire et al., 2000, Singhal, 2000).

Cathode is where oxygen from air undergoes reduction through the electrochemical response (Fergus et al., 2016). The oxygen molecule from air dissociates into oxide ion and traverses the electrolyte. The formation of oxide ion is because of the electronic charges from the anode flow through outside the electrolyte and produces electrical power then accepted by oxygen molecule to form oxide ion (Haile, 2003). The design requirements of cathode based on the previous studies are thin and porous, high electronic conductivity and high ionic conductivity (Singhal, 2000, Maguire et al., 2000).

2.4 Cathode materials for IT-SOFC

Reducing the operating temperature of SOFC indirectly sacrifices the efficiency of conventional used cathode which is lanthanum strontium manganese (LSM). Thus, another perovskite commonly known as LSCF has been used as cathode for IT-SOFC owing to its advantages such as high ionic and electronic conductivity that leads to smaller polarization resistance. Besides, to achieve low polarization resistance, a higher porosity of cathode material will increase the diffusivity of oxygen molecules through the electrode surface is needed. The better conductivity of cathode material should reduce the polarization resistance and increase power density. Besides LSCF, there are various type of perovskite cathode material such as $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ (SSM) (Li et al., 2014) and $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Fe}_y\text{Co}_{1-y}\text{O}_{3-\delta}$ (BSCF) (Peña-Martínez et al., 2009).

LSCF is a ceramic powder that has potential as economical and high efficiency in producing purer O_2 (Haikal Mustafa et al., 2017). Besides, LSCF perovskite as cathode material shows a high thermal and chemical stability and high electrocatalytic activity in reducing environment (Marinha et al., 2011, Mostafavi et al., 2015). Furthermore, LSCF compounds has higher oxygen vacancies which allowing for ORR happens on the cathode surface (Muhammed Ali et al., 2018).

2.5 Method producing cathode material

Different methods of synthesis for preparation of LSCF powders have been applied such as solid- state reaction (Haikal Mustafa et al., 2017, da Côte et al., 2013), sol- gel (Ismail et al., 2016, Ghouse et al., 2010) , co- precipitation (Mostafavi et al., 2015), spray pyrolysis (Beckel et al., 2007), combustion (da Conceição et al., 2011),

microwave- assisted glycine nitrate (Muhammed Ali et al., 2018) and citrate hydrothermal method (Garcia et al., 2013).

Conventional solid- state method is a method that involves simple procedures and requires high calcination temperature to form a product (Haikal Mustafa et al., 2017, Mostafavi et al., 2015, da Côrte et al., 2013). This method is commonly used by researchers as it is simple and low cost to run (da Côrte et al., 2013). (Li et al., 1999) recommended that solid state reaction can produce huge amount of perovskite materials and easily to be handled compared with EDTA pyrolysis and modified citrate pyrolysis method. Besides, (Athayde et al., 2016) also stated that solid state reaction is a simple process which can give more perovskite powders with a few parameters involve.

There was various type of LSCF nanomaterials had been developed by several researchers. The performance of LSCF perovskite cathode material had been compared among researchers by years to find the best method and material that can be applied at intermediate temperature. Ghouse et al., (2010) prepared the LSCF powder by using sol-gel method. It was found that the crystallite sizes of LSCF powders about 15 to 23 nm. Another research from da Côrte et al., (2013) synthesized the LSCF powder by using conventional solid-state method. They found that the crystallite sizes increased 9.6 to 26 nm when calcined from 700 to 1000°C which the range was too far compared with sol-gel metho. Furthermore, Garcia et al., (2013) was proposed another method prepared LSCF powder by using citrate- hydrothermal synthesis. As result, the crystallite size obtained 53 nm at 900°C with lowest R_p was 0.34 $\Omega.cm^2$ at 750°C. However, the crystallite size was still bigger than the result from solid state and sol- gel method which means this method was not recommended to apply at intermediate temperature.

CHAPTER THREE

RESEARCH METHODOLOGY

3.1 Flow Chart Process

LSCF-CuO perovskite material were synthesized by solid- state route as illustrated by the flow chart in Figure. 3.1. Each sequence need to be conducted properly and accurately as the experiment was conducted at high temperature which was 600°C, 700°C, 800°C and 900°C.

3.2 Preparation of Solid- State Method

The LSCF was synthesized by conventional solid state method. The starting materials, Lanthanum nitrate hexahydrate ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, MERCK®, 99%), Strontium nitrate ($\text{Sr}(\text{NO}_3)_2$, Grade AR, Friendemann Schimdt Chemical, 99%), Cobalt nitrate-hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, ChemAR®, 99%), Ferum nitrate-nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, ChemPur®, 99%), and Ethyl alcohol ($\text{C}_2\text{H}_5\text{OH}$, R&M Chemicals, 95% V/V denatured) were mixed together and crushed about 15 min then transferred into a beaker. The mixture was heated at 100°C for 6 h for removing excess nitrate and ethanol. The mixture was transferred into the close lid crucible and be calcined at desired temperature 600°C, 700°C, 800°C and 900°C.

