Studies on the Densification and Grain Growth Mechanisms of Polycrystalline Ceramic Based on $LaYO_3$

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APPROVAL AND DECLARATION SHEET

This thesis titled Studies on the Densification and Grain Growth Mechanisms of Polycrystalline Ceramic Based on $LaYO_3$ was prepared and submitted by Najwa Shafiqa Binti Anwar (Matric Number: 1330410933) and has been found satisfactory in terms of scope, quality and presentation as partial fulfillment of the requirement for the award of degree of Master of Science (Materials Engineering) in Universiti Malaysia Perlis (UniMAP).

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LIST OF ABBREVIATIONS

La	Lanthanum
Y	Yttrium
O_2	Oxygen
H_2	Hydrogen
La_2O_3	Lanthanum Oxide
Y_2O_3	Yttrium Oxide
$LaYO_3$	Lanthanum Yttrium Oxide
SOFC	Solid Oxide Fuel Cell
ABO_3	Perovskite structure
XRD	X-ray Diffraction
SEM	Scanning Electron Microscope
IS	Impedance Spectroscopy
Pt	Platinum
Ni	Nickel
Cu	Copper
Zn	Zinc
Ag	Silver
Mg	Magnesium
Nb	Niobium
CO	Carbon monoxide
CO_2	Carbon dioxide
YSZ	Yttria Stabilized Zirconia
LSGM	Lanthanum Gallate, Strontium and Magnesium doped
SDC	Samarium Doped Ceria
ScSZ	Scandia Stabilized Zirconia
TSS	Two-step Sintering
RC	Resistance-capacitance

LIST OF SYMBOLS

2θ	Diffraction angle
λ	wavelength
%	percentage
°C	degree Celsius
μ	micro
tan δ	dielectric loss
σ	conductivity
Z	impedance
Y	conductivity
ε	permittivity
M	Electric Modulus

LIST OF EQUATIONS

KAJIAN MENGENAI PENUMPATAN DAN MEKANISMA TUMBESARAN IRA BAGI SERAMIK POLIHABLUR BERDASARKAN $LaYO_3$

ABSTRAK

$LaYO_3$ adalah seramik polihabluran dengan struktur jenis oksida perovskit. $LaYO_3$ disintesis menggunakan kaedah sintesis keadaan pepejal. Pada mulanya, sampel dipanaskan antara 1200 °C hingga 1500 °C selama 10 jam dan perlahan-lahan disejukkan dalam udara. Kehadiran fasa kedua iaitu otorombik menunjukkan sifat polimorfisme $LaYO_3$. Fasa struktur monoklinik tulen telah berjaya disintesis selepas dipanaskan pada 1500 °C selama 10 jam dan lindap-kejut dalam cecair nitrogen. Selepas itu, serbuk $LaYO_3$ monoklinik tulen telah dipelet menggunakan penekanan sestatik dan telah difabrikasi oleh kaedah pensinteran dua langkah. Bagi pensinteran langkah pertama (T_1), pelet telah dipanaskan pada 1300 °C selama 1 minit dan kemudian dilindap-kejut ke dalam cecair nitrogen. Pelet kemudiannya dipanaskan pada suhu yang agak rendah antara 1000 °C hingga 1250 °C dan ditandakan sebagai T_2 selama 15 jam masa pegangan. Dengan meningkatkan T_2, ketumpatan relatif meningkat daripada ~87% kepada ~95%. Peratusan pengecutan juga meningkat secara linear. Mikrostruktur menunjukkan keseragaman. Saiz butiran adalah berkadar terus dengan ketumpatan relatif. Cole-cole plot daripada impedans menunjukkan satu separuh bulatan menyumbang kepada fenomena pukal sampel $LaYO_3$ yang telah disinter. Kekonduksian sampel yang disinter antara 1000 °C hingga 1200 °C berada dalam lingkungan 2 hingga 3×10^{-5} S/cm dan tenaga pengaktifan adalah kira-kira ~0.4 eV. Sementara itu, sampel yang disinter pada 1250 °C menunjukkan kekonduksian yang tinggi iaitu 8.41×10^{-3} S/cm dengan 1.4 eV kerana mempunyai kesan sempadan ira di dalam sampel. Oleh itu, peningkatan suhu T_2 menunjukkan pengalir ionik yang tinggi dengan tingkah laku elektrik yang insulatif menyumbang kepada pembentukan pertumbuhan ira yang lebih besar.

