A study on ionic conductivity and SOFC performance of doped CeO₂ ceramics under millimeter-wave irradiation heating

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Abstract

Solid oxide fuel cell (SOFC) is a promising candidate for alternative energy source due to its high efficiency that meets the global energy needs and at the same time has less adverse environment impact. However, frequently addressed important issues in SOFC are its durability and high cost due to high operation temperature. Therefore, the ultimate target is the development of high efficiency SOFC that operates at low temperature.

Interest in applying microwaves (MW) as heating source to replace conventional heating is growing. Unique characteristics of MW that does not exist in other heating methods such as rapid, volumetric, and selective heating have attracted researchers to exploit MW irradiation heating in materials processing. Significant developments have taken place by using MW in materials processing due to its advantageous.

This research work addressed the important characteristic that MW could offer, known as 'non-thermal effect' or also described as 'specific MW effect'. The aim of this work is to utilize the MW non-thermal effect in order to improve the conductivity of electrolyte material of SOFC and subsequently, improve the SOFC performance.

First, this dissertation reports the electrical conductivity of promising electrolyte candidate for intermediate-temperature SOFC; Gd or Sm doped CeO₂ with various dopant concentrations ranging from 10-25 mol% measured under MW irradiation heating, and the result was compared to that obtained under conventional heating. In this work MW with frequency of 24 GHz which is categorized as MMW was used. It is found that, the degree of conductivity enhancement could be controlled by thermal environment of measurement setup, dopant type and dopant concentration. At 400 °C the conductivity enhancement for different types of dopant and dopant concentrations under optimized thermal environment differed between 3 to 13 times. The conductivity enhancement linearly decreased with temperature because the effect of MMW was more pronounced at lower temperature. The influence of MMW heating on the conductivity is thoroughly discussed by analyzing the activation energy and absorption property of the samples. Taken together, the results obtained in this work identified that conductivity was

improved because of apparent activation energy was reduced due to MMW non-thermal effect which induced the ionic conductivity in the electrolyte.

In the second part of this dissertation, cell performance of single cell under MMW irradiation heating was discussed. Using 20 mol% Sm doped CeO₂, La_{0.8}Sr_{0.2}MnO₃, and NiO-20SDC cermet as the electrolyte, cathode and anode, respectively, a button-type electrolyte-supported single cell was fabricated. Initially, the single cell and measurement condition were optimized by tested the cell with various parameters, namely, NiO-20SDC anode composition, gas concentration, cathode printing temperature and electrolyte thickness. The cell performance was greatly dependent on these parameters, and the effect on the open circuit potential and power density was described. For the first time, performance of single cell under MMW irradiation heating was demonstrated. The cell performance was improved approximately 62% and 52%at 630 °C and 734 °C, respectively when heated under MMW irradiation. The improvement trend has the same tendency with the conductivity enhancement where both conductivity and performance enhancement were larger at lower temperature. This finding indicates that cell performance was improved because of higher conductivity of the electrolyte obtained under MMW irradiation heating due to MMW effect.

Chapter 1

Introduction

1.1 Global power generation

Historically, global energy consumption has risen rapidly from the past century, and it is strongly influenced by economic growth and population. As from now on strong economic growth and expanding populations are expected, accordingly, energy consumption will increase. One of the major challenges faced by energy sector is challenge in meeting global energy demand, as reported that by the year 2040, world energy consumption will increase to 40-50% [1-4].

Another major challenge is to fight against climate changes or global warming and pollution. The primary source of energy that used in the world uses fossil fuel such as coal, natural gas and petroleum to generate power. Such power generators, known as combustion engines generate electricity by converting heat energy produced from combustion of fuels to mechanical energy and finally to electrical energy. Even though the internal combustion engine has proven to be an affordable and effective means of generating energy, however, the variety of fuels used to generate electricity all have some impact on the environment, especially to the air pollution. The energy sector is the largest source of air pollution emissions [5-8]. Today, societies continue to face environmental problems created by the combustion of carbon-based fuels. For example, carbon dioxide, the primary product of combustion, causes global climate changes because of the enormous concentrations it has reached in the atmosphere [9-11]. As energy sector become the predominant source of air pollution, it is critical to develop low-emission energy-generation technologies that reduce greenhouse gas emissions.

1.2 Fuel cell technology as a clean energy source

In the past decade, the pace of research in energy field has been rapid, driven by the requirements for clean energy source and high energy density electric generator. Fuel cell technology offers an attractive combination of highly efficient fuel utilization and environmentally-friendly operations. In fundamental principle, fuel cell generates electrical energy when hydrogen and oxygen reacts, producing water and heat as the by-products. Fuel cell will generates electrical power as long as fuel is supplied, and fuel can be instantly replenished. Also, because fuel cell has fewer moving parts, it is quiet during operation. Fuel cell is different from combustion cell where it directly converts the chemical energy to electrical energy without any combustion involved, therefore the efficiency is higher, of up to 60%. Furthermore, the heat by-product can be used in other appliances as heat energy, for example for water heater which is called as co-generation [12-15]. Fig. 1.1 shows the data adapted from Fuel Cell Energy. Inc report, comparing the efficiency and emissions of fuel cell and other internal combustion-based power generations. It clearly shows that fuel cell is the cleanest power while provides highest efficiency.



Figure 1.1: Comparison of efficiency and emission produce by various power generation systems (*Direct fuel cell-turbine, **Direct fuel cell-energy recovery generator) [16].



Energy density (Wh/kg)

Figure 1.2: Comparison of the energy density and output power performance between various power generation systems [17].

Fuel cell is often compared to batteries because both convert the energy produced by a chemical reaction into usable electric power. Figure 1.2 shows the energy density and output power density of various power storage devices namely capacitor, lead cell, lithium ion cell, nickel-metal hydride (Ni-MH) cell and fuel cell. Compared with other cells, the energy density of the fuel cell is impressive. With its significantly higher energy density which means higher energy storage, fuel cell open up opportunities in a wide range of applications such as for portable consumer electronics, stationary energy generation, auxiliary power, and so on. The closest competitor of fuel cell, Li ion cell is widely used to power electronic devices and sensors due to its higher output power density, but their well-known drawbacks, namely discharge rate, recharge capability, safety concerns, and disposal issues, have forced the power systems researchers to investigate the potential application of fuel cell and develop high power density fuel cell [18-19].

Fuel cells are classified by the type of material used for electrolyte, as can be seen in Table 1.1 [20-22]. The type of fuel cell determines the electro-chemical reaction that take place, the kind of catalyst required, operating temperature, types of fuels required, design and field of application. There are five major types of fuel cells; polymer electrolyte membrane fuel cell

(PEMFC), alkaline fuel cell (AFC), phosphoric acid fuel cell (PAFC), molten carbonate fuel cell (MCFC), solid oxide fuel cell (SOFC).

	PEMFC	AFC	PAFC	MCFC	SOFC
Electrolyte	solid	potassium	phosphoric	molten	ceramic
	polymer	hydroxide,	acid	carbonate	
		(KOH)		salt	
Operating temperature, °C	60-140	150-200	180-200	600-700	700-1000
Efficiency, %	40-50	50	40	45-55	50-60
Power density, kW/m ²	3.8-6.5	1.0	0.8-1.9	1.5-2.6	0.1-1.5
	Portable,	Space,	Medium to	Large	Medium to
Applications	stationary,	military,	large power	power	large power
Applications	automotive	sub-	generation	generation	generation
		marines,			
		transport			

Table 1.1: Classification of fuel cells

1.2.1 Background of Solid Oxide Fuel Cell

Solid oxide fuel cell uses a hard ceramic as the electrolyte and operates at high temperatures range, as high as 1000 °C. Of the several types available, as can be seen in Fig. 1.3, SOFCs have high efficiency and excellent long-term performance stability. Specifically, because the system operates in the high temperature range, fuels can be reformed within the fuel cell itself, eliminating the need for external reforming and allowing the units to be used with a variety of hydrocarbon fuels.

Furthermore, at high temperature electrochemical reaction is possible to occur at the electrodes simply by supplying fuel and air without using an expensive noble metal catalysts, thereby reduce the cost. SOFC also generates higher quality waste heat which is useful in combined applications, for example stationary power generator needs heat for fuel gasification, and residential equipped with SOFC system can use the heat to produce hot water from water heater for residential application. In addition, the water can be recycled to produce the steam needed to reform the fuel. Due to these benefits, SOFC appears to be one of the promising fuel cell system [17,23,24].



Figure 1.3: Cell efficiency and power generating scale of various power systems [17]

The basic configuration of an SOFC is illustrated in Fig. 1.4. The single cell is composed of dense electrolyte, porous anode and porous cathode. Oxygen from air is supplied to anode, and hydrogen as the fuel to the cathode. The electrolyte separates the air and fuel compartment. Electrolyte allows only oxygen ion (or hydrogen ion for proton conducting electrolyte). Negatively charge oxygen ion (O^{2-}) migrates through the electrolyte and electrochemically react with hydrogen at cathode. This reaction produces water and only small amount of carbon dioxide if hydrocarbon used as fuel at cathode. Electrons generated at the anode travel through an external load to the cathode, completing the circuit and supplying electric power along the way. As long as there's fuel, air, and heat the process continues producing clean, reliable, and affordable energy.



Figure 1.4: Basic diagram of solid oxide fuel cell.

The reactions at both electrodes and full reaction are as follows [25]:

The reaction at cathode

$$\frac{1}{2}$$
 O₂ + 2 e⁻ \longrightarrow O²⁻

The reaction at anode

$$\mathrm{H}_2 + \mathrm{O}^{2-} \longrightarrow \mathrm{H}_2\mathrm{O} + 2\,\mathrm{e}^{-1}$$

The unit cell reaction

$$\frac{1}{2}O_2 + H_2 \longrightarrow H_2O$$

Figure 1.5 shows the timeline of brief history of the development of SOFC. Globally, research and development (rnd) in SOFC has expanded in all aspects. Collaborations in rnd between academician-industry-goverment have accelerated rapidly until commercialization of SOFC has been realized by Bloom Energy (U.S), Ceres Power (U.K), Ene-Farm (Japan) and to date rnd continues to build better fuel cell.



Figure 1.5: Timeline of research and development in SOFC [26].

1.2.2 SOFC components and the state-of-the-art materials

The main components for fabricating SOFC are electrolyte, cathode and anode. Each component has to meet certain requirements. The requirements for each component are given below.

Solid electrolyte

An electrolyte used in SOFC is a ceramic material which can conduct ion O^{2-} (or H⁺). An electrolyte must be used to provide a pathway for the ions to flow, via hopping mechanism. An electrolyte must fulfill few requirements before it can be used as the electrolyte of SOFC, as listed below:

- 1. Possesses high ionic conductivity
- 2. Has low or negligible electronic conductivity
- 3. Thermodynamic stable from room temperature to working temperature
- 4. Stable in both reducing and oxidizing atmospheres at the working temperature
- 5. Sufficient mechanical strength

- 6. Dense to ensure gas tightness
- 7. Has matching thermal expansion compatible with that of electrodes and other components
- 8. Has chemical compatibility between electrodes materials

Above mentioned requirements limit the choice of electrolyte materials to stabilized zirconia (ZrO_2) , doped ceria (CeO_2) and lanthanum gallate $(LSGM: (LaSr)(GaMg)O_3)$. Each material has its own advantages and disadvantages.



Figure 1.6: Conductivity of selected electrolyte materials, yttria doped zirconia (YSZ), lanthanum strontium gallate (LSGM) and gadolinium doped ceria (CGO) [27].

Stabilized zirconia electrolytes have been the most favored electrolyte for SOFCs, however they are able to operate in temperature range from 850-1000 °C, whereas at lower temperature range the internal resistance is too large, thus the efficiency or power density is not satisfying. Although the conductivity is significantly lower, this materials are advantageous because of their outstanding mechanical stability [27,28].

The doped ceria electrolytes are attractive for low-temperature (<800 °C) SOFCs because they offer a significantly higher ionic conductivity, but they become mixed conductor and exhibit dimensional change due to reduction of Ce⁴⁺ to Ce³⁺ under reducing environment, resulting in an internal short circuit of the cell. Consequently, a decrease open circuit voltage (OCV) and an additional fuel utilization even under OCV-conditions takes place, therefore efficiency of the system decreases [29-31].

Lanthanum gallate based electrolytes exhibit an even higher ionic conductivity compared to stabilized ZrO_2 and doped CeO_2 , which is benefit for low operating temperature SOFC. However, the problems associate with LSGM includes long term stability due to Ga evaporation in a reducing atmosphere resulting in the formation of new phases, low mechanical stability of LSGM, as well as high cost of Ga [32,33].

Figure 1.6 compares the conductivity of the most promising materials for electrolyte, namely yttria doped zirconia (YSZ), lanthanum strontium gallate (LSGM) and gadolinium doped ceria (CGO) as a function of inverse temperature. Electrical conductivity is a vital property for electrolyte because it governs the cell performance.

Doped Ceria (CeO₂) as a solid electrolyte

Pure stoichiometric cerium oxide or ceria (CeO₂) forms the fluorite structure ($I4/mmm Pm\overline{3}m$) over the whole temperature range from room temperature to the melting point at 2400 °C. This fluorite structure is built on the basis of a Ce⁴⁺ cation face centered cubic (FCC) packing with oxygen ions located in the tetrahedral sites of the structure, as illustrated in Fig. 1.7 [34]. Pure CeO₂ is not a good ion conductor. Introducing lower valence dopant in Ce⁴⁺ site to create oxygen vacancy, oxygen ion conductivity can be introduced dramatically. The conductivity is strongly dependent on the characteristics of the dopant elements and their concentrations. CeO₂ doped with alkaline earths or rare earths has received considerable attention due to the conductivity improvement. Fig. 1.8 illustrates conductivity of CeO₂ with various dopants. It shows that dopant size greatly influence the conductivity, where dopants having similar size with Ce⁴⁺ show higher conductivity.

However, one major drawback of doped CeO_2 that has been discussed by researchers is it shows irrefutable electronic conductivity at high temperature and under low oxygen partial pressure. The electronic conductivity acts as a short-circuit pathway through the electrolyte and effectively reduces the SOFC efficiency. Nevertheless, the range of oxygen partial pressures over which the electrolyte is predominantly ionic widens as the temperature is reduced. Below 700 °C, the degree of electronic conductivity is thought to be low enough to allow acceptable SOFC operation. Furthermore, it is reported that CeO_2 doped with Gd^{3+} , Sm^{3+} and Y^{3+} are relatively less reducible and the ionic conductivity is well established [35-37].

Electrodes

Electrode is the layer through which reactants are transported to electrolyte-electrode interface where the electrochemical reaction takes place. Efficient delivery of reactants can be achieved if electrode effectively allows gas flow and distribute it over the reaction surface. In SOFC, the primary function of the fuel electrode (anode) is to promote the electrochemical oxidation of fuels. When a hydrocarbon fuel such as methane is used as the fuel, additional functions of the anode may include internal reforming or partial oxidation of the fuel. Meanwhile, air electrode (cathode) promotes the electrochemical reduction of O_2 from air or oxygen gas. These electrochemical processes at anode and cathode require a series of elementary reactions which involves the transfer of electrons.

The requirements for anode and cathode in SOFC includes:

- 1. High electronic conductivity
- 2. Porous microstructure for gaseous diffusion
- 3. High electrocatalytic activity for the electrodes reaction
- 4. Thermodynamic stability from room temperature to working temperature
- 5. Sufficient mechanical strength
- 6. Thermal expansion that match with other cell components
- 7. Minimum reactivity with electrolyte and interconnection

These stringent electrochemical and mechanical requirements greatly restrict the number of suitable electrodes candidate materials.



Figure 1.7: CeO₂ crystal structure



Figure 1.8: Ionic conductivity of doped ceria at 800 °C against the radius of dopant cation [31].

The most common anode material is porous Ni-ceramic in which nickel provides the electronic conductivity and ceramic provides the oxygen-ion conduction, thus Ni to ceramic ratio plays important role to achieve high electrical conductivity [38].