At the same time, copper oxide (CuO) was prepared by crushing the copper nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, R&M Chemicals, 99%) into small pieces. The ethyl alcohol was added and mix with the mixture and crushed about 15 min. The mixture then was transferred into the close lid crucible and be calcined at desired temperature 600°C, 700°C, 800°C and 900°C.

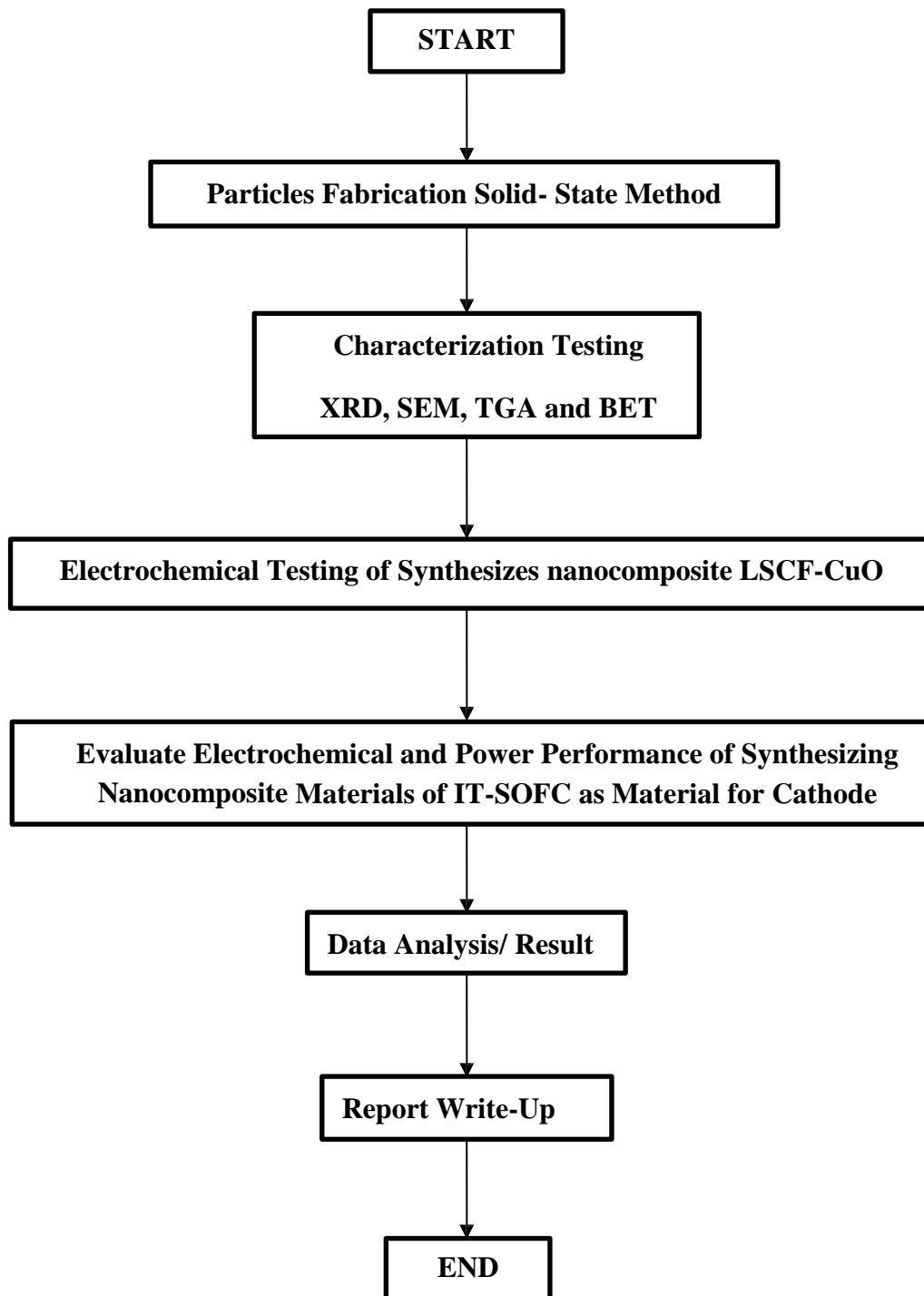


Figure. 3.1: Synthesizing of LSCF-CuO perovskite material process flow chart

The resulted LSFC and CuO powders were crushed well together with weight ratio 1:1 to get LSCF-CuO type cathode. The mixture sample then be calcined again at the same temperature for 6 h. This method was to ensure that the formation of composite LSCF-CuO will be formed well after calcination.

3.3 Characterization Analysis

3.3.1 XRD Analysis

The calcined powder was characterized by X-ray diffraction (XRD) by using Xpert-Highscore plus with Cu K α radiation. The diffraction patterns obtained within range from 10 θ to 90 θ for the entire sample. The raw data of XRD obtained had been done by data treatment before analysing the phase and composition in the sample.