STUDIES ON THE DENSIFICATION AND GRAIN GROWTH MECHANISMS OF POLYCRYSTALLINE CERAMIC BASED ON $LaYO_3$

ABSTRACT

$LaYO_3$ is a polycrystalline ceramic with the perovskite type oxide structure. $LaYO_3$ was prepared using solid state synthesis method. Initially, the sample was heated between 1200 °C to 1500 °C for 10 hours and slowly cooled in air. The existence of secondary phases that belongs to orthorhombic shows the polymorphism properties of $LaYO_3$. Pure phase monoclinic structure was successfully synthesized after heated at 1500 °C for 10 hours and rapidly cooled in liquid nitrogen. Then, the pure monoclinic $LaYO_3$ powder was pelletized using cold isostatic pressing and been fabricated by two-step sintering method. For the first-step sintering (T_1), pellets were heated at 1300 °C for 1 minute and then quenched into liquid nitrogen. The pellets were then reheated at the relatively lower temperature between 1000 °C to 1250 °C and denoted as T_2 for 15 hours holding time. By increasing T_2, the relative density increased from ~87 % to ~95 %. Percentage of shrinkage also linearly increased within error. Microstructural analysis shows homogenous microstructure. The grain size was directly proportional to the relative density. Cole-cole plot from complex impedance of sintered $LaYO_3$ shows one semicircle contribute to the bulk phenomenon responsible. The conductivity for samples sintered between 1000 °C to 1200 °C were in the range of 2 to 3×10^{-5} S/cm and the activation energy is about ~0.4 eV. Meanwhile, sample sintered at 1250 °C shows high conductivity that is 8.41×10^{-3} S/cm with 1.4 eV because phenomenon responsible in the sample have grain boundary effect. Therefore, increasing T_2 temperature shows high ionic conductor with electrically insulative behaviour that contribute by larger formation of grain growth.

CHAPTER 1

INTRODUCTION

1.1 Background

The ever-increasing energy demand triggered by the deficiency of fossil fuels has led us to seek alternative power sources. These fossil fuels were formed by natural processes of buried organisms, which are non-renewable resources, and it raises serious environmental concerns and economic effects (Abas *et al*., 2015). Fuel cell is the most attractive alternative power source because it can produce clean and efficient electricity to meet the future challenges (Afif *et al.,* 2016; Kirubakaran *et al*., 2009; Radenahmad *et al.,* 2016).

Fuel cells are considered an excellent alternative energy resource from the environmental point of view because fuel cells are quiet and produce negligible emissions of pollutants. Furthermore, the efficiency ranges from 40 to 60% depending on the type and design of fuel cells because different types of fuel cells have varied efficiencies. Moreover, the primary fuel source for the fuel cell is hydrogen that can be

obtained from natural gas, coal gas, methanol, and other fuels containing hydrocarbons (Stambouli & Traversa, 2002).

Initially, fuel cells were used in closed environments such as space technology and submarines, where cost is not an issue. NASA began using fuel cells in the late 1950s and continues to do so today. Fuel cells were used in the Apollo and Gemini spacecrafts, and now in space shuttles. Currently, there are many uses for fuel cells, including:

I. Transportation: All the major automakers are working to commercialize a fuel-cell car. Fuel cells are powering buses, boats, trains, planes, and scooters, even bicycles.
II. Stationary: More than 2500 fuel cell systems have been installed all over the world − in hospitals, nursing homes, hotels, office buildings, schools, utility power plants, and an airport terminal, providing primary power or backup.
III. Residential: Fuel cells are ideal for power generation, either connected to the electric grid to provide supplemental power and backup assurance for critical areas, or installed as a grid-independent generator for on-site service in areas that are inaccessible by power lines. The waste heat from a fuel cell can be used to provide hot water or space heating for a home.
IV. Portable Power: Miniature fuel cells for cellular phones, laptop computers and lightweight electronics are on their way to market. These small fuel cells generally run on methanol, an inexpensive wood alcohol also used in windshield wiper fluid.
V. Landfill/Wastewater Treatment: Wastewater treatment plants and landfills are using fuel cells to convert the methane gas they produce into electricity. (Garche, 2013; Giddey *et al.,* 2012; Gong, 2005; Laosiripojana *et al*., 2009; Liu *et al.,* 2016; Minh, 2004; Serincan, 2016).

Fuel cell is a device that converts chemical energy into electrical energy similar to battery but slightly differs in its electrochemical process. The output from a fuel cell is a stable direct current (DC) of about one-volt. Fuel such as natural gas (CH_4) or methanol (CH_3OH) and oxygen (from air) are required to operate fuel cell.