For cathode material, the most common type is perovskite-based LaMnO₃. Strontium is normally used to dope into La site and becomes $La_{1-x}Sr_xMnO_3$ (LSM), which can enhance the electronic conductivity. Further dope or replacement of manganese with other elements such as cobalt and iron (LSCF) increased the electrical and mechanical properties of LSM [39].

1.2.3 Challenges in SOFC technology

One current concern in SOFC technology is its high operating temperature. The main challenges of the operation of SOFC at high operating temperatures include [40-42]:

1. Unstable chemical and mechanical properties.

High temperature thermal cycles not only induce a substantial thermal stress at electrolyteelectrode-interfaces, but it also increases the inter-diffusion kinetics which can change the chemistry of the adjoining components.

2. Slow startup.

Herein, a period of cell heating is required in order to reach the operating temperatures. Hence, start-up times for SOFC operation are time consuming.

3. Sealing problems.

Material choices for sealant at high temperature is limited, thus requires expensive interconnect and integration of materials for SOFC stacks. The sealant must have a thermal expansion which is reasonably close to that of the other materials involved and sealant should not react with joining parts.

To solve the problems regarding the high-temperature SOFC, operation temperature must be reduced. However, reducing operating temperature results in decrease in performance of the cell. This is because at low temperature the resistance (ohmic loss) increases especially in electrolyte and decreases the reaction at electrodes by the result of increasing polarization at both electrode. Therefore, many attempts has been done by researches in order to improve the performance of SOFC at low temperature. Continuous research works includes synthesizing new materials for SOFC components, fabricating new cell design, development of SOFC system and so on [43,44].

1.3 Microwave as a heating source

1.3.1 Background

Microwave (MW) radiation is the term associated with any electromagnetic radiation in the microwave frequency range of 300 MHz-300 GHz. This range lies between radio wave frequencies (RF) and infrared (IR) frequencies in the electromagnetic radiation spectrum. The corresponding wavelength is from 1 mm to 1 m. MW has wide range of applications for instance for communications, radar and heating, and each applications requires certain frequency. The application of MW for heating was discovered by chance when scientists were doing research related to radar system during World War 2. After the potential of MW in heating process was recognized, interest in applying MW in materials processing as an alternative heating method increased profoundly [45].



1.3.2 Theory of microwave irradiation heating

Figure 1.9: Effective loss factor as a function of the frequency due to dipolar and conduction mechanisms [46].

When materials are irradiated, MW-materials interaction occurs through polarization; displacement of charge through the formation and rotation of dipoles, and conduction; charges transport processes. The principle of MW heating attributes from both processes when MW energy is converted to thermal energy as the losses. Due to the forces applied by MW are rapidly changing, for example 2.45×10^9 cycle per second at frequency 2.45 GHz, it resulted material warming due to the losses. During polarization, reorientation loss occurs when dipole molecules are unable to follow extremely rapid reversal of electric field. On the other hand, loss in conduction is due to ohmic loss during the movement of ions within the material and collision with other species. Loss is characterized by relative loss factor, ε ["]. Figure 1.9 illustrates effective loss factor due to dipoles and conduction in certain range of frequency [46].

Not all materials can be heated by MW. Heating behavior of materials depends on the ability of the materials to absorb MW when irradiated and that ability controlled by the material's dielectric properties, frequency of MW energy, and the temperature of the materials [47,48]. Figure 1.10 illustrates the interaction of MW with different materials. Generally, MW-materials interaction can be divided into three groups; transparent, opaque or reflector and absorber, depending on how it interacts with MW. Transparent materials having low dielectric loss could not be heated and can be a good choice for insulator. Metals reflect and do not absorb MW energy, therefore metals are not effectively heated by MW. Meanwhile, absorptive materials having high dielectric loss can be heated by MW because they can absorb MW energy well.



Figure 1.10: Microwave interaction with different materials.

MW heating is the result of absorption of MW energy by a material. When electric field is

applied to a materials, total power absorbed, P can be calculated by [49] :

$$P = \sigma |E|^{2} = 2\pi f \varepsilon_{0} \varepsilon_{eff}^{"} |E|^{2} = 2\pi f \varepsilon_{0} \varepsilon_{r}^{'} \tan \delta |E|^{2}$$
(1.1)

where σ is total effective conductivity, E is electric field, f is MW frequency, ε_0 is free space permittivity, ε_{eff} is relative effective dielectric factor, ε_r is relative dielectric constant and $\tan \delta$ $(\varepsilon''/\varepsilon')$ is energy loss required to store a given quantity of energy.

Eq.1.1, demonstrates that dielectric properties of materials have strong influence on power absorption. For optimum coupling, a balanced combination of moderate *E*, to permit adequate penetration, and high loss (maximum ε_{eff} and tan δ) is required.

1.3.3 Characteristics of microwave irradiation heating

Heating mechanisms under conventional and MW irradiation heating are fundamentally different, as listed in Table 1.2. Each characteristic interrelates with all others. Under conventional heating, heat is transferred from the furnace or heater by heat conduction, convection or radiation to the surface of materials before transferred to the inner part of the materials. This process is apparently time and energy consuming because heat should be transferred from one medium to other medium gradually. In contrast, under MW irradiation heating materials generate heat on their own by direct interaction with MW, which is called as self-heating, so that materials are heated from the inner side towards the outer side. The illustration of heat transfer under conventional and MW irradiation heating is shown in Fig.1.11.

Conventional Heating	Microwave Irradiation Heating		
Conduction, convection	Energetic coupling		
External to internal	Molecular level		
Non-selective	Selective		
Superficial	Volumetric		
Slow	Rapid		

Table 1.2: Conventional versus microwave irradiation heating characteristic.

MW irradiation heating offers selective heating, where heating mechanism is dependent on how material absorbed MW energy. Due to self-heating, each part of the heated materials generates heat volumetrically, so even for those objects with complicated shape, materials can be heated relatively uniform. Selective heating would be a great advantage for some processes where only target components should be heated while other components and surrounding should be maintain at lower temperature.

MW also offers rapid heating and allows rapid response which means process start and end (switch on and off) can be controlled instantly. In addition, the amount of heat energy generated inside the heated material can be controlled easily by the adjustment of MW power. MW rapid heating and self heating lead to other benefits such as low cost, high efficiency and clean energy [50,51].



Figure 1.11: Heat transfer in a) conventional and b) microwave irradiation heating. Arrows show the direction of heat transfer.

1.3.4 Microwave processing of materials

Since MW offers many advantages in terms of energy efficiency, performance and features that not achievable with other techniques, it opens up opportunities for processing a wide range of materials. The increasing interest in application of MW technology has prompted a considerable amount of research in this area and MW has accepted as an alternative method for materials processing. Figure 1.12 gives overview of published literatures of MW processing of various materials. From this chart, it shows that the largest publication is on ceramic materials.

Many successful work in ceramics processing has been reported. MW has been used as an

alternative heating method in advanced materials, for example in synthesis [52,53], sintering [54-56] and joining [57,58]. Researchers have found that the processing temperature is lower when using MW irradiation heating compared to conventional heating due to internal heating [49,59]. In addition, it has been reported that processing materials under MW increases reaction rate and decreases activation energy. Moreover, MW processing resulted in improvement of properties such as density, hardness, strength and so on. Such differences phenomena occur in MW processes and improvement in material properties have been discussed with regard to MW effect, either because of self-generated heating or non-thermal effect which explains conversion of absorbed MW energy directly to process energy.



Figure 1.12: Published literature in microwave processing materials [60].

1.3.5 Higher frequency microwave

The power generated from any microwave (MW) source depends on its operating frequency and construction. Due to availability and feasibility, MW with frequency of 9.15 MHz and 2.45 GHz have been the most widely used. This type of MW is specifically known as centimeter wave (CMW) because of its wavelengths are in centimeters range. CMW is most frequently generated by magnetron. In some applications, higher MW power is required. Gyrotron with higher frequency is able to provide output power from kilowatts to megawatts. Gyrotron with frequency in the range of 30 GHz to 300 GHz has corresponding wavelength in the range of millimeter, thus MW associates with this frequency range is known as millimeter wave (MMW). Nevertheless, gyrotron with frequency of 24 GHz and 28 GHz are also commonly considered as MMW due to the similarity of their characteristics [61-63].

Due to high stability of generated frequency and power level, MMW is superior to CMW. MMW offers better heating efficiency even for poor dielectric loss materials, more uniform radiation which lead to homogeneous processing and higher MW effect [64]. In addition, due to the shorter wavelength the depth of penetration is smaller and the incident radiation power is lost in the shorter depth, allowing the near surface treatment of the material. Moreover, thermal run-away which can lead to hotspot in heated materials under MMW is lesser. Furthermore, processing metal under MW can cause local concentration of electric field which leads to metal sparking or arcing. This phenomenon can be avoided by using MMW during materials processing involving metal especially at high temperature.

1.4 Scope and objectives

High operation temperature is a major issue in SOFC which leads to problems regarding cell durability, high energy and cost, and start-up time. Researchers have adopted many approaches in order to develop high-efficiency SOFC that operates at lower temperature. This includes developing new materials for electrolyte, anode and cathode, reducing thickness of electrolyte to reduce ohmic loss via fabrication of anode, cathode or metal supported cell, exploiting nan-otechnology, developing new design of stack cell and single-chamber SOFC, and many more [65].

The use of microwave in materials processing provides an alternative heating approach. Unique characteristic of microwave which promotes internal reaction within materials, not only lead to significant reduction in processing time and energy because of rapid and selective heating, but also results in properties improvement that might not be achieved by other methods [46,66]. Despite the complex interactions between microwave and materials are still debatable, many successful work in materials processing has been reported and exciting new MW processes are being explored.

The main goal of this study is to exploit the benefits of microwave heating technology to replace conventional heating in SOFC system in order to lower the operation temperature of SOFC. To achieve this goal, fundamental investigation on the influence of microwave energy on the material properties must be done. Investigation on electrical conductivity under microwave irradiation heating of solid electrolyte material for SOFC was carried out by Kishimoto et.al, where they reported that the conductivity of stabilized ZrO_2 improved remarkably when measured under microwave irradiation heating compared to that under conventional heating [67-69]. As higher conductivity can be obtained under microwave irradiation heating, this finding is beneficial for development of intermediate-temperature SOFC (IT-SOFC) which operates at lower temperature. Doped CeO₂ and stabilized ZrO₂ are categorized in the same crystal structure group which is fluorite-type, and it possesses higher conductivity that stabilized ZrO₂. As mention earlier, the conductivity of stabilized ZrO₂ improved under MMW irradiation heating, therefore it is expected that same trend might be occurred, where conductivity of doped CeO₂ could be enhanced too. Otherwise, new phenomena might be observed in doped CeO₂.

Comparative study of the conductivity of $Ce_{1-x}Gd/Sm_xO_{2-x/2}$ and its performance under conventional and microwave irradiation heating is the main focus in this research. $Ce_{1-x}Gd/Sm_xO_{2-x/2}$ was chosen because this material shows high potential as electrolyte for IT-SOFC. Microwave power source with frequency of 24 GHz was used in this study. The corresponding wavelength for 24 GHz is 12 mm, therefore it can be specifically categorized as millimeter-wave. Thus, throughout this thesis 'millimeter-wave (MMW)' is used instead of 'microwave (MW)'.

To achieve the objectives, study was performed according to the specific aims, as follows:

- 1. Determine the optimum thermal environment for conductivity measurement under MMW irradiation heating.
- Study the influence of MMW irradiation heating on the electrical conductivity of Ce_{1-x}Gd/Sm_xO_{2-x/2}.
- 3. Identify the microwave effect on the ion conduction.

4. Evaluate the single cell performance under MMW irradiation heating.

Because the influence of MMW irradiation heating on the ion transport is relatively new, reported data is limited. Thus, this thesis also aim to provide new beneficial scientific data and knowledge in addition to existing ones to give clearer view of the theory.

1.5 Outline of the thesis

This doctoral thesis presents the research work carried out within a period of three years. It is divided into four chapters. Follows are brief description of each chapters:

Chapter 1: Introduction and research background

This thesis starts with the introduction and comprehensive review of the solid oxide fuel cell and microwave technology. It covers the principle and problems involved in SOFC and the advantages of microwave which leads to the motivation of this study. Scope of the research work and thesis outline are described in this chapter.

Chapter 2: Electrical conductivity of doped ceria under millimeter-wave irradiation heating

This chapter begins with the introduction of the material studied in this research, $Ce_{1-x}M_xO_{2-x/2}$. Detailed flows of the methodology starting from sample preparation, characterization, experimental setup for conductivity measurement under conventional and MMW irradiation heating including the optimization of thermal environment, absorptivity measurement under MMW irradiation heating and investigation of ionic transport number are described here. Then, the results for each measurements are discussed.

Chapter 3: Performance of single cell under millimeter-wave irradiation heating

This chapter begins with the introduction of the performance evaluation of SOFC. Then, fabrication of single cell including the preparation of each part of the cell is describes in details. The measurement setup for performance evaluation under conventional and MMW irradiation heating is given here. This includes the conditioning process prior to measurement, optimal single cell and system conditions, and thermal insulation for measurement under MMW. The performance of single cell under conventional and MMW irradiation heating is compared and discussed.

Chapter 4: Conclusions

Finally, this thesis ends with conclusions derived from this research, giving the answer to the objectives of this study. Some recommendations are also given for future work.

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Chapter 2

Electrical conductivity of doped ceria under millimeter-wave irradiation heating

2.1 Introduction

This chapter presents the electrical conductivity of a promising candidate, doped CeO_2 for solid electrolyte material of SOFC under MMW irradiation heating. Results were compared to that obtained under conventional heating and detailed discussion was given to give clear understanding on the effect of the MMW on the charge carriers transportation in this material.

In defect-free solid electrolyte, ions are trapped in their lattice and rarely can escape from the lattice site. For ionic conduction to occur, it requires either some sites are vacant, so that ions can hop into the neighboring vacancies, or there are interstitial ion which can hop into adjacent interstitial sites. In this study, the former defect structure was exploited by doping CeO_2 with trivalent cation into the Ce⁴⁺ site in order to increase the conductivity by the formation of oxygen vacancies. The concentration of oxygen vacancy in the lattice is important as it will affect the kinetics of the conduction process. Fig. 2.1 (a) and (b) show the crystal structure of CeO₂ and migration paths of an oxygen ion in the cubic symmetry fluorite system, respectively [1].

The Kroger-Vink notation for the defect chemistry of trivalent cation doped CeO_2 is [2]:

$$M_2O_3 \xrightarrow{CeO_2} 2\,M_{Ce}' + V_o^{\bullet\bullet} + 3\,O_o^x$$

where, M_2O_3 is dopant oxide, M_{Ce}' is negatively charged dopant cation at Ce⁴⁺ site, $V_o^{\bullet\bullet}$ is

positively charged oxygen vacancy and O_o^x is zero charged normal oxygen ion.



(a) Fluorite structure

Figure 2.1: Schematic view of (a) crystal structure and (b) oxygen migration path in the fluorite structure [1].

By increasing the temperature, ions can move more easily. The temperature dependence of ionic conductivity is usually given by Arrhenius equation:

$$\sigma = \frac{\sigma_0}{T} \exp\left(\frac{E_a}{RT}\right) \tag{2.1}$$

where, σ is ionic conductivity, σ_0 is pre-exponential factor, T is absolute temperature, E_a is activation energy and k is Boltzmann constant. Conductivity commonly displayed in graph of log σT against T^{-1} . As can be predicted by Arrhenius equation, this graph shows a linear relationship between log σT and T^{-1} .