3.3.2 SEM and EDX Analysis

The calcined LSCF-CuO powder was been analysed by using Scanning Electron Microscopy (SEM) using Quanta FEG 650. The acceleration voltage was 15-20 kV, using backscattering electron. The behaviour of the microstructure of the sample was defined at 500 nm or 5 μ m. The average weight sample used is around 0.2 g per sample. The sample was observed at 500 nm or 5 μ m to define the particle distribution size of the sample and the overall cross-section image for LSCF-CuO. The average particle size was recorded from random particle for each sample. Besides, the sample also be analysed by Energy-Dispersive X-ray (EDX) analysis by using Quanta FEG 650 on behaviour of microstructure at 5 μ m or 500 nm. This analysis to determine the element that presence in the sample to support the XRD analysis data.

3.3.3 TGA Analysis

The precursor LSCF for solid state method was analysed by using a TGA analyser model Pelkin Elmer STA 600, from room temperature to 900°C with air flowrate of 50 cm³/min and heating rate of 5°C/min in air. The weight loss of the sample will be recorded during the process in exothermic process.

3.3.4 BET Analysis

Brunauer–Emmett–Teller (BET) is an analysis to measure the specific surface area and total pores volume of the LSCF-CuO. The sample was being taken with average 0.2 g per sample. BET analysis will calculate the porosity volume based on the SEM analysis that had shown the particle size image and cross- sectional area of LSCF-CuO sample.

3.3.5 Electrochemical Impedance Spectroscopy

The electrochemical performance of LSCF-CuO and SDC symmetrical cell was analyzed in EIS furnace system (model ZIVE SP2). The symmetrical cell was attached by silver wires and the surface area of the cathode was been recorded which was 0.95 cm². The EIS was measured at open circuit air with frequency range from 0.1 Hz to 1 MHz with signal amplitude of 10 mV and 5 mV for each sample for temperature between 600°C to 800°C.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Chemical and physical characterization of LSCF-CuO nanoparticles

4.1.1 XRD analysis

Figure. 4.1. showed the X-ray diffraction patterns of LSCF-CuO powders calcined between 600°C and 900°C. The results found that the formed of single phase of perovskite LSCF-CuO at the temperature 800°C and above. However, some unknown peaks had been identified between 10o and 30o degree at temperature below than 800°C. The data represent the small amount of secondary phases which was La_2O_3 or SrO_3 (Darbandi and Hahn, 2009) based on the cell parameter of JCPDS No. (5-602). The LSCF and LSCF-CuO peak patterns had been compared as shown in Figure. 4.2. The peak patterns of LSCF and CuO had been identified and suits well with the cell parameter of JCPDS No. (37-1493) and the data from (Lu et al., 2012). Besides, it shown that when the calcination temperature increased, the intensity of LSCF-CuO perovskite also increased indicates better crystallization and greater crystal size.

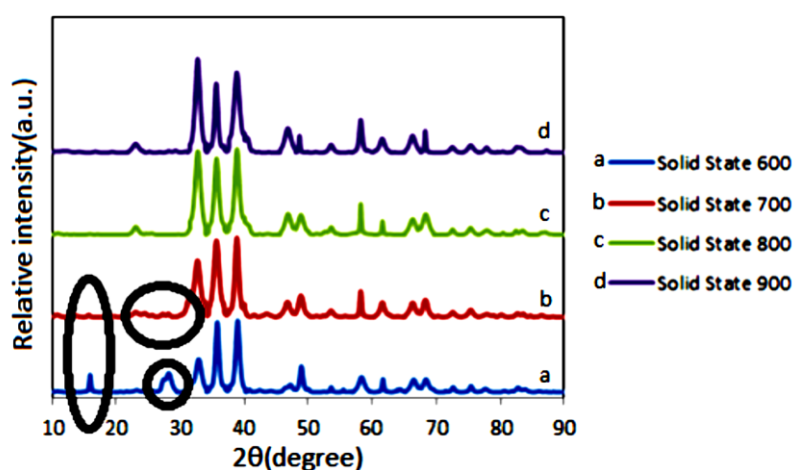


Figure. 4.1: XRD peak patterns with different temperature

From Figure. 4.1, the optimum temperature for perovskite LSCF-CuO for solid state route was 800°C. It was indicated that the addition of CuO was able to reduce the temperature from 900°C to 800°C as the LSCF optimum temperature was 900°C and above. Besides, the addition of CuO can reduce the activation energy in the formation of perovskite LSCF. Furthermore, CuO was able to form a single-phase perovskite with LSCF at specified temperature. Thus, LSCF-CuO powder will give better result for the next analysis such as SEM and TGA analysis.