The fuel gas is fed into the fuel electrode (porous anode in a solid state) where the hydrogen is oxidized ($H_2 \rightarrow 2H^+ + 2e^-$). Oxygen in air is fed into the oxidant electrode (porous cathode in a solid form) where it is reduced ($O_2 + 2e^- \rightarrow O^{2-}$). Ions of hydrogen or oxygen are conducted by an electrolyte layer (liquid or dense solid) which is sandwiched between the two electrodes. From proton (hydrogen ion, H^+) conducting electrolyte fuel cells, water is formed at the cathode/electrolyte side according to the equation;

$$2H^+ + ½O_2 + 2e^- \rightarrow H_2O \quad (1.1)$$

For oxygen ion (O^{2-}) conducting electrolyte fuel cells, water is formed at the anode/electrolyte side;

$$H_2 + O^{2-} \rightarrow H_2O + 2e \quad (1.2)$$

The overall reaction in the fuel cell is;

$$H_2 + ½O_2 \rightarrow H_2O \quad (1.3)$$

Fuel cells have five different types which are Alkaline Fuel Cell (AFC), Solid Polymer Fuel Cell (SPFC) and Phosphoric Acid Fuel Cell (PAFC) that are operated at relatively low temperatures (< 200 °C). Furthermore, Molten Carbonate Fuel Cell (MCFC) is performed at about 650 °C and Solid Oxide Fuel Cell (SOFC) operates between 650 and 1000 °C. Table 1.1 shows the main characteristics and applications of

each fuel cell, in terms of operating temperature. For a particular fuel cell, the application fields are based on its properties and performance. Based on this comparison, clearly the overall properties of SOFC can be superior to other types of fuel cell if their high operating temperature can be reduced (Stambouli & Traversa, 2002). To realize this possibility, the new electrolyte materials with higher ionic conduction than the conventional YSZ are required (Jacobson, 2010).

Table 1.1: Type of fuel cell and their characteristics and applications (Steele & Heinzel, 2001)

Type	T_{op} (°C)	Characteristics	Applications
AFC	50 ~ 100	• High power density (A/m^2) • High Pt loadings • Pure O_2, no CO_2, no CO • Very expensive	• Space vehicles • Automobile
SPFC	50 ~ 100	• Easy design • High Pt loading • Pure H_2 (>99.99%), no CO • Moderate current density	• Space and military • Automobile
PAFC	~ 200	• Commercially successful • Available in a few to 300 kW • Tolerant to CO_2 but low CO • High reliability • High cost ($2000 to $3000 per kW)	• Electricity-heat cogeneration • Power in remote areas (near natural gas supply lines) • Automobile
MCFC	600 ~ 700	• Corrosive • Internal natural gas-reforming • Need CO_2 for cathode • CO is usable fuel • No Pt but Ni catalyst • High-grade heat available	• Medium to large (2 kW ~ 2 MW) cogeneration power systems • Load levellers in electric utilities • Not suitable for small power plants or for transportation use
SOFC	~ 1000	• Very high temperature • Simple in design • Internal natural gas-reforming • No catalyst needed • CO is usable fuel • Cell are difficult to produce • High-grade heat available	• Cogeneration plant • Potential use in transportation sector if the operating temperature can be reduced

1.1.1 Solid Oxide Fuel Cell (SOFC)

Solid oxide fuel cell (SOFC) is an all-solid device that operated between 600 ~ 1000 °C. In contrast to other types of fuel cells, where the electrochemical reactions occur at the gas-liquid-solid three-phase-zone, reactions in SOFC occur at the gas-solid two-phase contact. The corrosive electrolyte is no longer a problem in SOFC, as two porous ceramic electrodes are separated by a dense oxide-ion conducting ceramic electrolyte. Fuel (H_2 or CO) is fed to the anode and reacts with oxygen ions to form water (or CO_2) while releasing electrons to the external circuits. On the other hand, oxygen is fed to the cathode and accepts electrons from the external circuit to form oxygen ions. Electrons flow from the anode through the external circuit to the cathode (Badwal *et al.*, 2014; Mahato *et al.*, 2015; Timurkutluk *et al.*, 2016).

Figure 1.1 shows the operating principles of SOFC with flow directions for each species and with captions for each cell component. The focus of this research study is on electrolyte materials and hence only oxygen-ion conducting SOFC will be reviewed in the next chapter.

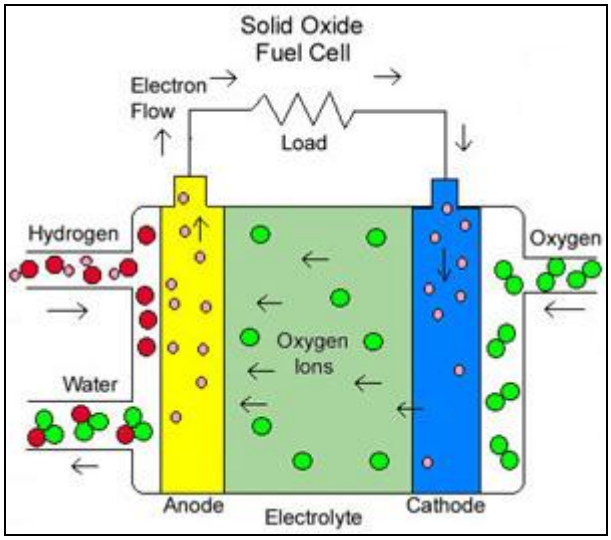

Figure 1.1: Operating principle of SOFC and its components (Kawamoto, 2008).