Due to strong function between the dopant size and the binding energy, the choice of dopant is vital aspect to be considered in order to optimize the ionic conductivity in ceria. The difference of charge between dopant and vacancy resulted in attraction which may lead to reduction in conductivity. Dopant must has the minimum interaction so that small energy needed to separate the interaction before ions has the ability to migrate [3,4]. In addition, the ionic size of dopant should be similar with host cation and possesses minimum charge different to minimize the distortion of lattice from the ideal cubic fluorite structure [5,6]. Studies have found that Gd³⁺ and Sm³⁺ exhibit smallest binding energy which leads to higher conductivity [7-9]. In this project Gd³⁺ and Sm³⁺ were chosen as the cation dopants because of the aforementioned reasons. The ionic radii of cations is tabulated in Table 2.1.

Table 2.1: Ionic radii of host cation and dopant cations in Gd/Sm doped CeO_2 .

Ion	Ionic radius, pm	Reference
Ce ⁴⁺	114	[10]
Gd^{3+}	105	[10]
Sm ³⁺	108	[11]

The specific scope and objectives of the experiments in this chapter are:

- 1. Synthesis Gd/Sm doped CeO₂ electrolyte material.
- 2. Measure the conductivity of Gd/Sm doped CeO_2 under MMW irradiation heating, and identify the influence of the thermal environment on the conductivity.
- 3. Compare the conductivity of Gd/Sm doped CeO₂ under conventional heating and MMW irradiation heating.
- Analyze the effect of MMW irradiation heating on the activation energy of Gd/Sm doped CeO₂.
- 5. Verify the MW effect on conduction process of Gd/Sm doped CeO_2 .
- 6. Measure the ionic transport number of doped CeO_2 .

2.2 Experimental

2.2.1 Synthesis of doped CeO₂

10-20 mol% Gd-doped CeO₂ (hereinafter 10GDC, 15GDC, 20GDC) and 10-25 mol% Smdoped CeO₂ (hereinafter 10SDC, 15SDC, 20SDC, 25SDC) powder were prepared via conventional solid state method by using cerium nitrate hexahydrate (Ce(NO₃)₃ · 6H₂O) (Nacalai Tesque, Inc., Japan), gadolinium nitrate pentahydrate (Gd(NO₃)₃ · 5H₂O) (Mitsuwa Chemical Co. Ltd., Japan) and samarium nitrate hexahydrate, 99.9% (Sm(NO₃)₃ · 6H₂O) (Kishida Chemical Co. Ltd., Japan). Required precursor powders were completely dissolved by continuous mixing and stirring in ethanol for 1 h using magnetic stirrer with rotary speed of 360 rpm at room temperature. Obtained slurry was heated under sodium lamp to remove the liquid phase, and then the powder was calcined at 1000 °C for 2 h in argon atmosphere with flow rate of 100 ml/min. Next, powder was ball-milled in an ethanol dispersion using planetary type mill (Pulverisette, Fritsch, Germany) for 1 h operated at 200 rpm. Obtained powder was pelletized under uniaxial press at 15 MPa for 1 min, followed by cold-isostatic press at 125 MPa for 1 min. Green pellets were sintered in a conventional chamber furnace at 1550 °C for 5 h with heating and cooling rate of 5 °C/min. Obtained samples have pale brown-yellowish color.

2.2.2 Phase analysis

Crystal phases of samples were identified by using powder X-ray Diffraction with CuK_{α} (XRD; Multiflex, Rigaku, Tokyo, Japan) in the range of 20 - 80°. Data were inspected using JADE (Materials Data, Inc., (MDI)) software and compared with database.

2.2.3 Density measurement

The apparent densities, ρ of samples were determined by Archimedes method using water as the liquid. ρ was calculated using the following equation:

$$\rho = \left(\frac{W}{W - (W_1 - W_L)}\right) \times \rho_L \tag{2.2}$$

where, W is sample mass, W_1 is sample mass in water, W_L is water mass and ρ_L is water density. Then, apparent relative density, ρ_r was determined as follows:

$$\rho_{\rm r} = \frac{\rho}{\rho_{\rm th}} \tag{2.3}$$

Theoretical density, $\rho_{\rm th}$ was calculated using following equation:

$$\rho_{\rm th} = \frac{MZ}{N_{\rm A}V} \tag{2.4}$$

where, *M* is molecular weight, *Z* is number of atoms in unit cell, N_A is Avogadro's number (6.02×10^{23}) and *V* is volume of unit.

2.2.4 Electrochemical impedance spectroscopy

To investigate the conductivity of the Gd/Sm doped CeO_2 , the impedance is measured as a function of the frequency of the alternating current (a.c) source. Measurement was carried out by two-probe method using impedance analyzer (Modulab Xm, Solatron, U.K) under conditions shown in Table 2.2.

Table 2.2: Measurement conditions for impedance measurement.

Temperature	400-1000 °C
Temperature interval	50 °C interval
Frequency	0.1 Hz - 1 MHz
Points per decade	15 (in logaritmic)
Voltage amplitude	300 mV

Sample

For impedance measurement, pellet sample was cut into approximately $4.0 \times 4.0 \times 10.0 \text{ mm}^3$ rectangular sample using low-speed diamond disc saw blade (Maruto Instrument Co., Ltd.). Electrode contact was made by painting $4.0 \times 4.0 \text{ mm}^2$ surfaces with platinum paste (Nilaco Corp., Japan) and connected with platinum wire. Then, sample was heat-treated at 1100 °C for 10 min to obtain good contact between the electrodes and sample. Fig. 2.2a shows the schematic view of sample used for conductivity measurement.



Figure 2.2: Schematic view of samples used for impedance measurement.

Measurement under conventional heating

For measurement under conventional heating, sample was heated using standard electric tube furnace, as shown in Fig.2.3. Data at each temperature was collected after holding the temperature for 1 h to ensure stability of sample temperature. Sample setup for measurement under conventional heating is shown in Fig 2.4.



Figure 2.3: Tube furnace for impedance measurement.



Figure 2.4: Schematic view of experimental setup in conventional tube furnace for impedance measurement.

Measurement under MMW irradiation heating

The source of MMW used in this study is from permanent magnet gyrotron system (PMGS) (GYCOM Ltd., Russia), as can be seen in Fig. 2.5. The specification of the PMGS is tabulated in Table 2.3. Sample was heated using fixed frequency of 24 GHz. Temperature was controlled by adjusting the voltage of the high voltage power supplied (HVPS) and electron beam current of cathode filament power supply (CFPS). Typically voltage was in the range of 12.0-15.0 kV, and current range was 0.450-0.550 A. Sample was heated to each measurement temperature and temperature was held until stable temperature was achieved. To eliminate the extrinsic factor that can affect the data, same sample for each composition was used in measurement under conventional and MMW irradiation heating. Sample arrangement is based on previously developed sample set up as illustrated in Fig. 2.6 [12-15]. An additional sample which has same composition and dimensions with conductivity measuring sample was used to monitor the temperature, as can be seen in Fig. 2.2b. Thermocouple was inserted carefully to avoid measurement error and positioned inside the additional sample. Samples were sandwiched between susceptors to assist heating and prevent heat radiation. 5SDC was chosen as susceptor as it possesses lower electrical conductivity than samples and has similar MMW absorption properties with samples. The space between the two samples and the susceptors was filled with boron nitride (BN) powder. BN powder served as the electrical insulator between sample and susceptor, and to provide effective thermal transport due its high melting point, low MMW absorption, low dielectric loss, high thermal conduction [16]. Finally, sample was surrounded

by alumina fiber board to prevent thermal radiation.



Figure 2.5: Permanent magnet gyrotron system (PMGS) used as the heating source for millimeter-wave irradiation heating.

Power	up to 3kW
Wave type	continuous wave (CW)
Frequency	24 GHz (single frequency)
Magnetic field strength	0.44 T
Output radiation	H ₁₁ mode of circular waveguide



Figure 2.6: Schematic view of experimental setup for impedance measurement under millimeter-wave irradiation heating.

Optimization of thermal environment for impedance measurement under millimeter-wave irradiation heating

MMW offers direct internal heating which allows materials to be heated from the inner side towards surface, thus temperature distribution of direct MMW heating is different from the conventional heating, as illustrated in Fig. 2.7, where temperature of inner side of sample is higher than the surface. During MMW processing, temperature control is vital aspect in order to obtain homogeneous temperature throughout the sample and to optimize microwave effect. To prevent temperature gradient between inner part and surface, the use of thermal insulator and susceptor become essential in any MMW processing. Fig. 2.8 illustrates that temperature gradient in the sample could be minimized by using susceptor-assisted MMW heating. Commonly the role of susceptor is as an external heat generator especially when using MW with lower frequency. Alumina fiber board is a typical thermal insulator used in microwave processing to control the heat loss from sample. It has been reported that material and configuration of susceptor and insulator play important role to ensure effective MW heating which requires maximum energy input from MW source and minimum radiation loss from target sample [17-20]. Careful consideration on susceptor and thermal insulator should be given in MW processing.

Therefore, in this study, to achieve effective MMW heating, a preliminary study on the effect of susceptor and fiber board on thermal environment for conductivity measurement under

MMW was done. Measurement was performed by using 20SDC as the sample representative under nine different environments as tabulated in Table 2.4. Here, thermal environment was controlled by changing the upper and lower susceptor thickness, and configuration of fiber board. Measurement setup is illustrated in Fig. 2.9.

	1	1	1	1
Environment	Upper susceptor	Lower susceptor	Fiber board	Open channel on
	thickness, mm	thickness, mm	size ^{<i>a</i>}	fiber board
1	1.0	3.5	Medium	nil
2	2.0	3.5	Medium	nil
3	3.0	3.5	Medium	nil
4	2.0	3.0	Medium	nil
5	2.0	3.8	Medium	nil
6	2.0	3.5	Small	nil
7	2.0	3.5	Large	nil
8	2.0	3.5	Medium	1
9	2.0	3.5	Medium	2

 Table 2.4: Thermal environments for conductivity measurement under MMW irradiation heating.

^{*a*}Fiber board size: small $4.0 \times 4.0 \times 2.0$ mm³, medium $6.0 \times 6.5 \times 2.0$ mm³, large $9.0 \times 9.5 \times 2.0$ mm³



Color code: Blue for cold spot, red for hot spot.

(b) Temperature profile.

Figure 2.7: Temperature profile in a sample during direct heating under millimeter-wave irradiation.



Figure 2.8: Temperature distribution in a sample under susceptor and fiber board assisted millimeter wave irradiation heating.



Figure 2.9: Schematic view of experimental setup for impedance measurement for optimizing thermal environment. Insert: Middle fiber board without/with open channel(s).

Determination of bulk conductivity, $\sigma_{\rm dc}$

Total electrical conductivity in polycrystalline is contributed by three main regions, as can be seen in Fig. 2.10 :

- 1. ①,④ electrode-electolyte interface
- 2. ② grain boundary (intergrain)
- 3. (3) bulk (intragrain)

Contribution of each mechanism to the total conductivity can be interpreted separately because conductivity mechanism is frequency dependence. Frequency range and corresponding phenomena is presented in Fig. 2.11. In this study, frequency dependence of bulk conductivity of doped CeO_2 collected from a.c impedance method was analyzed by using universal dielectric response (UDR), which describes the complex conductivity due to ion-hopping [21,22]. Theoretical value was calculated by applying widely used equivalent circuit which described the a.c behavior of electrochemical system, shown in Fig. **??**. This equivalent circuit involves elements made up from capacitance and conductance that contribute to the grain boundary (g.b) and bulk ion conduction.



Figure 2.10: Phenomena contribute to total ionic conduction in polycrystalline: ①,④: electrode-electrolyte interface conduction ②: grain boundary conduction and ③: bulk conductivity.



Figure 2.11: Possible interpretation for conductivity mechanisms dependent on frequency.



Figure 2.12: Equivalent circuit consisted of capacitance (C) and conductant (G) that contribute to the grain boundaries (g.b) and bulk ion conduction.

The complex conductivity is given by:

$$\sigma^* = \sigma'(\omega) + i\sigma''(\omega) \tag{2.5}$$

Ion hopping described by UDR:

$$\sigma'(\omega) = \sigma_{\rm dc} + \sigma_0 \omega^{\rm s} \tag{2.6}$$

$$\sigma''(\omega) = \left[\tan\left(\frac{s\pi}{2}\right) \sigma_0 \omega^{\rm s} + \omega \varepsilon_0 \varepsilon_\infty \right]$$
(2.7)

The complex conductivity becomes:

$$\sigma^* = \sigma_{dc} + \sigma_0 \omega^s + i \left[\tan\left(\frac{s\pi}{2}\right) \sigma_0 \omega^s + \omega \varepsilon_0 \varepsilon_\infty \right]$$
(2.8)

where σ_{dc} denotes the d.c bulk conductivity i.e. intra-grain conductivity of mobile O^{2-} ions, σ_0 is temperature-dependent coefficient. Conductivity increases as a power of the frequency, with exponent s (s < 1). Here, ε_0 is the permittivity of free space and ε_{∞} is the high-frequency permittivity due to optical phonon. The measured complex conductivity data were fitted using nonlinear least-squares fitting.

2.2.5 Millimeter-wave absorptivity

To investigate the correlation between conductivity enhancement and MMW energy absorptivity, heating behavior of samples during irradiation was observed. For each composition, two pellets of 16 mm diameter and 2 mm thickness were used in this experiment. In order to ensure stable temperature measurement, lower sample was designed with a channel at the center which was used to place the thermocouple, as shown in Fig. 2.13. Thermocouple was inserted between the pellets, then sample was covered by alumina fiber board to prevent heat loss. By heating the sample at fixed MMW power input (current: 0.18 A, voltage: 9 kV) time-dependence sample temperature was recorded. Note that for absorptivity measurement only, instead of PMGS, gyrotron oscillation heating system with frequency of 24 GHz was used.



Figure 2.13: Schematic view of experimental setup to investigate the heating behavior of samples under fixed millimeter-wave irradiation heating.

2.2.6 Ionic transference number, t_{ion}

Ionic transference number, t_{ion} for doped CeO₂ was measured via electromotive force, *EMF* method using oxygen gas concentration cell. Disc sample with thickness of 1.0 mm and diameter of 16.0 mm was used as the electrolyte. Pt paste was applied on both surfaces of sample, then heat-treated at 1100 °C for 10 min, which served as electrodes. The schematic illustration of the sample for *EMF* measurement can be found in Fig. 2.14. Sample was mounted in the sample holder of SOFC Single Cell Evaluation Unit (FC-400H, CHINO Co., Japan), as illustrated in Fig. 2.15. Gas sealing was done prior to the measurement by heating the system in the

tube furnace at 850 °C to melt the glass ring. Different concentrations of O_2 gas was supplied to anode and cathode. Concentration of oxygen gas was controlled by supplying and adjusting the concentration of N_2 gas using Log Mix flow meter. Gases were supplied to the anode and cathode with total flow rate of 200 ml/min at each electrode. Measurement was done at temperature 600-1000 °C.

The cell is given by:

 O_2 (P'O₂ (high pressure)), Pt |doped CeO₂ |Pt,O₂, (P''O₂ (low pressure))

Reaction occurs at cathode (high oxygen partial pressure, $P'O_2$, reduction process);

$$O_2 + 4 e^- \longrightarrow 2 O^{2-}$$

Reaction occurs at anode (low oxygen partial pressure $P''O_2$, oxidation process);

$$2 O^{2-} \longrightarrow O_2 + 4 e^{-}$$

Theoretical EMF was calculated using Nernst equation, described by:

$$E = \left(\frac{RT}{4F}\right) \ln\left(\frac{P'O_2}{P''O_2}\right) \tag{2.9}$$

where, *R* is universal gas constant 8.3144 JKmol⁻¹, *T* is temperature, *F* is Faraday constant (9.648534 × 10⁴ Cmol⁻¹), $P'O_2$, $P''O_2$ is oxygen pressure at high and lower region, respectively.

Ionic transference number, t_{ion} was calculated from the equation shown below:

$$t_{\rm ion} = E_{\rm observed} / E_{\rm theoretical} \tag{2.10}$$



Figure 2.14: Schematic diagram of sample for EMF measurement.



Figure 2.15: Schematic view of *EMF* measurement.