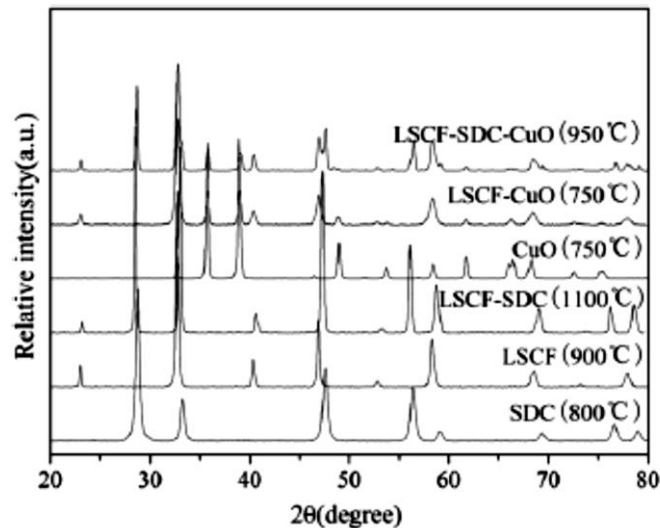
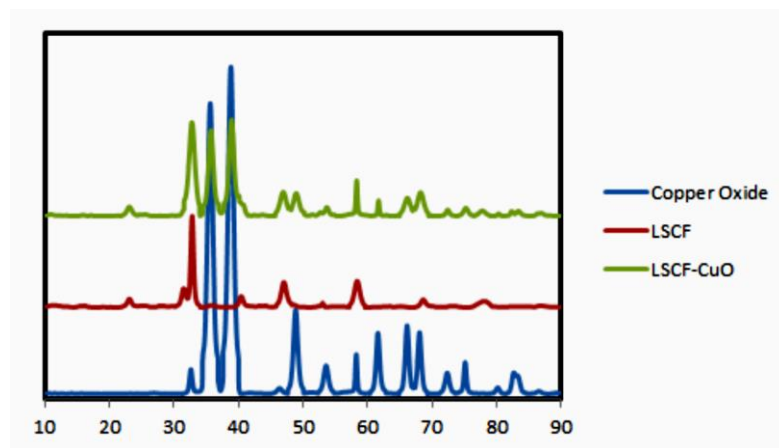


Figure. 4.2: XRD analysis identified phase

4.1.2 EDX analysis

EDX analysis was conducted to identify the presence of element in the samples. Figure. 4.3 shows the presence of each elements in the sample with different temperatures. It was found that there were no impurities found in the sample and the sample was highly pure with La, Sr, Co, Fe and CuO elements. This was because these elements did not perform single phase perovskite completely due to insufficient calcination temperature.

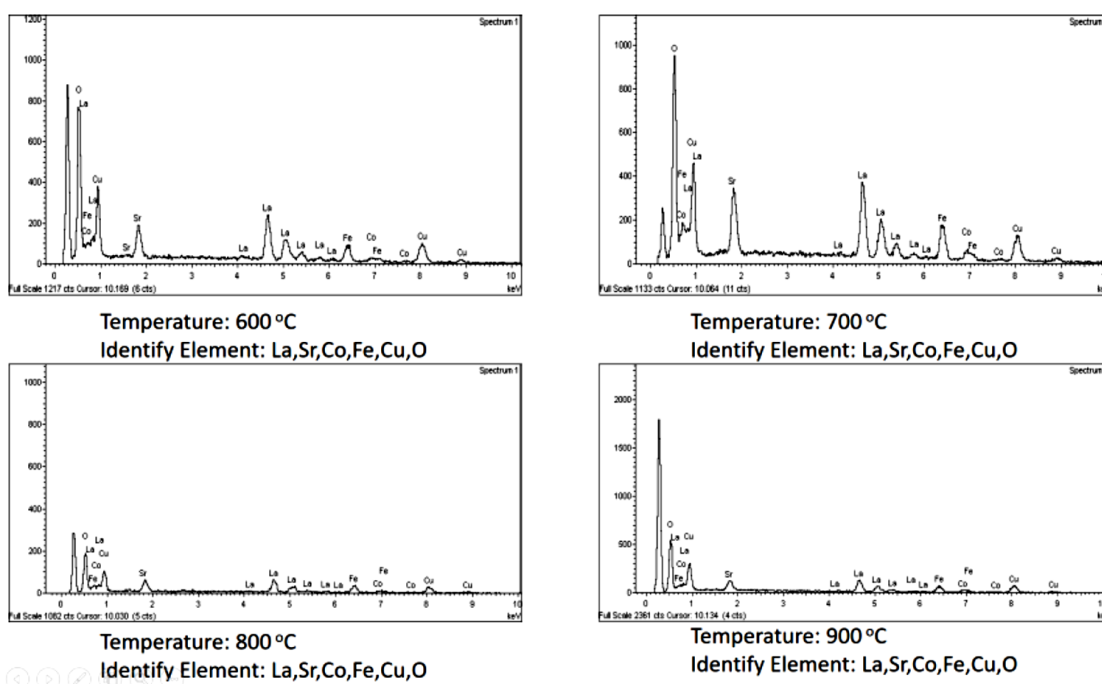


Figure. 4.3: EDX analysis for solid state route

4.1.3 SEM analysis

The LSCF-CuO sample was conducted under SEM analysis to analyse the microstructure of LSCF-CuO cathode material. Figure. 4.4 shows the microstructure of LSCF-CuO cathode material under 5 μm and 500 nm magnifications. These samples showed that the increasing of calcination temperature would increase the specific surface area of the structure, but the polarization resistance would be increased.