1.1.2 Basic components of SOFCs

There are specific material requirements and criteria that need to be satisfied before they can be considered as cathode, anode or electrolyte for SOFC application. These requirements are necessary to ensure the electrochemical reactions that occur at high temperatures will be at the most optimum condition, efficient and safe. These are criteria for cathode, anode and electrolyte (Badwal *et al*., 2014; Stambouli & Traversa, 2002; Yokokawa *et al*., 2001; Yamamoto, 2000)

i. Cathode

The criteria for the cathode material are:

(1) High electrocatalytic activity for oxygen reduction

(2) High electronic conductivity

(3) Stability in the oxidizing atmosphere and at high-temperature

(4) Thermal expansion compatible with other cell components

(5) Porous for efficient oxygen transport

ii. Anode

For the anode material, the criteria are:

(1) Effective oxidation catalysis

(2) High electronic conductivity

(3) Stability in the reducing anodic environment and at high-temperature

(4) Thermal expansion compatible with other cell components

(5) Porous for easy fuel transport

(6) Tolerance to sulphur contaminants and hydrocarbon fuels

iii. Electrolyte

Criteria for electrolyte materials are:

(1) High oxygen ion conductivity and negligible electronic conductivity

(2) High stability under both oxidizing and reducing atmospheres

(3) Stability at high-temperature

(4) Thermal expansion compatibility with electrode materials

(5) High density to prevent fuel transport to the cathode

Table 2.1 summarizes the most important material requirements for each component of SOFC in terms of electrical conductivity, stability, compatibility, and porosity (Minh & Takahashi, 1995).

Table 2.1: Requirements for SOFC components (Minh & Takahashi, 1995)

Component	Requirements				
	Conductivity	Stability	Compatibility	Porosity	Thermal expansion
Anode	High electrical conductivity	Chemical, phase, morphological, and dimensional stability in fuel environment	No undesirable chemical interactions or interdiffusion with adjoining cell components	Porous	Thermal expansion match with adjoining components
Electrolyte	High ionic conductivity. Negligible electrical conductivity	Chemical, phase, morphological, and dimensional stability in fuel and oxidant environment	No damaging chemical interactions or interdiffusion with adjoining cell components	Fully dense	Thermal expansion match with adjoining components
Cathode	High electrical conductivity	Chemical, phase, morphological, and dimensional stability in oxidant environment	No damaging chemical interactions or interdiffusion with adjoining cell components	Porous	Thermal expansion match with adjoining components
Interconnect	High ionic conductivity. Negligible electrical conductivity	Chemical, phase, morphological, and dimensional stability in fuel and oxidant environment	No damaging chemical interactions or interdiffusion with adjoining cell components	Fully dense	Thermal expansion match with adjoining components

1.2 Problem Statement

Nowadays, fuel cell is attracting much interest as power generation system with high energy conversion efficiency and almost no emission of air pollutant. Among the various types of fuel cell, SOFCs have many advantages such as variety of fuel, long life and environmental friendly system. Therefore, the development of SOFC is highly important. The conventional SOFCs are operated at high temperature about ~1000 °C and special alloy required for encapsulation. The drawbacks using high temperature are high operation cost, costly maintenance, phase stability of the materials and its compatibility was affected. So, the development of SOFCs at relatively lower operating temperature (< 1000 °C) require suitable electrolytes materials with reasonable high conductivity as an alternative for YSZ.

Conventional solid electrolyte, yttria stabilized zirconia (YSZ) have very low conductivity about 4.52×10^{-6} S/cm and it formed resistive layers between electrodes. Strontium magnesium doped lanthanum gallate (LSGM) was used as typical electrolyte has high ionic conductivity 1.7×10^{-1} S/cm but the limitation of LSGM is to get phase pure because existence of secondary phases. $LaYO_3$ has been proposed as a potential electrolyte because it shows ion conduction with oxide ion transport number is unity with conductivity is 5.8×10^{-4} S/cm at 1000 °C and activation energy are 1.22 eV (calculated) and 1.3 eV (experimental). Therefore, further improvements are required to enable $LaYO_3$ to become suitable electrolyte at < 1000 °C operation temperature.