2.3 Results and discussions

2.3.1 Phase confirmation and sample density

XRD patterns of all prepared samples are shown in Fig. 2.16 and Fig. 2.17. All data agreed well with the JCPDF (34-0394) data without any presence of secondary phase, confirming that all samples possess single phase.

Lattice parameter, unit volume, density are tabulated in Table 2.5. Lattice parameter values are obtained from [11,23-25]. All the prepared samples were dense where the relative densities were over 95%, which achieve the requirement for electrolyte material for SOFC.

 Table 2.5: Lattice parameter, lattice volume, theoretical density, observed density and relative density of prepared samples.

Lattice	Volume,	Density _{th} ,	Density _{obs} ,	Density _{rel} ,
parameter, Å	mm^3	g/cm ³	g/cm ³	%
5.417	158.96	7.233	7.0108	96.9
5.420	159.22	7.240	6.9305	95.7
5.422	159.40	7.251	7.0262	96.9
5.439	160.90	7.117	7.0542	99.1
5.427	159.88	7.167	6.9479	96.9
5.429	159.93	7.170	6.9858	97.4
5.443	161.21	7.118	6.7871	95.4
	Lattice parameter, Å 5.417 5.420 5.422 5.439 5.427 5.427 5.429 5.443	LatticeVolume,parameter, Åmm³5.417158.965.420159.225.422159.405.439160.905.427159.885.429159.935.443161.21	LatticeVolume, mm³Density _{th} , g/cm³parameter, Åmm³g/cm³5.417158.967.2335.420159.227.2405.422159.407.2515.439160.907.1175.427159.887.1675.429159.937.1705.443161.217.118	LatticeVolume, mm³Density _{th} , g/cm³Density _{obs} , g/cm³parameter, Åmm³g/cm³g/cm³5.417158.967.2337.01085.420159.227.2406.93055.422159.407.2517.02625.439160.907.1177.05425.427159.887.1676.94795.429159.937.1706.98585.443161.217.1186.7871



Figure 2.16: XRD patterns of GDCs.



Figure 2.17: XRD patterns of SDCs.

2.3.2 Optimized thermal environment for impedance measurement under millimeter-wave irradiation heating

The way a material is heated by MW depends on the material itself including its shape, size, and dielectric properties, as well as the nature of the MW equipment used including the surround thermal environment. Therefore, in this experiment, to identify thermal environment for measurement of conductivity under MMW irradiation heating that provide optimum MMW effect on sample, the influence of upper susceptor thickness, lower susceptor thickness, fiber board size and fiber board configuration was investigated, and the results were discussed below.

The results of conductivity of 20SDC under nine different thermal environments (refer Table 2.4) are shown in Fig. 2.18. For comparison, conductivity measured under conventional heating is also plotted here. All measurements under MMW irradiation exhibit higher conductivity value than under conventional heating with noticeable different enhancements. Enhancements of conductivity at 400 °C differ in wide range which is 3 to 9 times showing that the effect of MMW heating is greatly dependence on surrounding ambiance.

For materials that have poor absorptivity, i.e metals may not couple with MW power efficiently especially at room temperature, thus heating process at the initial stage is difficult. Material that possesses high dielectric loss, commonly silicon carbide (SiC) is used as a susceptor where it works as a converter of MW energy into heat. Then the heat will be used to heat the low dielectric sample by heat transfer [26-30]. In contrast, in this study, doped CeO₂ is a dielectric material that able to absorb MMW energy well and is heated readily from low temperature. Susceptor used in this work was 5SDC which has similar absorption property with samples. During the MMW irradiation heating, sample and suceptors were heated simultaneously. Due to self-heating, sample was heated internally, resulted in temperature gradient between the inner part and surface. If no susceptor was used, temperature gradient will be larger at high temperature because of the heat loss by radiation from the surface to the surrounding. Susceptor provided external heating source, so that homogenize temperature distribution within the sample could be achieved. The trade-of relationship among MMW heating and heat loss, as illustrated in Fig. 2.19, results in the optimum susceptor thickness which provides maximum MMW effect and minimum heat loss.



Figure 2.18: Conductivity of 20SDC under various thermal environment.



Figure 2.19: Energy absorbed and loss by sample under millimeter-wave irradiation heating, using (left) thick susceptor, (right) thin suceptor.

To give clear view on effect of each environment, results of respective parameters dependence of conductivity in lower temperature range are shown separately in Fig. 2.20, 2.21, 2.22 and 2.23, for the influence of the thickness of upper susceptor, the thickness of lower susceptor, fiber board size, and fiber board configuration, respectively. Dashed lines indicate the value of conductivity obtained from conventionally heated sample at each temperature.

Effect of upper susceptor thickness

Firstly, as shown in Fig. 2.20 the effect of upper susceptor thickness of 1.0 mm, 2.0 mm and 3.0 mm which corresponding to Environment 1, 2 and 3 (refer Table 2.4), respectively were studied. It is significant that conductivity value can be controlled by adjusting the thickness of the susceptor at upper side, where it can be seen that using different thickness resulted in different conductivity. Susceptor with thickness of 2.0 mm shows highest enhancement at all temperatures. Using 2.0 mm upper susceptor could allow relatively more MMW energy to interact directly with sample and offer better prevention of heat radiation. When using upper susceptor with thickness of 1.0 mm, although direct MMW interaction was larger, the heat radiation was also large so that the overall MMW heating effect was lower, leads to lower conductivity. In contrast, for upper susceptor of 3.0 mm, the heat radiation was prevented well but the benefit of MMW self-heating was reduced, resulted in lower conductivity. In conclusion, upper susceptor with thickness of 2.0 mm.



Figure 2.20: Conductivity of 20SDC under various upper susceptor thickness.

Effect of lower susceptor thickness

Fig. 2.21 shows the result of conductivity dependence on lower susceptor thickness of 3.0 mm, 3.5 mm and 3.8 mm, which corresponding to Environment 4, 5, and 6 (refer Table 2.4), respectively. Thinner lower susceptor resulted in lower conductivity compared thicker lower susceptor. Same explanation as influence of upper thickness can be given where, the thinner the susceptor, the larger the heat loss, thus lowered the effectiveness of MMW heating. Increasing the thickness of the lower susceptor from 3.0 mm to 3.5 cm increased the conductivity, but further increase up to 3.8 cm did not show any significant change.

From the results of the effect of upper and lower thickness on the conductivity, it indicates that susceptor with specific thickness can maximize the prevention of heat radiation from sample surface, thus minimize thermal gradient between surface and inner part of sample, as well as maximize the effect of MMW irradiation directly to the sample, which consequently leads to effective MMW heating.



Figure 2.21: Conductivity of 20SDC under various lower susceptor thickness.

Effect of fiber board size

The results of the influence of size of alumina fiber board on the conductivity which measured under Environment 2, 6, and 7 (refer Table 2.4) are shown in Fig. 2.22. Obtained result shows no significant change was observed on conductivity value regardless of fiber board size, even though smaller fiber board was expected to give higher conductivity due to high degree of penetration of MMW irradiation to the sample. Alumina fiber board has low thermal conductivity (0.0014 W/cm°C) and transparent to MMW due to low dielectric loss so it can ensure penetration of MMW energy with negligible decreasing intensity [16]. These characteristics enable alumina used as thermal insulator to keep sample temperature up to 1000 °C for conductivity measurement. It can be said that alumina fiber board that had been used in this work is porous enough to allow penetration of MMW energy to reach sample and it also free from impurity that might absorb MMW energy, which can reduce percentage of energy to be absorbed by sample. In fact, prior to measurement, the fiber board was heat-treated at 1000 °C for 1 h to release unnecessary organic impurities.



Figure 2.22: Conductivity of 20SDC under various fiber board size.

Effect of configuration of fiber board

Fiber board configuration plays vital influence on the heating effectiveness. Results from measurement under Environment 2, 8 and 9 (refer Table 2.4) to study this effect can be seen from Fig. 2.23. Result shows that different fiber board design lead to remarkable difference in conductivity, especially when fiber board with two open channels was used, conductivity dropped drastically when compared to the result obtained by using fiber board without open channel. Fiber board with open channel was expected to increase the MMW energy dose directly onto sample. However, this configuration resulted in larger heat loss from the sample, thus resulted in ineffective MMW heating. Therefore, fiber board without open side was found to be desirable to minimize heat loss from the sample arrangement.



Figure 2.23: Conductivity of 20SDC under various fiber board open channel.

The influence of upper and lower susceptor thickness, fiber board size, and fiber board configuration on the MMW effect and heat radiation is concluded in Table 2.6:

 Table 2.6: Conclusion of the effectiveness of each parameter on MMW heating and heat radiation during MMW irradiation heating.

	Thick	Thin	Fiber board	Fiber board	Fiber board
	susceptor	suceptor	No channel	One	Two
				channel	channels
MMW effect	Low	High	High	High	High
Heat radiation	Low	High	Low	Moderate	High

It can be concluded that, combining the optimum susceptor and fiber board which leads to high efficient MMW heating can results in high conductivity. By analyzing results obtained here, Environment 2, shown in Table 2.7 which resulted in the highest conductivity was chosen to be used for further conductivity measurement under MMW irradiation.

Upper susceptor	Lower susceptor	Fiber board size,	Open channel on
thickness, mm	thickness, mm	mm^3	fiber board
2.0	3.5	6.0 imes 6.5 imes 2.0	nil

Table 2.7: Optimized thermal environments for conductivity measurement under MMW irradiation heating.

2.3.3 Conductivity enhancement under MMW irradiation heating

Conductivity measurement under MMW irradiation heating for 10GDC, 15GDC, 20GDC, 10SDC, 15SDC, 20SDC and 25SDC was performed under previously determined optimal thermal environment (refer Table 2.7) and the results are discussed here.



Figure 2.24: Frequency dependences of the measured complex conductivities (σ' and σ " represents real part and imaginary part, respectively) and their fitted spectra by universal dielectric response (UDR) for the 15GDC at 600 °C under conventional (Conv) and millimetre-wave (MMW) irradiation heating. σ_{dc} is bulk conductivity.

Conductivity values were determined by UDR fitting. An example of typical curve fitted by using UDR is presented in Fig. 2.24. Data shown here are for conductivity of 15GDC obtained under conventional and MMW irradiation heating at 600 °C, which is used as a representative of other samples. The intrinsic bulk conductivity, σ_{dc} corresponds to the real part of complex impedance, σ' at d.c frequency. For ionic conductivity, frequency corresponding to the ion hopping is obtained approximately 10^4 - 10^5 Hz for real part of complex conductivity. It can be seen in this figure that data were well fitted by the UDR in this frequency range. Furthermore, it can also be noticed that, the σ_{dc} obtained when measured under MMW irradiation heating was higher compared to that measured under conventional heating.

Same approach was used to determine the σ_{dc} for data obtained at other temperatures and samples, and curves were similar. Determined data were compiled in Arrhenius plots, as can be seen in Fig. 2.25 and Fig. 2.26 for GDCs and SDCs, respectively. Results from conductivity under conventional heating are comparable with the data reported in literatures [23,31]. As can be seen from these figures, conductivity improved significantly when measured under MMW irradiation heating for all measured samples, especially at lower temperature. Conductivity enhancement was calculated for each sample, as follow:

$$\text{Enhancement} = \sigma_{\text{MMW}} / \sigma_{\text{Conv}}$$
(2.11)

At 400 °C, for example, conductivity for conventionally heated 10GDC was 5.71×10^{-4} S/cm, and when measured under MMW irradiation heating, the conductivity increased to 7.29×10^{-3} S/cm, recorded the enhancement of conductivity was approximately 13 times. Conductivity of 15GDC and 20GDC enhanced slightly lower which is 10 and 11 times, respectively. The degree of enhancement was also dependent on dopant concentration, as we can see this effect profoundly in SDCs, where conductivity of 10SDC, 15SDC, 20SDC and 25SDC increased by 4, 10, 9, and 3 times, respectively under MMW irradiation heating. However, the conductivity enhancement decreased with increasing temperature, which can be explained by higher heat radiation at higher temperature, resulted in lower effectiveness of MMW heating.



Figure 2.25: Conductivity of GDCs under conventional and MMW irradiation heating. Conductivity enhancement at 400 °C is shown by the upside arrow.



Figure 2.26: Conductivity of SDCs under conventional and MMW irradiation heating. Conductivity enhancement at 400 °C is shown by the upside arrow.

In order to find the optimum structure that provide highest conductivity in conventional and MMW irradiation heating, conductivity dependence on dopant concentration was compared between these two methods. The results for the isothermal plots of conductivity as a function of dopant concentration at 400 - 600 °C under conventional and MMW irradiation heating are shown in Fig. 2.27, 2.28, 2.29 and 2.30. It is well-known that in conventional heating, conductivity is strongly dependent on amount of defect which directly resulted from dopant concentration which associates with vacancies concentration and trapping effect of the oxygen vacancies by the dopant ions. As can be seen in Fig. 2.27 and 2.28 for GDCs and SDCs, respectively, from lower to optimum dopant concentration, increasing the dopant concentration resulted in increasing vacancies, thereby improved the conductivity, which shows that oxygen vacancies concentration was the predominant effect that contributes in conductivity process. At composition of 15GDC and 20SDC, samples achieve optimum conductivity and further dopant addition decreased the conductivity. The decrease in conductivity after optimum dopant concentration can be explained by the interaction between dopant-vacancy clusters (Gd/Sm_{Ce}- $V_0^{\bullet \bullet}$) which give the trapping effect that hindered the hopping process [32]. As the result, conductivity under conventional heating increased in the following order; $\sigma_{dc} 20$ GDC $< \sigma_{dc} 10$ GDC $< \sigma_{d$ $\sigma_{\rm dc}$ 15GDC for GDCs and $\sigma_{\rm dc}$ 10SDC $< \sigma_{\rm dc}$ 15SDC $< \sigma_{\rm dc}$ 25SDC $< \sigma_{\rm dc}$ 20SDC for SDCs.

Meanwhile under MMW irradiation heating, besides defect structure another important factor that was expected to contribute in conduction process is energy supplied from the MMW, which dependent on how the materials can absorb the energy from MMW source and use it in the process. As plotted in Fig. 2.29 and 2.30, same order was observed except for 15SDC and 25SDC, where conductivity of 15SDC was higher than 25SDC resulted in change of the order to $\sigma_{dc}10SDC < \sigma_{dc}25SDC < \sigma_{dc}15SDC < \sigma_{dc}20SDC$. The switch between 15SDC and 25SDC is due to different degree of conductivity enhancement influenced by MMW. For example at 400 °C conductivity of 15SDC and 25SDC enhanced by 10 and 3 times, respectively. This result shows that MMW effect was larger in 15SDC. Consequently, the conductivity of 15SDC outperformed the conductivity of 25SDC.



Figure 2.27: Composition dependence of conductivity for GDCs under conventional heating.



Figure 2.28: Composition dependence of conductivity for SDCs under conventional heating.


Figure 2.29: Composition dependence of conductivity for GDCs under millimeter-wave irradiation heating.



Figure 2.30: Composition dependence of conductivity for SDCs under millimeter-wave irradiation heating.

Table 2.8 compares the similar conductivity value obtained under conventional and MMW irradiation heating for optimum composition of GDCs and SDCs which is 15GDC and 20SDC, respectively. Conductivity value for 15GDC and 20SDC obtained at 550 °C under conventional heating was similar with the value obtained at 400 °C under MMW irradiation heating. This result shows that by using MMW as the heating source, conductivity of sample can be improved at lower temperature.

Sample	$\sigma_{\rm MMW}$ at 400 °C,	$\sigma_{\rm Conv}$ at 550 °C,
	Scm^{-1}	Scm^{-1}
15GDC	8.975×10^{-3}	8.701×10^{-3}
20SDC	6.257×10^{-3}	8.465×10^{-3}

 Table 2.8: Comparison of conductivity value of 15GDC and 20SDC under conventional heating and millimeter wave irradiation heating.