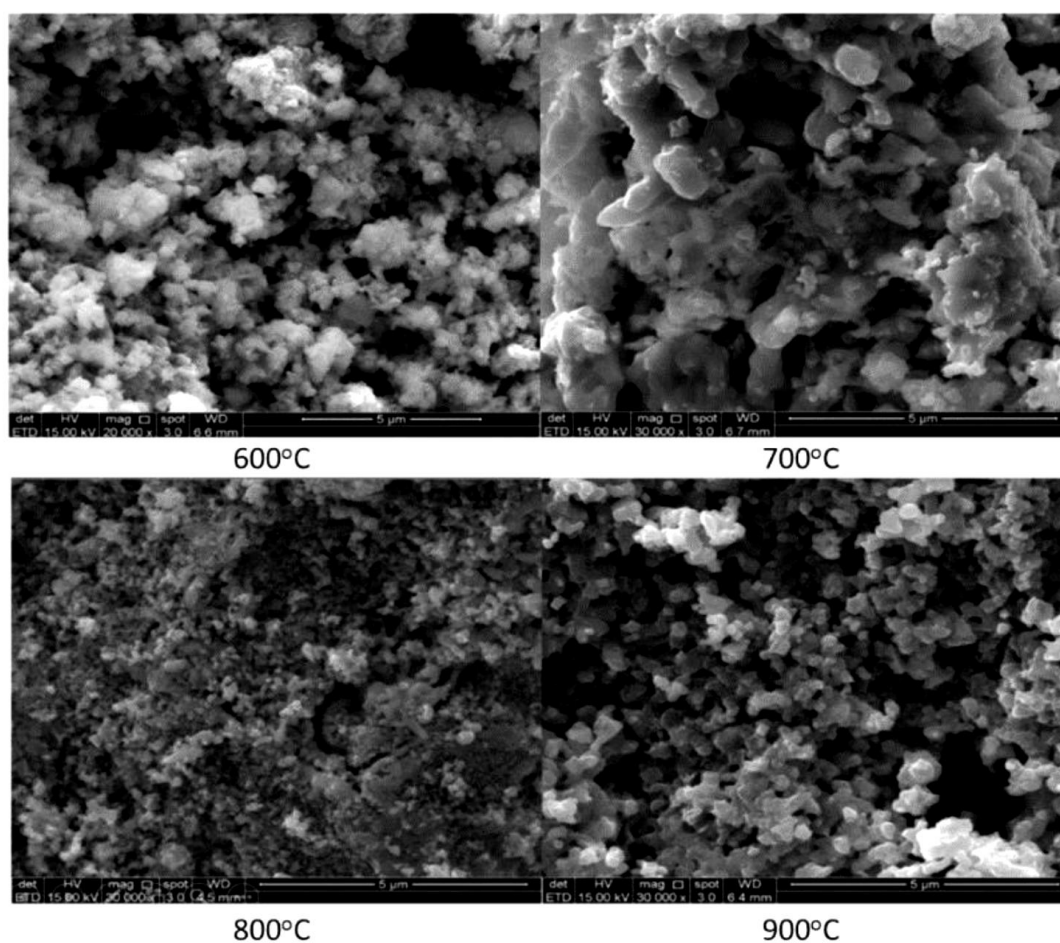


Figure. 4.4: SEM image of the LSCF-CuO powder calcined at 600°C, 700°C, 800°C and 900°C at 5 μm magnification

Figure. 4.5 showed that the average particle size of microstructure of single phase perovskite LSCF-CuO cathode material. Based on the figure, the particle size increased as the temperature increased as increasing sintering temperature lead the particle in bulk form thus the specific surface area and total pore volume were decreased. This could be proven by conducting the BET analysis to support this result. Besides, the increasing of particle size will lead the polarization resistance also increased due to particle size increased.