Millimeter-wave effect on the activation energy of ion conduction process

The influence of microwave on materials processing which leads to different results from that obtained from other methods has been reported due to different in activation energy, E_a , where researchers found that apparent activation energy obtained from microwave processing was smaller than that obtained from other methods [33]. The E_a is a important thermodynamic parameter in thermal-induced processes including ion conduction which can give a insight into mechanism that involves during the processes. The reduction of E_a in microwave processing is usually explained in regards of thermal effect providing local heating which causes the processes to be more rapid, or non-thermal effect that improves atomic diffusion.

In this study, the E_a in ionic conduction process is the minimum energy that ion must possesses in order to migrate in its lattice. For ionic conduction process, E_a can be determined from the slope of the conductivity graph, based on Arrhenius equation [34]:

$$\sigma T = \sigma_0 \exp\left(-\frac{E_{\rm a}}{kT}\right) \tag{2.12}$$

where, σ is ionic conductivity, σ_0 is pre-exponential factor, *T* is absolute temperature, E_a is total activation energy and *k* is Boltzmann constant.

There are two energies that contribute to total activation energy in ionic conduction, i.e. charge carrier migration energy, $E_{\rm m}$ and ion-defect clusters dissociation energy, E_0 . Ion-defect cluster in doped CeO₂ is cation-vacancy cluster. In wide temperature range, transition temperature appears where gradient change in Arrhenius plot can be observed. At higher temperature ionic conductivity depends only on $E_{\rm m}$ because all the clusters are dissociated and mobile. Lower than transition temperature, conductivity depends on $E_{\rm m} + E_0$, leading to a steep slope in Arrhenius plots. In other words, there is conductivity drop or discrepancy compared with extrapolated line of higher temperature plot to lower region, reflecting the E_0 . The discrepancy equals zero at temperature region higher than transition temperature, and it becomes larger with decreasing temperature. Therefore, $E_{\rm m}$ and E_0 can be separately calculated as described:

At higher temperature region:

$$E_{\rm a} = E_{\rm m} \tag{2.13}$$

At lower temperature region:

$$E_{a} = E_{m} + E_{0} \tag{2.14}$$

In this work, doped CeO₂ shows transition temperature at 600 °C where it can be noticed that the gradient of Arrhenius plots changed at this temperature regardless the dopant types and dopant concentration. Nevertheless, the degree in the gradient change depends on dopant type where we can see the gradient change was more obvious in GDCs compared to SDCs. In addition, compositions with low dopant content show smaller gradient change, which was apparent in SDCs. An example of gradient change is given in Fig. 2.31 for 10GDC. Therefore, E_0 was calculated from gradient at below 600 °C, meanwhile E_m was determined from gradient at above 600 °C.

As can be seen from the Arrhenius plots, at lower temperature region, E_0 calculated from the gradient obtained under conventional and MMW irradiation heating, denoted as $E_{0(\text{Conv})}$ and $E_{0(\text{MMW})}$, respectively have noticeable difference. The reduced E_0 under MMW irradiation heating resulted in higher conductivity because lower energy must be overcome by ions to become mobile. At higher temperature region, $E_{\rm m}$ obtained from gradient under conventional heating, denoted as $E_{0({\rm Conv})}$ was slightly higher compared to that obtained under irradiation heating, denoted as $E_{0({\rm MMW})}$, showing that reduction in $E_{\rm m}$ also has certain contribution to the conductivity enhancement under MMW irradiation heating. Fig. 2.32a and 2.32b compare the $E_{0({\rm Conv})}$, $E_{0({\rm MMW})}$, $E_{0({\rm Conv})}$ and $E_{0({\rm MMW})}$. It is apparent from these graphs that both $E_{\rm m}$ and E_0 were lower for samples measured under MMW irradiation heating compared to that under conventional heating without any exception even though the enhancement was as low as three times.



Figure 2.31: Gradient change in Arrhenius plot of 10GDC.





Figure 2.32: Activation energy obtained from conventional heating and millimeter-wave heating: a) for Gd-doped CeO₂, b) for Sm-doped CeO₂. $E_{m(conv)}$: migration energy obtained from conventional heating, $E_{0(conv)}$: dissociation energy obtained from conventional heating, $E_{m(MMW)}$: migration energy obtained from millimetre-wave irradiation heating $E_{0(MMW)}$: dissociation energy obtained from millimetre-wave irradiation heating.

Sample	$E_{\rm m(MMW)}/E_{\rm m(Conv)}$	$E_{0(\text{MMW})}/E_{0(\text{Conv})}$
10GDC	0.78	0.11
15GDC	0.78	0.10
20GDC	0.84	0.10
10SDC	0.92	0.05
15SDC	0.80	0.26
20SDC	0.80	0.26
25SDC	0.93	0.33

Table 2.9: Ratio of migration energy, $E_{\rm m}$ and dissociation energy, E_0 obtained from millimetre-wave irradiation to the conventional heating for each sample.

Table 2.9 presents the ratio of activation energy obtained from MMW irradiation heating to that obtained from conventional heating, which is an indicator to give insight into the difference of energy value obtained from these heating methods, where the larger the ratio the smaller the difference between the energies. In another way, it illustrates energy reduction when heated under MMW irradiation heating, where larger the ratio, smaller the energy reduction. As can be seen from the table all samples show the same tendency where $E_{m(MMW)}/E_{m(Conv)}$ were significantly larger than $E_{0(MMW)}/E_{0(Conv)}$. $E_{m(MMW)}/E_{m(Conv)}$ were in the range of 0.78 to 0.93, indicating that the E_m obtained from MMW irradiation heating. On the other hand, $E_{0(MMW)}/E_{0(Conv)}$ was small, in the range of 0.05 to 0.33 demonstrates that there was large reduction of E_0 when heating under MMW irradiation heating. From this result, it can be concluded that E_0 was greatly affected by MMW irradiation for both GDCs and SDCs, showing that the predominant factor leading to higher conductivity for MMW irradiation heated samples is the reduction of E_0 .

Observed phenomena from this study in doped CeO_2 is different from the reported data for stabilized ZrO_2 , where it is found that, only E_{m} was profoundly reduced under MMW heating [35,36]. It shows that although both materials have fluorite structure, MMW effect might be different depends on the nature of the type of cation, such as interaction between cation and oxygen ion in the lattice structure. In the case of stabilized ZrO_2 , the influence of MMW irradiation heating on the E_0 is relatively very small, thus reduction in E_{m} due to MMW energy becomes the dominant factor that reduced the total activation energy, resulted in improvement in conductivity. Such reduction in E_{m} by MMW effect also occurred in doped CeO₂. In contrast, in doped CeO₂, apart from reduction in E_{m} , an additional significant reduction in E_0 also contributes to total reduction in E_{a} . Even though comprehensive investigation have yet to be done on MMW effect including the electric and magnetic components of MMW, considering the possibility of doped CeO₂ to be reduced under MMW could explain the individual results shown by stabilized ZrO_2 and doped CeO_2 . Reduction of Ce^{4+} to Ce^{3+} produces electrons which distribute in lattice and interact with other charges. When reduction occurs, the concentration of clusters of negatively charged Gd³⁺/Sm⁴⁺ in Ce⁴⁺ cation site and positively charged oxygen vacancy decreases, causing the E_0 to reduce. A recent study found that microwave energy improves the reduction of Cu²⁺ in CuO to Cu⁺ producing Cu₂O by direct transformation of electromagnetic energy to chemical energy [37]. In addition, it has been reported that the association energy of electron is lower than association energy of ion meaning that less energy required by electron to overcome the interaction before it migrates [38,39]. This interpretation corresponds with the result of reduction of E_0 in this work. Therefore, the additional reduction of E_0 in doped CeO₂ might be due to the increased electron concentration induced by MMW. On the contrary, such phenomenon might not occur in stabilized ZrO₂ due to high stability of Zr^{4+} . This explains the difference of influence of MMW on the association energy in doped CeO_2 and ZrO_2 .

A possible explanation for this finding is that reduction in activation energy is attributed to the absorbed MMW energy which becomes one of energy contributor in conduction process apart from thermal energy. Numerous studies in regards to the enhancement of mass transport and solid state reaction rates in microwave processing have been reported. The researchers mostly explain the observation of reduction in activation energy as the result of microwave non-thermal effect that leads to enhancement in the process involved [37,40,41]. Similar to the present study, in the case of same conductivity value, as illustrated in Fig. 2.33 in conventional heating, the only energy source for conduction process to occur originates from thermal energy. Meanwhile, in MMW heating, an additional energy absorbed from MMW plays important part to facilitate the charge carriers transport, thus resulted in lower apparent activation energy.



Figure 2.33: Reaction coordinates diagram of conduction process under conventional and millimeter irradiation heating for same conductivity value.

Verification of millimeter-wave effect on conductivity of doped CeO₂

The existence of microwave specific effects which resulted in distinct phenomena from what can be attained under conventional heating have been discussed in literatures. The ionic conductivity in doped CeO_2 studied in this work was found to improve due to reduction in activation energy. Therefore, the origin of the reduction in activation energy should be clarified.

Two possible phenomena in diffusion process under electromagnetic-wave irradiation can be differentiated between [42]:

1. Localized heating effect, P which is given by

$$P \propto \varepsilon_0 \varepsilon^{''} |E|$$
 (2.15)

2. Ponderomotive driving force, PMF, which is given by

$$PMF \propto \left(\frac{\varepsilon}{2}\right) \frac{\partial |E|}{\partial x}$$
 (2.16)

where ε_0 is free space permittivity, ε'' is dielectric loss factor, ε is dielectric constant and *E* is electric field.

From these equations, it can be described that, firstly, for localized heating model, it describes that under constant electric field, energy flow rate is directly proportional to the dielectric loss factor, ε'' of material. Localized heating occurs when the reaction molecules absorb energy from microwave then selectively enhance the process that take place. Secondly, based on the *PMF* model given, the exerting force is directly proportional to the dielectric constant, ε of material. *PMF* is explained as a nonlinear electromotive force that a charged particle experiences in the presence of oscillating electromagnetic fields. Ponderomotive forces can cause particle acceleration and energization [43].

To verify the effect of localized heating on the conductivity enhancement of doped CeO₂, the absorptivity of samples under constant electric field was investigated by observed the heating behavior. The heating behaviors of GDCs and SDCs is shown in Fig. 2.34 and Fig. 2.35, respectively. From the absorption property measurement, temperature elevation as a function of MMW irradiation time was obtained and heating rate of each sample was determined from the gradient of these curves. Heating rate here represents the dielectric loss factor, ε ["] which is the ability of the material to convert absorbed MMW energy to thermal energy.

Heating rate was used to clarify the correlation between conductivity enhancement and localized heating phenomenon. Graph of conductivity enhancement versus heating rate is plotted in Fig. 2.36. Correlation between conductivity enhancement and localized heating interpreted using correlation coefficient, r that measure the strength of the linear association between conductivity and localized heating. The greater the value of r, the stronger the relationship and for the positive relationship, the strongest relationship is indicated by r equals 1, meanwhile requals zero for the weakest relationship. Data obtained in this work were in random pattern and r was very small which is 0.125, showing that there is almost no correlation between conductivity enhancement and heating rate. Thus, it is sufficient to say that the conductivity enhancement of GDCs and SDCs is not due to localized heating phenomenon.



Figure 2.34: Heating profile of GDCs under constant millimeter-wave power.



Figure 2.35: Heating profile of SDCs under constant millimeter-wave power.



Figure 2.36: Conductivity enhancement ($\sigma_{dc}(MMW)/\sigma_{dc}(Conv)$) at 400 °C versus heating rate of samples irradiated under constant millimeter-wave power.

K. I. Rybakov and J. H. Booske et al. have demonstrated ion diffusion in solid under electromagnetic-wave irradiation and explained the *PMF* phenomenon induces driving force on mobile charges and mass transport in solids [44-46]. In the present study, MMW effect was found to be more pronounced in cation-vacancy dissociation energy, which the initial process for charge carriers before becomes mobile in crystal lattice. In the case of *PMF* phenomenon, as shown in Eq. 2.16, if the power is constant, higher ε results in larger *PMF*. It has been reported that, at frequency of 24 GHz and higher yttria stabilized ZrO₂ with two different additives having high and low dielectric constant, the ε " values for both samples were similar and unchanged at such high frequency. In contrast, value of ε was larger for YSZ contains additive having high dielectric constant. Higher ε resulted in an improvement in strain rate under MMW irradiation heating, proving that the improvement was attributed to *PMF*, while the effect of localized heating remained [47]. In addition, it also has been reported that Ti_{0.5}W_{0.5} with Gd₂O₃ additive showed somewhat larger microwave dielectric constant compared to Sm₂O₃ additive [48]. In this study, slightly larger conductivity enhancement of GDCs than SDCs might be due to higher dielectric constant of GDCs compared to SDCs. Taken together, it shows that the conductivity enhancement in this work could be attributed to dielectric constant, suggesting the role of *PMF* in promoting conductivity which results in higher conductivity in doped CeO_2 under MMW irradiation heating. From the viewpoint of MMW non-thermal effect which explains that when molecules absorb energy from MMW, the energy will not immediately convert to heat but instead induce additional driving force (*PMF*) which assist ion mobility in diffusion process.

2.3.4 Ionic transference number, t_{ion}

Ionic transference number, t_{ion} in electrolyte describes the fraction of the total current carried by oxygen ion. For the ideal electrolyte for SOFC, it must shows t_{ion} equals to 1 relative to theoretical value determined by Eq. 2.9. Electrolyte possesses t_{ion} deviating from 1 is known as mixed conductor due to charge carriers are mixed of ion and electron.

In order to investigate the t_{ion} , the electromotive force, *EMF* was measured at open circuit or without any ohmic load for 20SDC as the representative of doped CeO₂ samples in this study due to high conductivity in both conventional and MMW irradiation heating. The *EMF* of 20SDC measured under various oxygen partial pressure, $P'O_2:P''O_2 = 0.500:0.025$, 0.500:0.050, 0.500:0.075 and 0.500:0.100 at temperature range 600-1000 °C is presented in Fig. 2.37. Obtained *EMF* showed good relation with temperature and oxygen partial pressure as predicted by Eq. 2.9, where *EMF* increased with temperature increase, and increasing the oxygen partial pressure at one electrode side decreased the *EMF*.

From the *EMF* values, the t_{ion} was determined using Eq. 2.10 and the result obtained at 600-1000 °C is shown in Fig. 2.38. t_{ion} at all temperatures was found to be unity under measured conditions which means *EMF* obtained in this work has the same value as expected for SOFC electrolyte that obey the Nernst-Einstein equation. Therefore, the electrical conduction in measured oxygen pressure range at temperatures between 600-1000 °C was proved to be purely ionic.

However, under reducing atmosphere or too low oxygen partial pressure, $< 10^{-15}$ atm, many studies have reported that the *EMF* of doped CeO₂ deviated from theoretical value, due to unstable Ce^{4+} reduced to Ce^{3+} , consequently, electrons appears to involve in conduction process. Any electronic conductivity of the electrolyte would degrade energy efficiency of SOFC since the motion of electronic defects would translate to a short-circuiting current resulting in a loss in cell voltage [49-51]. Nevertheless, few studies have reported that the reduction of ceria based electrolyte could be suppressed by reducing operation temperature, operating cell with highly humidified fuel, co-doping in CeO_2 and coating of stabilized zirconia thin film on the CeO_2 surface [52,53].



Figure 2.37: *EMF* for oxygen concentration cell: $P'O_2$ (high pressure), Pt |20mol% doped CeO₂ |Pt,O₂, ($P''O_2$ (low pressure)) as a function of temperature at various $P''O_2$ (low pressure). $P'O_2$ was constant at 0.5 atm.



Figure 2.38: The ionic transference numbers, t_{ion} as a function of temperature at various $P''O_2$ (low pressure). $P'O_2$ was constant at 0.5 atm.