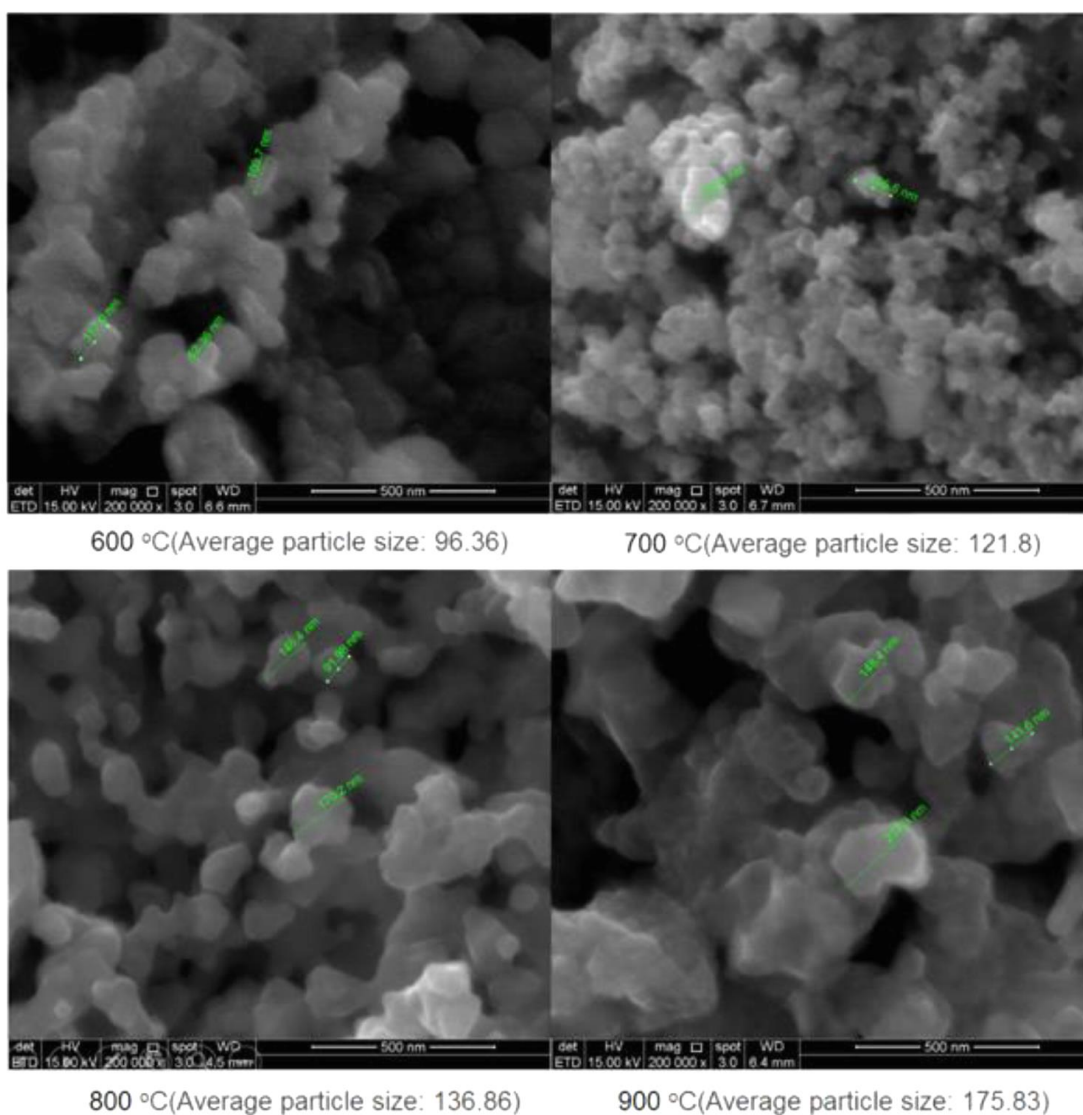


Figure. 4.5: SEM image of the LSCF-CuO powder calcined at 600°C, 700°C, 800°C and 900°C at 500 nm magnification

4.1.4 Thermogravimetric Analysis (TGA)

Figure. 4.6 showed TGA curve for weight loss of LSCF precursor against temperature for solid state route. Thermal decomposition was divided into three phases. The first phase occurred in which from 30°C to 400°C assigned to the loss of adsorbed water, decomposition of nitrate and metal-citrate complexes. The second phase indicated that the weight loss as nitrate decomposition until reach up to 500°C. This phase happened in which the formation of single phase perovskite LSCF began. The final phase indicated that the small weight of the sample due to formation of oxygen vacancies occurred then the sample started to stabilize at approximately 650°C. Thus, the overall weight loss from the analysis was about 38.5 w.t%.