2.4 Summary

Single phase polycrystalline 10-20 mol% Gd-doped CeO₂ (abbreviated as 10GDC, 15GDC, 20GDC) and 10-25 mol% Sm-doped CeO₂ (abbreviated 10SDC, 15SDC, 20SDC, 25SDC) having relative density over 95% of theoretical density were successfully synthesized via solid state conventional method. Electrical conductivity of the samples was measured under conventional heating in tube furnace and under millimeter-wave (MMW) irradiation in permanent magnetic gyrotron system (PMGS) with 24 GHz, 3kW, and the results were compared.

Under MMW irradiation heating, sample's thermal environment was found to have significant influence on the conductivity of the sample. By changing the configuration of measurement setup to obtain different thermal environment by using various susceptor thickness and fiber board design, the conductivity could enhanced between 3 to 9 times for 20SDC. The enhancement was attributed to the effectiveness of MMW irradiation heating which strongly depends on direct exposure of MMW to the samples that results in self-heating and heat loss by radiation from the samples to the surrounding. The higher the MMW effect and the lower the heat radiation lead to the efficacy of MMW irradiation heating, consequently increased the conductivity.

Using optimized thermal environment for conductivity measurement setup conductivity of all samples was measured. Conductivity for all samples under MMW irradiation heating was improved compared to that under conventional heating. Nevertheless, improvement was dependent on dopant types and dopant concentration, where it differs from 3 to 13 times. Overall, doped CeO_2 with Gd resulted in larger enhancement compared to Sm. Meanwhile, 15GDC and 20SDC show highest enhancement for respective dopant type. Results from activation energy indicates that cation-vacancy dissociation energy reduced significantly compared to migration energy under MMW irradiation heating. MMW absorptivity verified that conductivity enhancement has no correlation with heating rate, which represent the effect of localized heating on the conductivity. Therefore, it is suggested that conductivity enhancement of doped CeO_2 could be attributed to ponderomotive force (PMF) that presence in electromagnetic field, which provided an additional energy to facilitate ion conduction in crystal structure, consequently enhanced the conductivity.

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Chapter 3

Performance of single cell under millimeter-wave irradiation heating

3.1 Introduction

In previous chapter, the enhancement of ionic conductivity of Gd and Sm doped CeO_2 electrolyte under MMW irradiation was proven and discussed. To verify the practicality of using MMW energy in order to improve SOFC efficiency, a working fuel cell using those materials as the electrolyte should be fabricated and tested. Therefore, in this chapter, performance of a single cell under MMW irradiation heating was compared and discussed to that obtained under conventional heating. A single cell was fabricated and its overall performance was evaluated by using the most ubiquitous characterization technique, comparing the current density-voltage (*I-V*) and current density-power density (*I-P*) which provides an overall quantitative evaluation of cell performance. Example of typical *I-V* and *I-P* curve can be seen in Fig. 3.1. This curves give information about the maximum voltage available during zero current load or known as open circuit voltage (OCV), voltage and power generated at certain current, and maximum power which is commonly used during comparison of cells performance. Fuel cell is designed to operate at or below the maximum power density.



Figure 3.1: Typical current density-voltage (*I-V*) and current density-power density (*I-P*) of SOFC [1].

Nernst equation for H_2 - O_2 fuel cell with oxide ion conductor describes:

$$OCV = E_0 + \frac{RT}{2F} \ln \frac{P_{H_2} \cdot P_{O_2}^{-1/2}}{P_{H_2O}}$$
(3.1)

where E_0 represents the ideal electromotive force under standard conditions, F is the Faraday constant (96484 Cmol⁻¹), R is the gas constant (8.314 JK⁻¹mol⁻¹), T is absolute temperature, 2 is the number of electrons involved in the reactions and P is the partial pressures refer to the reactants and products in form of gas at the standard pressure of 1 atm.

In practice, when using mixed ion-electron conductor as the electrolyte such as doped CeO_2 , theoretical value of OCV can not be achieved due to electron leakage resulted from reduction of Ce^{4+} to Ce^{3+} . As described by Wagner's equation, OCV for mixed ion-electron conductor can be estimated by using following equations [2]:

$$\mathbf{OCV} = t_{\mathrm{ion}} \times \frac{RT}{4F} \ln \frac{P_{\mathrm{O_2}}'}{P_{\mathrm{O_2}}''}$$
(3.2)

$$t_{\rm ion} = \frac{R_{\rm e}}{R_{\rm i} + R_{\rm e}} \tag{3.3}$$

where P_{O_2}' and P_{O_2}'' are the partial pressures of oxygen at the cathode and anode, respectively, and R_i and R_e refer to the ionic and electronic resistances of the electrolyte, respectively. Generally, t_{ion} does not remain constant within the electrolyte. Therefore, Wagners equation is more appropriately expressed as follows:

$$OCV = \frac{RT}{4F} \int_{P_{O_2}'}^{P_{O_2}'} t_{ion} d\ln P_{O_2}$$
(3.4)

Voltage of an ideal cell would maintain while supplying current as determined by above equations, however a real fuel cell produces less voltage than predicted voltage. This phenomenon occurs due to irreversible losses or polarizations in the cell. There are three major losses that contribute to voltage losses, namely ohmic loss, activation loss, and concentration loss. Careful data analysis may discriminates between the variation sources of loss within a cell. The real voltage output of a fuel cell can be written as:

$$V = V_{\rm theory} - \eta_{\rm ohm} - \eta_{\rm act} - \eta_{\rm conc}$$
(3.5)

where V is real output voltage, V_{theory} is thermodynamically predicted output voltage, and η_{ohm} , η_{act} and η_{conc} is ohmic loss, activation loss and concentration loss, respectively.

Each loss is briefly explanation as follows [3-5]:

1. Ohmic loss

Loss that caused by material resistance to ion-flow and electron-flow through the electrolyte, and the anode and cathode, respectively.

2. Activation loss

Loss that represents voltage loss to overcome the activation barrier associated with the electrochemical reactions at anode and cathode.

3. Concentration polarization

Loss due to mass transport, usually associates with depletion of charge carrying reactants caused by slow diffusion from the bulk of the gas channels through the porous electrodes.

To date, majority of fuel cell fabrication is based on electrolyte-supported, cathode- supported, anode-supported or metal-supported cell. The design of the fuel cell has strong influence on the cell polarizations, thus polarization curve displays different shape depends on the design. In this study, single cell was fabricated as electrolyte-supported cell. This type of cell utilizes a thick electrolyte to provide mechanical support for thin anode and cathode. High efficiency of the cell can be achieved by minimization of ohmic resistance of the electrolyte.

Examples of performance and polarization curves of electrolye-supported and anode- supported cell having comparable cell thickness are given in Fig. 3.2 and 3.3, repectively [6]. It can be seen that for electrolyte-supported cell, the highest polarization which contribute to voltage loss originates from ohmic loss, most probably from the ionic resistance in electrolyte. Overall performance of anode-supported cell is superior compared to electrolyte-supported cell due to thicker electrolyte of electrolyte-supported cell. From the polarization curve, particular component that results in high polarization can be identified to be focused on for improvement.

The scope and objectives of the experiments in this chapter are as follows:

- Synthesis electrolyte (Ce_{0.8}Sm_{0.2}O_{1.9} (20SDC)), anode NiO-20SDC and cathode (La_{0.8}Sr_{0.2}MnO₃ (LSM)) materials for SOFC cell.
- Fabricate single electrolyte-supported SOFC cell.
 Cell: H₂, NiO-20SDC | 20SDC | LSM, O₂
- 3. Optimize the cell and measurement system such as composition of anode material, cathode heat treatment temperature, electrolyte thickness and gas concentration.
- Measure and compare the overall cell performance under conventional and MMW irradition heating.



Figure 3.2: Cell voltage, polarization and power density vs. current density trace of electrolyte-supported cells [6].



Figure 3.3: Cell voltage, polarization and power density vs. current density trace of anode-supported cells [6].

3.2 Experimental

3.2.1 Preparation of electrolyte material

For powder and pellet preparation of electrolyte material same method as in 2.2.1 was used. The electrolyte materials used for measurement of single cell performance was $Ce_{0.8}Sm_{0.2}O_{1.9}$ (20SDC). Both flat surfaces of sintered pellet with diameter of approximately 16 mm were ground using Dr. Lap grit 9 μ m to obtain desired thickness and smooth surfaces.

3.2.2 Preparation of anode material:NiO-20SDC cermet

Nickel oxide (NiO)-20SDC cermet was chosen as anode material. By using NiO instead of Ni metal, the porosity can be increased during the reduction process [7]. NiO-20SDC cermet anode powder with various weight ratios (NiO:20SDC = 50:50, 60:40, 65:35 wt%) was synthesized by mechanically mixing NiO (Kanto Chemical Co.Inc Cica Reagent) and as-prepared 20SDC powder in an ethanol dispersion using planetary type mill (Pulverisette, Fritsch, Germany) for 1 h operated at 200 rpm. The slurry was then heated under natrium lamp to evaporate the liquid phase. Obtained mixture NiO-20SDC then was calcined for 1 h at 1000 °C with heating and cooling rate 5 °C/min.

The resultant powders were mixed with 1 wt% polyethylene glycol, PEG (Wako Pure Chemical Industries) (PEG:NiO-20SDC cermet = 3:7 wt%) using conditional mixer for 2 min in order to form anode paste.

3.2.3 Preparation of cathode material:La_{0.8}Sr_{0.2}MnO₃ (LSM)

 $La_{0.8}Sr_{0.2}MnO_3$ powder was prepared using the solid state reaction method by mixing stoichiometric amount of La_2O_3 (Kojundo Chemical Laboratory Co., Ltd.), SrCO₃ (Kojundo Chemical Laboratory Co., Ltd.) and MnCO₃ (Ishizu Seiyaku Ltd.) using planetary type mill (Pulverisette, Fritsch, Germany) for 1 h or 3 h operated at 200 rpm in ethanol dispersion. Obtained slurry was then heated under natrium lamp to evaporate the liquid phase. Next, obtained powder was calcined in muffle furnace (Koyo) for 950, 1100, 1200, 1250 or 1300 °C for 2, 6, or 8 h. The resultant powders were mixed with 1 wt% polyethylene glycol, PEG (Wako Pure Chemical Industries) (PEG:LSM= 3:7 wt%) using conditional mixer for 2 min in order to form cathode paste.

3.2.4 Fabrication of electrolyte supported single cell

20SDC was chosen as the electrolyte to study the performance of SOFC due to high conductivity in both conventional and millimeter-wave irradiation heating. The flat surface of approximately 16 mm in diameter of sintered 20SDC pellet was sufficiently ground to remove the roughness on the surface after sintering process. It is important for preparing of electrodes screen printing process. Cell prepared was electrolyte-supported cell.

LSM cathode paste was painted onto the other side of electrolyte and heat-treated at various temperature in the range of 1100 to 1300 °C for 1 or 4 h. NiO-20SDC cermet anode paste was painted onto the 20SDC pellet, then heat-treated at 1200 °C for 1h. This process was kept as consistence as possible to eliminate any cause that can resulted in different property in electrodes. The effective area of each electrode was 0.196 cm². Schematic view of prepared single cell can be seen in Fig. 3.4.



Figure 3.4: Schematic view of a) front view, b) upper view of electrolyte-supported single cell. Anode:NiO:Ce_{0.8}Sm_{0.2}O_{1.9}, electrolyte:Ce_{0.8}Sm_{0.2}O_{1.9}, cathode:La_{0.8}Sr_{0.2}MnO₃.

3.2.5 Sample setup and *I-V* measurement

Performance of single cell was done using SOFC Single Cell Evaluation Unit (FC-400H, CHINO Co., Japan). Schematic view of full SOFC test system is shown in Fig. 3.5. H_2 gas was generated using Hydrogen generator OPGU-2200 (Horiba Ltd., Japan.). H_2 and O_2 gas composition was controlled by mixing the gasses with N_2 gas. Gas flow rate was adjusted by using Log Mix flow meter.

Before cell was mounted in the system, Pt paste was applied on both electrodes to obtain better contact between the electrodes and Pt mesh current collector. A standardized conditioning procedure prior to measurement was performed because the performance can change drastically depending the factors like operating conditions and testing procedures. The conditioning process includes removing the remaining gas in the system, glass sealing, gas leakage inspection, reduction of NiO to Ni of anode material and cell stabilization. The experimental flow of conditioning process is shown in Fig. 3.7. Conditioning process was done in conventional tube furnace. Prior each measurement, the evaluation unit was purged with N₂ gas to eliminate remaining gases from previous measurement. Firstly, the unit was heated up to 850 °C and held for 1 h to melt the glass ring. Gas leakage test was performed to ensure complete tightness on both electrodes side by measuring the *EMF* using O₂ gas concentration cell. After that, N₂ was purged again for 2 h to remove remaining O₂ especially in fuel side. Next, NiO anode was reduced to Ni by flowing 50%H₂-50%N₂ at rate of 100 ml/min for 2 h at 800 °C.

After conditioning was performed, single cell performance test was done by flowing O_2-N_2 mixed gases into the cathode side, and H_2-N_2 mixed gases into the anode side. The overall gas flow rate was constantly kept at 200 ml/min at each electrode. Voltage response to the controlled current load was monitored by using Potentiostat/Galvanostat (HA-151, Hakuto Denko.Ltd., Japan). *I-V* data were collected at temperature range of 600 - 800 °C after allowing the system to stabilize for 30 min at each measuring temperature. Voltage data were recorded after 2 min holding time per current load.



Figure 3.5: Schematic view of SOFC test station.







(b) Schematic view of closed up of temperature measurement.



N₂ purge flow rate 100ml/min for 2 h

Gas sealing : 850 °C

Leak test: EMF measurement of $\rm O_2$ concentration cell, at 800 $^{\circ}\rm C$

 N_2 flow rate 100ml/min for 2 h

Reduction of anode NiO \rightarrow Ni: flow H₂ at 800 °C for 2 h

I-V measurement under conventional heating

I-V measurement under MMW irradiation heating

Figure 3.7: Experimental flow of conditioning process before cell test.

Evaluation of cell temperature

Measurement of temperature need to be precisely monitored to avoid data misinterpretation. Real temperature of the sample was monitored by thermocouple which was inserted carefully between sample and diffusion plate to get direct contact with sample. Schematic diagram of thermocouple setup can be found in Fig. 3.6b. During conventional heating only, another thermocouple was located inside the furnace chamber to monitor the inner furnace temperature. Sample temperature was found to be higher compared to furnace setup temperature by 30 to 40 °C. It has been reported that gas mixture flow during measurement may lead to exothermic reaction that resulted in overheating especially when using platinum mesh because it could give catalytic effect [8].

I-V measurement under conventional heating

After conditioning process, measurement of cell performance was proceeded under conventional heating by heating the cell in tube furnace.

I-V measurement under millimeter wave irradiation heating

After measurement of cell performance under conventional heating was done, sample together with cell evaluation unit was removed from furnace and set into PMGS MMW chamber for measurement of cell performance under MMW irradiation heating.

Under MMW irradiation heating, sufficient thermal insulation is important to ensure that heat can be kept at desired measurement temperature, up to 800 °C. The picture of thermal insulator setup used in this work can be found in Fig. 3.8. For temperature control inside the MMW applicator, ZrO_2 pellets were used to monitor temperature to avoid overheating. Special attention should be taken to the thermal insulation configuration to avoid deterioration of the components of the cell evaluation unit. The schematic view of the details is illustrated in Fig. 3.9. Ceramic felt and fiber board act as thermal insulator while allowed MMW energy to reach cell because they are MMW transparent materials. Aluminium foil was used as MMW reflector to cover the pyrex tube in order to avoid this part to be heated by MMW and heat transferred to the plastic tube inside the equipment.









3.3 Results and discussion

3.3.1 Phase confirmation of materials for single cell

Anode material

Figure 3.10 shows XRD patterns of NiO-20SDC cermet powder with different weight ratios, namely 50wt%NiO-50wt%20SDC, 60wt%NiO-40wt%20SDC and 65wt%NiO-35wt%20SDC calcined at 1000 °C for 1 h. XRD patterns for all powders shows mixed peak of NiO and 20SDC, which agreed well with JCPDF #47-1049 for NiO and JCPDF #34-0394 for CeO₂ data. Any additional peak was not observed and the intensity of NiO peaks in composite anode powders increased with increasing weight ratio indicates that there was no chemical reaction between NiO and 20SDC.



Figure 3.10: XRD patterns of NiO-SDC cermet powder with various weight ratios, calcined at 1000 °C for 1h.

Cathode material

XRD patterns for LSM powders prepared under various conditions are shown in Fig. 3.11 and 3.12. Results in Fig. 3.11 are for powder ball-milled for 1 h, while results in Fig. 3.12 are for powders ball-milled for 3 h. Powder calcined at 950 °C shows mixed phase of LaMnO₃ (JCPDS#50-0298) and La₂O₃ (JCPDS#05-0602), indicates that at this temperature reaction between raw materials was unable to be completed in order to obtain desired material. By increasing the temperature, peaks which belong to La₂O₃ gradually disappeared. Powders were also calcined at 1250 °C and above, however the powder melted, hence no XRD result for these samples are shown here. No significant different was found when increasing the ball-milling time and calcination time. As the powder which was ball-milled for 1 h and calcined at 1200 for 1 h shows peaks that identical to the JCPDS data for LaMnO₃ with only small one additional peak at around 30°, this powder was used as cathode material in this study.



Figure 3.11: XRD patterns of La_{0.8}Sr_{0.2}MnO₃ ball-milled for 1 h and calcined for 2 h at different temperatures.



Figure 3.12: XRD patterns of La_{0.8}Sr_{0.2}MnO₃ ball-milled for 3 h and calcined at different time and different temperature.

3.3.2 Optimization of single cell and system conditions

Prior to comparison study between single cell performance under conventional and MMW irradiation heating, preliminary experiment was performed to find the optimum cell and system conditions for *I-V* measurement. This includes the investigation of the influence of gas concentration, electrolyte thickness, ratio of NiO-20SDC anode cermet and cathode heat treatment temperature on the performance of the single cell. The preliminary experiment was done under conventional heating only, and temperature was based on the furnace setup temperature .

Firstly, cell was tested under different temperatures to ensure the cell evaluation unit and measurement system were properly set up. Figure 3.13 shows current density-voltage (I-V) curve and current density-power density (I-P) curve of a single cell tested at different temperatures under conditions tabulated in Table 3.1. These curves shows typical curves for SOFC performance test, where cell voltage decreased when current load was increased. The voltage drop in the cell is commonly associated with three major polarizations which are ohmic polarization, activation polarization, and concentration polarization. Each polarization is contributed from many factors such as type of materials, morphology and microstructure, system conditions

and so on. However, from the *I-V* and *I-P* only, it is difficult to differentiate each polarization, so that other measurement such as impedance spectroscopy is required to verify detailed cell polarization leads to voltage drop.

From the *I-P* curve, it can be observed that, maximum power density increased linearly with temperature, where the maximum power density were 9.76, 13.56, 18.28 and 23.33 mW/cm² at 700, 750, 800 and 850 °C, respectively. This can be explained by decreasing of overall polarization of the cell when temperature was increased, resulted in higher overall performance at higher temperature.

The OCV obtained was deviated from the value described by Nernst equation (Eq. 3.1). For the ideal cell, the OCV is expected to be approximately 1.2 V. This observed phenomenon has been widely reported in mixed conductor doped CeO_2 under reducing atmosphere due to electron leakage. Nevertheless, as illustrated in Fig. 3.14, the OCV increased when the temperature was reduced because the ionic transference number increased with decreasing temperature, accordingly the OCV increased with decreasing temperature [9,10]. This result was in agreement with Wagner's equation (Eq.3.2) and literatures where it has been reported that at 800 °C, OCV of 0.8 V could be achieved [2,11,12].

Table 3.1: Measurement conditions for cell tested under various temperature. Cell: H₂, NiO-20SDC | 20SDC | LSM, O₂

Electrolyte thickness	1 mm
Anode	50wt%NiO-50wt%20SDC
Anode heat treatment	1200 °C, 1 h
Cathode	LSM
Cathode heat treatment	1100 °C, 4 h
Fuel	10%H ₂ -90%N ₂
Oxidant	$50\%O_2 - 90\%N_2$
Measurement temperature	700-850 °C



Figure 3.13: Current density-voltage (open symbols) and current density-power density (closed symbols) curves of single cell measured at various temperature.

Effect of gas concentration

The influence of gas concentration on the cell performance was investigated by using 10%H₂-50%O₂, 50%H₂-50%H₂ and 90%H₂-90%H₂. These gases were diluted with N₂. Figure 3.15 illustrates the *I-V* curve and corresponding *I-P* curve obtained from using various gas concentrations at 800 °C using cell with 2 mm thickness electrolyte. The cell and system conditions are tabulated in Table 3.2. From the result, it can be seen that the cell performance was strongly dependent on fuel and oxidant concentration, where larger the concentration resulted in better performance. The highest power density of 5.30 mW/cm² obtained when using 90%H₂-90%O₂. Lowering both gases to 50%H₂-50%O₂ decreased the power density to 3.57 mW/cm², and further reduction of H₂ concentration to 10%H₂-50%O₂ leads to power density dropped to 3.30 mW/cm².

Fig. 3.16 shows the maximum power density obtained from various gas concentrations measured at 600 - 800 °C. This graph shows clearly that at all temperatures, maximum power


Figure 3.14: Temperature dependence of OCV.

density increased linearly with gas concentration, where the highest maximum power density was obtained when using the highest gas concentration; $90\%H_2-90\%O_2$. This phenomenon could be explained by overpotential at anode and cathode decreased when high H₂ and O₂ concentration was used, while depletion of the reactants at low gases concentration increased the electrodes polarization. A study using impedance microscopy has identified and differentiated cell ohmic polarization and electrodes polarization under different H₂ concentration. It has been reported that cell ohmic resistance was not affected under various H₂ concentrations, while electrodes polarization increased when H₂ concentration decreased [13].

It also can be observed that the OCV varies with gas concentration. As illustrated in Fig. 3.17, at 800 °C, higher OCV was obtained when the gas concentration was increased. The OCV was 0.75, 0.78 and 0.81 V for 10%H₂-50%O₂, 50%H₂-50%O₂, and 90%H₂-90%O₂, respectively. From this result, it can be concluded that, for high rate reaction to occur at cathode and anode, polarization at both electrodes should be lowered by using high concentration of

both fuel and oxidant.

Table 3.2: Measurem	ent conditions for cell	l tested under v	arious gas	concentrations.
	Cell: H ₂ , NiO-20SD	C 20SDC LS	SM, O_2	

Electrolyte thickness	2 mm
Anode	50wt%NiO-50wt%20SDC
Anode heat treatment	1200 °C, 1 h
Cathode	LSM
Cathode heat treatment	1100 °C, 4 h
Fuel	10,50,90%H ₂
Oxidant	50,90%O ₂



Figure 3.15: Current density-voltage (open symbols) and current density-power density (closed symbols) curves of single cell with 2.0 mm thick electrolyte at 800 °C for different gas concentration

Effect of ratio of NiO-20SDC cermet

Besides performance of the electrolyte itself, efficiency of SOFC also determined by the anode. In order to obtain high performance cell, cell must be fabricated from an efficient anode.



Figure 3.16: Dependence of maximum power density on the gas concentration at various temperatures.



Figure 3.17: Dependence of OCV on the gas concentration.

Apart from the catalytic activities, the performance of anode predominantly dependent on its microstructure and transport properties.

In this work, performance of cells fabricated using NiO-20SDC cermet anode with three different compositions, i.e 50wt%NiO-50wt%20SDC, 60wt%NiO-40wt%20SDC and 65wt%NiO-35wt%20SDC, was measured and compared. The result for this measurement is shown in Fig.3.18. It should be noted that LSM cathode painting temperature was different, either 1100 or 1200 °C, as written in the graph legend. To observe the influence of anode composition, comparison was made by also considering the cathode painting temperature.

Firstly, for the cells with LSM painted at 1100 °C, comparing the cell with 50wt%NiO-50wt%20SDC and 60wt%NiO-40wt%20SDC anode, cell with higher NiO content shows higher performance, where the maximum power density at 800 °C was 34.26 and 53.08 mW/cm², respectively. Secondly, for the cells with LSM painted at 1200 °C, comparing the cell with 60wt%NiO-40wt%20SDC and 65wt%NiO-35wt%20SDC anode, the former resulted in significantly higher maximum power density, 96.04 mW/cm², while the latter generated 73.06 mW/cm². Fig. 3.19 presents the relationships between NiO content and maximum power density at 600, 700 and 800 °C. It is clear that increasing Ni content up to 60wt% resulted in highest power density, and further addition of the NiO leads to decreased in performance.

Anode effective conductivity and its microstructure are essentially important to explain anode performance. Firstly, in regards of the effective conductivity, anode must be electrically conducting. When NiO in anode is reduced to Ni metal phase, it provides electronic conductivity, meanwhile, 20SDC is ionic conductor and also electronic conductor in reduced atmosphere. Therefore, the ratio of the NiO and 20SDC is important to achieve effective conductivity which is required to obtained high cell performance. A study on the relationship between Ni content and electrical conductivity revealed that there is effective conductivity threshold, where at certain amount of Ni, conductivity increases abruptly, and further addition of Ni do not significantly affect the conductivity [14].

On the other hand, high performance anode requires as much as reaction site, which is called as three-phase boundary (TPB). TPB must possesses sites that allow H_2 gas, electrons and oxygen ions to react. For this reason, microstructure of the anode plays vital role to improve

its performance. Anode must be porous in order to increase the TPB length. It has been reported that porosity is dependent on Ni volume, where the higher Ni volume, the higher the porosity due to shrinkage of NiO particles during the reduction process creates the pore sites. However, too high Ni content leads to agglomeration of the particles, which accompanied by reduction of the porosity [15,16]. Detailed investigation on the influence of anode microstructure on the anode polarization by impedance measurement has found that high porosity resulted in long TPB length, slightly increased ohmic polarization, and reduced activation and concentration polarization of the anode [17].

From these points of view, 50wt%NiO-50wt%20SDC anode showed lower performance compared to the others mainly because of low effective conduction and less porous due to low Ni content. Highest performance of the cell with 60wt%NiO-40wt%20SDC anode might be explained by NiO-20SDC content at this ratio reached the high electronic-ion conductivity. Also, when the Ni content was increased, porosity increased. These two reasons resulted in high performance. Meanwhile, in the case of cell with 65wt%NiO-350wt%20SDC anode, the cell showed lower performance compared to 60wt%NiO-40wt%20SDC even though this anode was expected to be more porous due to high NiO content. Lower performance might be resulted from particle agglomeration produced due to high Ni content. This phenomenon leads to decrease in porosity, thus decreased gas transport and reaction rates.

Electrolyte thickness	1 mm
Anode	50-65wt%NiO:50-35wt%20SDC
Anode heat treatment	1200 °C, 1 h
Cathode	LSM screen printing 1100 °C, 4 h
Cathode heat treatment	1100 °C, 4 h or 1200 °C , 1 h
Fuel	90%H ₂ -10%N ₂
Oxidant	90%O ₂ -10%N ₂

Table 3.3: Measurement conditions for cell tested using different 20SDC-NiO cermet ratio. Cell: H₂, NiO-20SDC | 20SDC | LSM, O₂



Figure 3.18: Current density-voltage (open symbols) and current density-power density (closed symbols) curves of single cell with different ratio of NiO-20SDC anode at 800 °C.



Figure 3.19: Maximum power density dependent on NiO content at 600, 700 and 800 °C.

Effect of LSM cathode heat treatment temperature

The role of cathode in cell performance is important as anode. The concentration, activation, and total polarizations of the cathode contribute to the voltage loss, consequently decrease the cell performance. In this section, the influence of cathode heat treatment temperature on the cell performance was discussed.

Fig. 3.20 compares the performance of single cell obtained at 800 °C from cell with LSM heat-treated at 1100, 1200 and 1300 °C. The maximum power density could be produced was 53.08, 96.04, 102.68 mW/cm² at 1100, 1200 and 1300 °C, respectively. Maximum power density at other temperatures, as illustrated in Fig. 3.21 also confirm that by increasing temperature for cathode heat treatment temperature up to 1300 °C improved the cell performance.

The possible reason for this result is the improvement of the adherence of cathode to the electrolyte when increasing the temperature, thus decreased the contact resistance polarization of the cathode-electrolyte layer, consequently increased the performance. The another possible reason is, heating cathode at higher temperature resulted in microstructure improvement, where

this might increased the porosity of the cathode. As the result, the gaseous species transportation or diffusivity was increased, therefore decreased the concentration polarization. Decreasing both ohmic resistance and concentration polarization resulted in higher performance.

Table 3.4: Measurement conditions for cell tested using different temperature for LSM heat treatment. Cell: H₂, NiO-20SDC | 20SDC | LSM, O₂

Electrolyte thickness	1 mm
Anode	60wtNiO-40wt%20SDC
Anode heat treatment	1200 °C, 1 h
Cathode	LSM
Cathode heat treatment	1100-1300 °C, 1 h
Fuel	90%H ₂ -10%N ₂
Oxidant	90%O ₂ -10%N ₂



Figure 3.20: Current density-voltage (open symbols) and current density-power density (closed symbols) curves of single cell fabricated from various LSM heat treatment temperature at 800 $^{\circ}$ C.



Figure 3.21: Maximum power density dependent on LSM cathode heat-treated at various temperature.

Effect of electrolyte thickness

As can be seen in typical SOFC performance curve (Fig. 3.1), ohmic resistance loss is one of the key factors that contributes to cell overall voltage loss. The origin of ohmic resistance loss is from electrical resistance of ions flow in electrolyte and electrolyte-electrodes interface, as well as resistance of electrons flow in the electrodes. However, the electrons resistance is relatively very small compared to ions resistance. In this work, single cell was electrolyte-supported, so that the dominant factor that cause to the voltage loss originated mainly from ionic ohmic resistance. Ohmic loss in electrolyte is directly related to the thickness of cell components, thus in order to decrease the ohmic loss, thinner electrolyte is needed.

To observe the influence of electrolyte thickness on the cell performance, power density obtained using electrolyte with thickness of 1 mm was compared to that obtained using thickness of 2.0 mm. The measurement condition is tabulated in Table 3.5. Attempt was also made to measure cell with electrolyte thickness below 1.0 mm, however, measurement of the cell performance was not successful because of cell cracking which is believed occurred during glass sealing process. It took place due to low mechanical property of 20SDC and mismatch of coefficient of thermal expansion between 20SDC and glass [12]. This resulted in gas leakage which was proven by low *EMF*.

The *I-V* and *I-P* curves are shown in Fig. 3.22. The maximum power density obtained when using 1.0 mm and 2.0 mm at 800 °C was 102.86 and 51.07 mW/cm², respectively. Generally from this result, it can be seen that the cell performance improved significantly by using thin cell performance, where using half of the electrolyte thickness could improve cell performance by approximately two times. This result proved that voltage drop is strongly dependent on electrolyte thickness which determines the ohmic resistance.

The cell performance in this work was limited by the thick electrolyte used in the experiment, which resulted in high electrolyte ohmic loss, consequently deteriorate the cell performance. Higher cell performance in doped CeO_2 has been reported using electrolyte with thickness of few micrometers. These reported data were obtained by anode- or cathode-supported cell. However, it has been reported that, there is limitation in reducing electrolyte thickness of doped CeO_2 . At certain thickness, the resistance of ion flow through the electrolyte decreased, but electron density increased and become dominant in conduction process, leading to low performance [18,19].