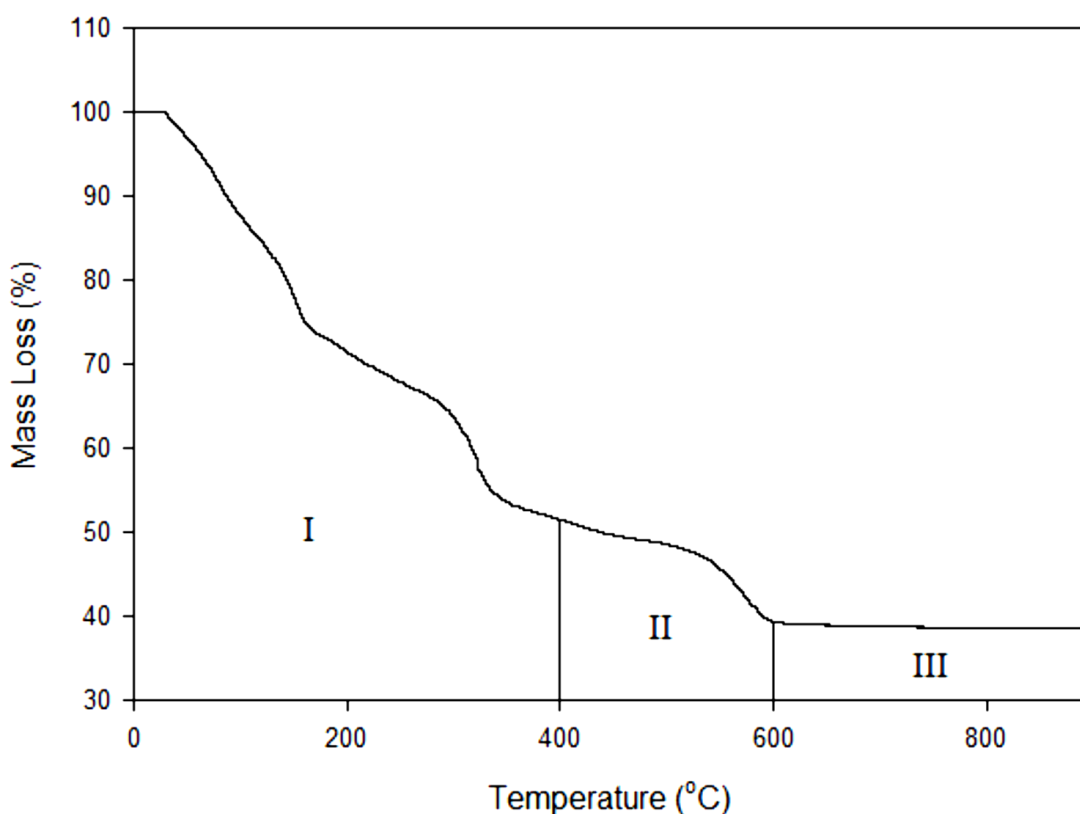


Figure. 4.6: TGA curves of the LSCF precursor for solid state route

4.1.5 BET analysis

The specific area and pore volume of LSCF microstructure from SEM analysis had been calculated by using BET analysis. This analysis was determined the specific surface area and pore volume of single phase perovskite LSCF-CuO material at different temperature. Table 4.1 showed the value of specific surface area and total pores volume for solid-state route.

Table 4.1: BET analysis for solid state route at various temperature

Sample (LSCF-CuO)	Specific surface area (m ² /g)	Total pores volume (cm ³ /g)
Solid State 600°C	13.33	0.0187
Solid State 700°C	4.55	0.0113
Solid State 800°C	3.22	0.0123
Solid State 900°C	1.47	0.0043

Based on the Table 4.1, the solid state at temperature 900°C had a lowest specific surface area and total pores volume compared with other temperatures. Besides, when the calcination temperature increased, the particle size also increased resulting of lower porosity.

4.2 Electrochemical characterization

The symmetrical cell of LSCF-CuO and SDC by configuration LSCF-CuO|SDC|LSCF-CuO had been conducted by using Electrochemical Impedance Spectroscopy (EIS). SEM image of cross section LSCF cathode layer on SDC electrolyte layer was shown in Figure. 4.7. The figure showed the LSCF electrode was attached well on the SDC electrolyte after been sintered at 1300°C. There were no other side reactions

occurred at interface LSCF-CuO and SDC layer after been sintered. Besides, the image shows there is no crack or peel-off between interface LSCF-CuO and SDC layers.

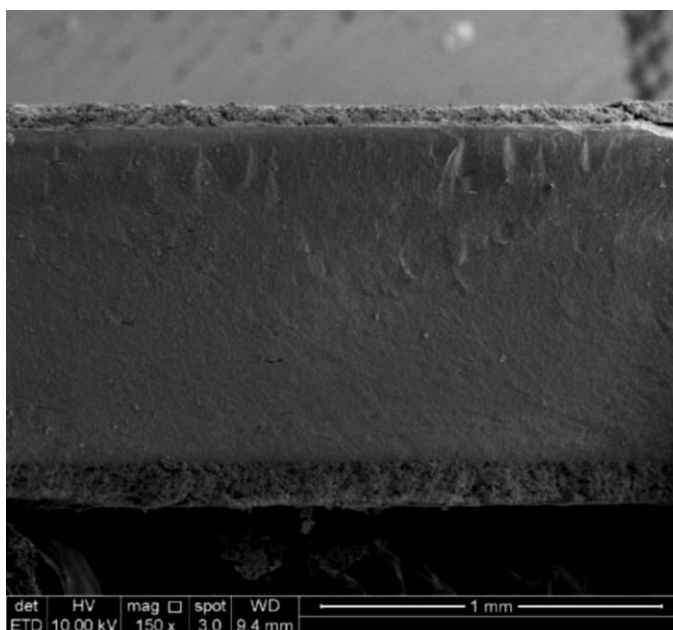


Figure. 4.7: Cross section SEM image of LSCF-CuO on SDC electrolyte layer



Figure. 4.8: Schematic diagram of equivalent fitting in ZMAN software

Figure. 4.8 shows the equivalent circuit that had been generated by ZMAN software. The parameters from the circuit were determined as L_s , R_s , R_1 , Q_1 referred to the inductance that allocated to the silver current-voltage probes of the EIS equipment. R_s is referring to electrolyte resistance and silver wire resistance (R_Ω). R_1 and Q_1 referred to low frequency arc low where R denoted as resistance at the frequency region and Q denoted as arc resistance constant phase element (CPE) at the frequency region. The value of capacitance

will be obtained based on the equation (4.1) to identify the resistance of the arc of polarization resistance of the cathode.

$$C = y^{\frac{1}{n}}(R^{\frac{1}{n}-1}) \quad (4.1)$$

Where:

$C = \text{Capacitance (F)}$

$y = Qy$

$n = Qa$

$R = \text{Resistance}$

Figure. 4.9 shows the impedance spectra of LSCF-CuO cathode sintering at different temperatures. The resistance polarization, R_p of the LSCF-CuO cathode at 800°C is about 0.41 $\Omega \cdot \text{cm}^2$ which was the smallest value compared with other temperatures. R_p for the LSCF-CuO cathodes, 600°C, 650°C, 700°C and 750°C were 29.53 $\Omega \cdot \text{cm}^2$, 9.31 $\Omega \cdot \text{cm}^2$, 3.14 $\Omega \cdot \text{cm}^2$ and 1.13 $\Omega \cdot \text{cm}^2$ respectively. It showed that increasing the sintering temperature would reduce the porosity and reaction area of the LSCF-CuO cathode, resulting in higher polarization resistance. On the other hand, decreasing the sintering temperature also increase more porosity, reaction area of the cathode, resulting in lower polarization resistance (Leng et al., 2008, Benel et al., 2013). Besides, addition of CuO can reduce the optimal temperature of the cathode from 900°C to 800°C showed that it had improved the properties of perovskite LSCF (Lu et al., 2012).

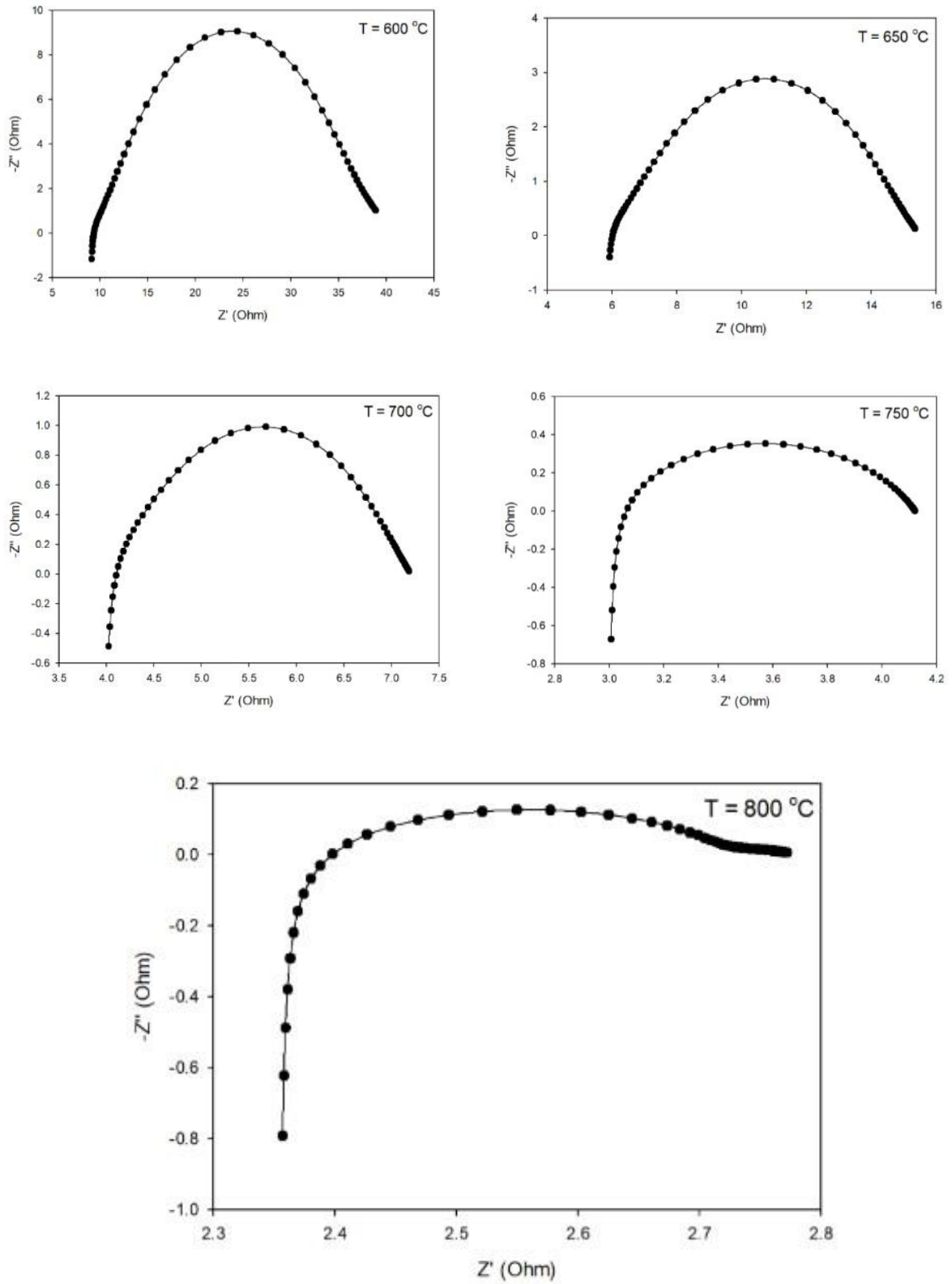


Figure. 4.9: Impedance spectra of LSCF-CuO cathodes at various calcination temperature