Electrolyte thickness	1 mm, 2 mm
Anode	60%wtNiO-40%20SDC
Anode heat treatment	1200 °C, 1 h
Cathode	LSM
Cathode heat treatment	1300 °C, 1 h
Fuel	90%H ₂
Oxidant	90%O ₂

Table 3.5: Measurement conditions for cell tested using different electrolyte thickness. Cell: H_2 , NiO-20SDC | 20SDC | LSM, O_2



Figure 3.22: Current density-voltage (open symbols) and current density-power density (closed symbols) curves of single cell with 1.0 and 2.0 mm thick electrolyte at 800 °C.

3.3.3 Cell performance under millimeter-wave irradiation heating.

Measurement under MMW irradiation heating was proceeded using optimized cell and measurement conditions, as tabulated in Table 3.6:

Table 3.6: Electrolyte-supported single cell and system conditions used for per-	ormance
comparison under conventional and MMW irradiation heating.	

Electrolyte	20SDC
Electrolyte thickness	1.0 mm
Electrodes area	0.19 mm^2
Anode composition	60wt%NiO-40wt%20SDC
Anode heat treatment	1200 °C, 1 h
Cathode composition	$La_{0.8}Sr_{0.2}MnO_3$
Cathode heat treatment	1300 °C, 1 h
Oxidant gas	90%O ₂ -10%N ₂
Fuel	90%H ₂ -10%N ₂
Temperature measurement	600-800 °C

For comparison of cell performance under conventional heating and MMW irradiation heating, temperature of sample was strictly evaluated as described in 3.2.5. Fig.3.23 and 3.24 compare the performance measured under conventional and MMW irradiation heating at 630 °C and 734 °C, respectively. It can be seen from these figures that cell performance measured under MMW irradiation was significantly higher than that obtained under conventional heating. At 630 °C, maximum power density increased from 16.63 mW/cm² to 26.86 mW/cm², recorded approximately 62% improvement. Meanwhile, at 734 °C, maximum power density increased from 53.59 mW/cm² to 81.27 mW/cm², recorded approximately 52% improvement.



Figure 3.23: Current density-voltage (open symbols) and current density-power density (closed symbols) curves of single cell measured under conventional (CONV) and MMW irradiation heating at 630 °C.



Figure 3.24: Current density-voltage (open symbols) and current density-power density-(closed symbols) curves of single cell measured under conventional (CONV) and MMW irradiation heating at 734 °C.

In consideration of cell tested in this work was designed as 1 mm thickness of electrolytesupported cell and both anode and cathode were relatively very thin, approximately 100-200 μ m, the influence of electrodes resistance to the cell performance is negligibly very small. Firstly, the total resistance, *R* that contributed to the overall cell performance is described as:

$$R = R_{\text{electrolyte}} + R_{\text{interface}} \tag{3.6}$$

The power, *P* delivered by the cell is given by:

$$P = IE_0 - I^2 R_{\text{electrolyte}} - I^2 R_{\text{interface}}$$
(3.7)

where, $R_{\text{electrolyte}}$ is the electrolyte resistance, $R_{\text{interface}}$ is resistance of ion transfer at the electrode/electrolyte interfaces, *I* is current and E_0 is open circuit voltage.

Using above equations, $R_{\text{interface}}$ was estimated by comparing *P* obtained for cell with thickness 1 mm and 2 mm. Theoretically, at same temperature and *I*, $R_{\text{electrolyte}}$ for 2 mm electrolyte is two times larger than 1 mm electrolyte. Meanwhile $R_{\text{interface}}$ for both cell should be constant. The relationship is described as:

$$\frac{P_1}{P_2} = \frac{IE_0 - I^2 R_{\text{electrolyte}} - I^2 R_{\text{interface}}}{IE_0 - I^2 R_{\text{electrolyte}} - 2I^2 R_{\text{interface}}}$$
(3.8)

where, P_1 and P_2 is power obtained using cell with 1 mm and 2 mm electrolyte, respectively.

From the calculation using data obtained at 600 and 700 °C under conventional heating, as can be seen in Fig. 3.25, it is estimated that $R_{\text{interface}}$ is extremely small compared to $R_{\text{electrolyte}}$. From this result, influence of $R_{\text{interface}}$ are negligible.



Figure 3.25: Current density-voltage (open symbols) and current density-power density (closed symbols) curves of single cell with 1.0 and 2.0 mm thick electrolyte at 600 and 700 °C.



Figure 3.26: Conductivity enhancement of 20SDC and performance enhancement of cell using 20SDC electrolyte at various temperature.

Therefore, for above reasons, cell performance improvement was considered to be associated with 20SDC electrolyte conductivity enhancement. Fig. 3.26 provides the relation between conductivity enhancement of 20SDC and maximum power density improvement in the temperature range of 600 to 750 °C. As discussed in previous chapter, the conductivity enhancement was linearly decreased with temperature because the effect of MMW was more pronounced at lower temperature. Same trend was observed for performance improvement where it decreased when temperature was increased. From these results, it can be seen that cell performance improvement correlated well with conductivity enhancement. Thus, it can be concluded that cell performance under MMW irradiation heating was improved due to enhancement of conductivity of the electrolyte which result from MMW effect.

3.3.4 Ionic transference number, t_{ion} under MMW heating

Electromotive force, *EMF* measurement was done to find the ionic transference number of 20SDC under MMW irradiation heating and the result was compared with that obtained under conventional heating. To avoid sample cracking during the measurement due to low mechanical properties of CeO_2 , sample with thickness of 2.5 mm was used. Pt was used as the electrodes.

Figure 3.27 compares the *EMF* values obtained under conventional and MMW irradiation heating at various oxygen partial pressures. Due to measurement limitation, *EMF* under MMW irradiation heating only can be obtained below 800 °C. It can be seen clearly that *EMF* values under MMW irradiation heating are similar to that obtained under conventional heating. Results of t_{ion} is shown in Fig. 3.28. All t_{ion} values were close to 1.0, showing that charge carriers for conduction process were ions, and do not change even under MMW irradiation heating.

From Fig. 3.23 and 3.24, the OCV was found to be lower when heated under MMW irradiation heating. As it was verified by the *EMF* measurement that t_{ion} remained unchanged under MMW irradiation heating, lower OCV obtained under MMW irradiation might be due to the occurrence of small crack inside the cell that resulted in gas leakage, during the movement of the evaluation set from conventional furnace to the MMW chamber. Nevertheless, despite the lower OCV, cell under MMW irradiation heating generated higher power density.



Figure 3.27: *EMF* under conventional and MMW irradiation heating for oxygen concentration cell : $P'O_2$ (high pressure), Pt |20mol% doped CeO₂ |Pt,O₂, ($P''O_2$ (low pressure)) as a function of temperature at various $P''O_2$ (low pressure). $P'O_2$ was constant at 0.5 atm.



Figure 3.28: The ionic transference number, t_{ion} under conventional and MMW irradiation heating as a function of temperature.

3.4 Summary

 $Ce_{0.8}Sm_{0.2}O_{1.9}$ (20SDC) electrolyte, NiO-20SDC anode and $La_{0.8}Sr_{0.2}MnO_3$ (LSM) cathode materials for SOFC were synthesized via conventional solid state route. Single electrolyte-supported button-type cell was successfully fabricated using these materials.

Initially, cell and measurement system were optimized by testing the cell under conventional heating using different anode cermet composition, cathode printing temperature, electrolyte thickness and gas concentration. Power density generated by the cell was found to have strong dependent on these parameters. The highest power density was obtained when cell with 1 mm electrolyte thickness, 60wt%NiO-40wt%20SDC anode painted at 1200 °C for 1 h, LSM cathode heat treatment temperature at 1300 °C for 1 h, 90%O₂-10%N₂ and 90%H₂-10%N₂ gases was used.

Next, cell electrochemical performance under conventional heating was compared to that under MMW irradiation heating. Cell performance under MMW irradiation heating improved compared to that measured under conventional heating. The improvement was in the same manner with the conductivity enhancement, where improvement was more pronounced at lower temperature. For the thick electrolyte-supported cell as used in this work, the dominant voltage loss could be ascribed to the electrolyte ohmic loss. A corollary of this, it is suggested that cell performance improved due to enhancement in ionic conductivity of the electrolyte resulted from MMW effect. Also, it is found that transference number for doped CeO_2 under MMW irradiation heating remained, similar to that obtained under conventional heating.

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Chapter 4

Conclusions and Recommendation

Conclusions

A study on the influence of millimeter-wave (MMW) on the ionic conductivity of one of the promising candidates of electrolyte material for solid oxide fuel cell (SOFC), $Ce_{1-x}Gd_x/Sm_xO_{2-x/2}$ was performed, aiming to obtain more insight into the ionic conductivity behavior under existence of MMW interaction. The key finding of this study is that the MMW specific effect has profoundly influenced the ionic conductivity of the $Ce_{1-x}Gd_x/Sm_xO_{2-x/2}$, where it improved the conductivity significantly. Specific findings in this work are summarized below.

Firstly, this study has shown that the influence of MMW effect on the conductivity was dependent on the thermal environment which experienced by sample. By modification of thermal environment, the conductivity of the sample could be varied. In this study, susceptor which used to assist heating process and alumina fiber board used as thermal insulator were considered in order to modify the thermal environment. It is found that susceptor thickness and fiber board insulator design affected the conductivity. In contrast, no significant difference was observed in conductivity when size of fiber board insulator was varied. Specific susceptor thickness and fiber board insulator configuration leads to a maximum MMW heating efficiency, thereby resulted in highest conductivity.

Secondly, it was demonstrated that ionic conductivity for all samples in this study enhanced significantly under MMW irradiation heating. Dopant type affected the enhancement degree, where in general, $Ce_{1-x}Gd_xO_{2-x/2}$ showed larger enhancement compared to $Ce_{1-x}Sm_xO_{2-x/2}$. In addition, dopant concentration also influence the conductivity enhancement. The implication of

this finding is that the degree of enhancement could be altered by changing the dopant or dopant concentration. Detailed investigation on the activation energy shows that the enhancement was ascribed to the reduction in ion migration energy and cation-vacancy dissociation energy. It appears that dissociation energy was reduced remarkably compared to migration energy, thus the dominant factor leads to conductivity improvement might be attributed to the reduction in dissociation energy. This study has found that MMW heating behavior was likely to show no direct correlation with conductivity enhancement, therefore eliminating the possibility of localized heating effect on ionic conduction process. It could be suggested that conductivity enhancement in $Ce_{1-x}Gd_x/Sm_xO_{2-x/2}$ owing to another potential phenomenon that may occur in MMW heated material, which is known as ponderomotive force (PMF). It is proposed that the existence of PMF provided an additional energy to facilitate ion conduction in crystal structure, hence the conductivity enhancement.

Next, results from performance of electrolyte-supported SOFC single cell by using doped $Ce_{0.8}Sm_{0.2}O_{1.9}$ as the electrolyte, $La_{0.8}Sr_{0.2}MnO_3$ as the cathode and NiO-Ce_{0.8}Sm_{0.2}O_{1.9} cermet as the anode under MMW irradiation heating demonstrate that overall cell performance improved under MMW irradiation heating. Electrolyte-supported cell was fabricated from thick electrolyte and very thin electrodes, therefore, overall cell polarization or loss is dominated by the electrolyte ohmic loss. Even though electrolyte-electrodes interface resistance and polarizations such as activation and concentration that related to anode and cathode might decrease too under MMW irradiation heating, these contributions is believed to be relatively very small. For that reason, the enhancement in cell performance could be due to the decrease of electrolyte ohmic loss as the result from the MMW effect. The enhancement in cell performance was found to be larger at lower temperature, which in the same manner as enhancement of ionic conductivity, suggesting that cell performance increased could be arised from increased ionic conductivity in electrolyte. Even though the result of cell performance was taken from $Ce_{0.8}Sm_{0.2}O_{1.9}$ only, this conclusions could be general for other $Ce_{1-x}Gd_x/Sm_xO_{2-x/2}$ because reasonable good agreement was observed in ionic conductivity and cell performance. It could be expected that samples that show higher conductivity enhancement should lead to higher cell performance under MMW irradiation heating.

In this study, MMW effect has been found to increase the conductivity of $Ce_{1-x}Gd_x/$ Sm_xO_{2-x/2} and improved the performance of SOFC. As samples show enhancement in conductivity due to MMW effect, towards the aim of lowering operation temperature of SOFC, MMW could potentially be a competent heating method. For instance, conductivity value for optimum sample for each dopant, Ce_{0.85}Gd_{0.15}O_{1.925} and Ce_{0.8}Sm_{0.2}O_{1.9} obtained at 550 °C under conventional heating was similar with the value obtained at 400 °C under MMW irradiation heating. Furthermore, cell performance improved more than 60% and 50% for Ce_{0.8}Sm_{0.8}O_{1.9} at 600 °C and 700 °C, respectively. This finding give potential implication with respect to lower temperature SOFC. By lowering the operation temperature, consequently, issues associate with high-temperature SOFC especially in regards to mechanical properties of the cell could be minimized. Furthermore, MMW has unique property which is called selective heating where only certain materials can absorb MMW energy and be heated. Materials with high dielectric loss, such as ceramic will be easily heated, meanwhile materials such as metal reflect the MMW, therefore will not be heated. By exploiting the selective heating property of MMW, less energy is required because it is used to heat only selected components. For application in SOFC, only ceramic cell should be exposed to MMW and other components of SOFC system should be kept at lower temperature by using metal wave guide that reflect MMW and shield other components from being irradiated. In addition, rapid MMW heating also offer time saving, hence can be cost effective heating method. Even though implementation of SOFC using MMW technology is still early to discussed due to complexity of SOFC itself, with the development in SOFC area and MMW technology this is not impossible.

Recommendation

A better understanding of MMW-material interaction in regards of ionic conductivity was achieved in this study. More work can be carried out to improve or expand this study.

In this study, effect of localized heating was verified by observing the heating behavior which represents the dielectric loss of the materials. Even though this result could prove the MMW effect on the ionic conduction process, it is suggested to investigate the dielectric constant of materials under millimeter-wave irradiation to give the solid evidence to the contribution of ponderomotive force in conduction process.

One of the limitations in fabrication of single cell was due to low mechanical property of doped CeO_2 which resulted in cell crack during the measurement, thus cell thinner than 1 mm was unsuccessfully measured. Theoretically, lowering the electrolyte thickness could lower the ohmic resistance, hence improve the cell performance. Therefore, it is suggested that for thinner cell, cell support-ring should be used in order to give extra support to the cell. In addition, cell cracking also might happened due to different of thermal expansion coefficient (TEC) between cell and glass seal, thus using glass seal that have similar TEC may avoid cell cracking. Furthermore, by performing the measurement at lower heating and cooling rate may also improve the measurement technique.

In this study, overall performance was compared based on voltage and power density generated by the cell. It would be interesting if this study is extended by performing impedance measurement under conventional and MMW irradiation heating in order to carefully investigate and differentiate each cell polarization such as ohmic, activation and concentration attributed by electrolyte, anode and cathode. This investigation may verify the contribution ionic conductivity enhancement of electrolyte to the cell performance enhancement. Furthermore, comparison study on cell performance under different oxygen partial pressure under conventional and MMW irradiation heating should be performed. This is important to observe the phenomena in MMW irradiation especially in doped CeO_2 due to the possibility of this material being reduced under reduced atmosphere.

Chapter 5

Publications and Presentations

Publications

- S.S.B. Che Abdullah, T. Teranishi, H. Hayashi, A. Kishimoto, Electrical conductivity of ceria-based oxide under 24 GHz millimeter-wave heating in varying thermal environments, J. Jpn. Soc. Powder Powder Metall. 63 (2016) 663-667. http://dx.doi.org/10.2497/jjspm.63.663.
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Presentations

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- <u>S.S.B. Che Abdullah</u>, T. Teranishi, H. Hayashi, A. Kishimoto, Influence of of quasimillimeter wave irradiation heating on the electrical conductivity of rare earth -doped CeO₂ for solid oxide fuel cell, The Ceramic Society of Japan, 29th Fall Meeting 2016, Sept 7-9, 2015, Hiroshima University, Japan.