Chapter 3

Methodology

The main target of this thesis is to characterize electrolytes for solid oxide fuel cells (SOFC). The electrolytes used in this work were both single material electrolytes; 3 mol% Y_2O_3 (Tetragonal Zirconia Polycrystals: TZP), 8 mol% Y_2O_3 doped ZrO_2 (Yttria stabilized Zirconia: YSZ) and ceria-based electrolyte of 10 mol% Gd_2O_3 doped CeO_2 (Gadolinia doped Ceria: GDC). The combination of TZP, YSZ and GDC were also studied as composite electrolytes, i.e., TZP/YSZ and GDC/YSZ. The sintering temperature and time were varied for all electrolytes to compare the effects on phases, mechanical and electrical properties. In addition, the effects of the composition ratio of the composite electrolytes on its properties were also investigated. An overview of the methodology used in this study is shown in Figure 3.1.

3.1 Materials and specimen preparation

3.1.1 Single material electrolytes

Zirconia-based electrolytes, 3 mol% Y_2O_3 (TZP from Magnesium Elektron Laboratory, UK) and 8 mol% Y_2O_3 doped ZrO_2 (YSZ from Tosoh, Japan), and a ceria-based electrolyte, 10 mol% Gd_2O_3 doped CeO_2 (GDC from Rhodia, France), were used in this study. Pellets of 13 mm diameter and 1 mm thick were made by uniaxially pressing 400 mg of powder at 1.38 MPa. The pellets were then sintered at 1450°C, 1500°C, and 1550°C in air for 1 and 2 hours at the heating and cooling rates of 180°C per hour.

3.1.2 Composite electrolytes

3 mol% Y_2O_3 doped ZrO_2 (TZP from Magnesium Elektron Laboratory, UK) powder was blended with 8 mol% Y_2O_3 doped ZrO_2 (YSZ from Tosoh, Japan) at the

weight ratio of 1: 3, 1: 1, and 3: 1. The composite of TZP/YSZ was ball-milled for 15 hours to make sure that the composition is homogeneous. After ball-milling, 400 mg of the powder was pressed at 1.38 MPa into pellets of 13 mm diameter and 1 mm thick using a uniaxial die. The pellets were then sintered at 1450°C, 1500°C, and 1550°C in air for 1 and 2 hours at the heating and cooling rates of 180°C per hour. 10 mol% Gd_2O_3 doped CeO_2 (GDC from Rhodia, France) powder was blended with YSZ in the same ratios of 1: 3, 1: 1, and 3: 1 and the same pressing and sintering procedures were followed.

3.2 Characterization Methods

3.2 .1 Density

The bulk density of the sintered pellets was measured using Archemedes method, ASTM C 373-88. The test specimens were dried in an oven at 150°C followed by cooling in a desiccator. The dry mass, D was determined to the nearest 0.0001 g. The specimens were placed in a pan of distilled water and boiled for 5 hours, taking care that the specimens were submerged in water at all times. After that, the specimens were soaked in water at room temperature for 24 hours. After impregnation of the test specimens, the mass, S was determined to the nearest 0.0001 g while suspended in water. Excess water was removed from the surface of the specimens before determining the saturated mass, M to the nearest 0.0001 g.

1 cm^2 of water weighs 1 g. The exterior volume, V (cm^2) can be calculated as follows:

$$V = M - S \qquad\qquad 3.1$$

The bulk density, B (g/cm^3), of the specimens is dry mass of the specimens divided by the exterior volume including pores as follows:
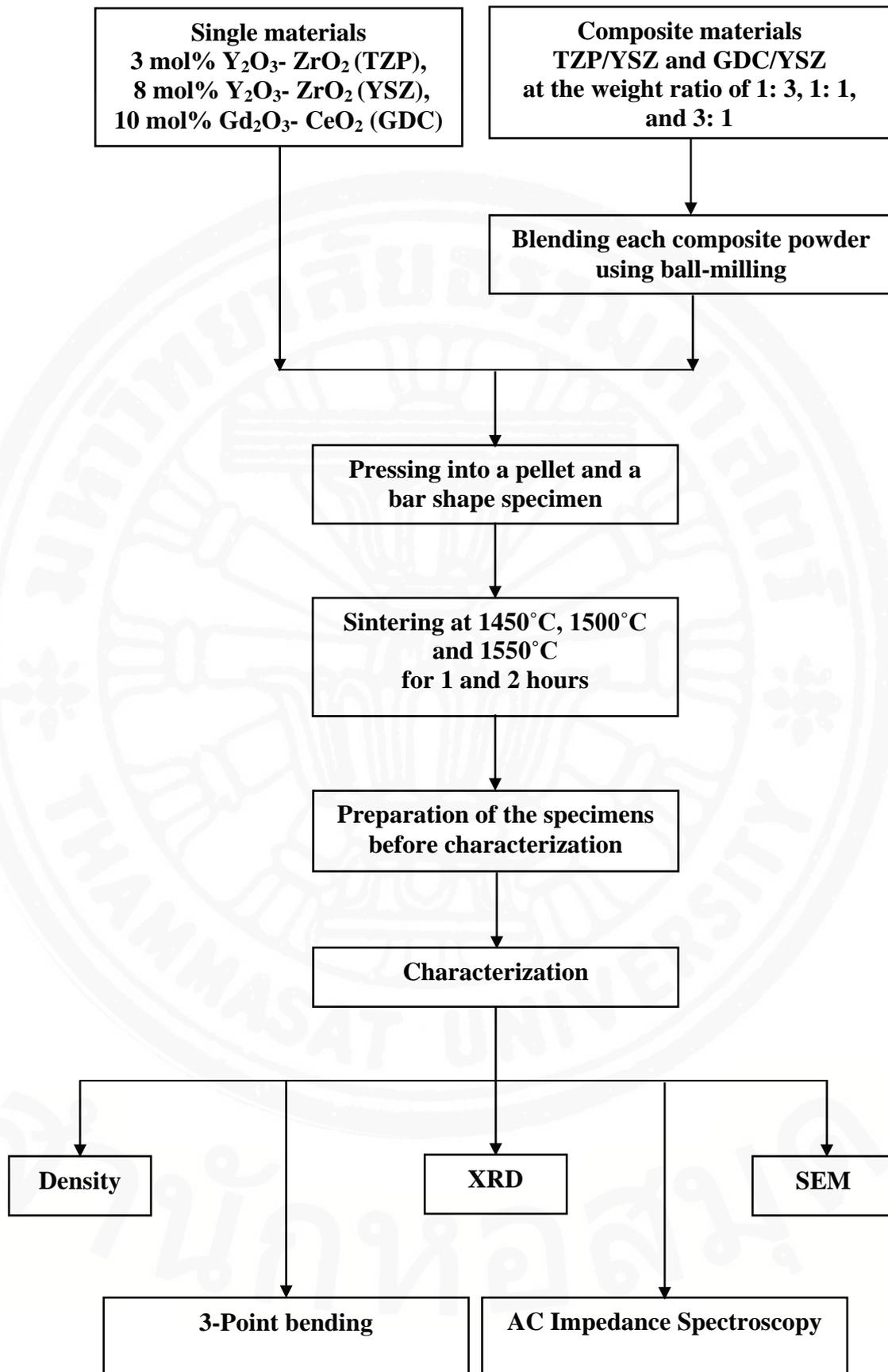
$$B = \frac{D}{M - S} \qquad\qquad 3.2$$

Single materials 3 mol% Y_2O_3- ZrO_2 (TZP), 8 mol% Y_2O_3- ZrO_2 (YSZ), 10 mol% Gd_2O_3- CeO_2 (GDC)		**Composite materials** TZP/YSZ and GDC/YSZ at the weight ratio of 1: 3, 1: 1, and 3: 1

Blending each composite powder using ball-milling

Pressing into a pellet and a bar shape specimen

Sintering at 1450˚C, 1500˚C and 1550˚C for 1 and 2 hours

Preparation of the specimens before characterization

Characterization

Density

XRD

SEM

3-Point bending

AC Impedance Spectroscopy

Figure 3.1 Overview of the methodology used in the study.

3.2.2 Phase Identification

An X-ray diffractometer (JEOL, model JDX-3530) using Cu-Kα target in the 2θ range from 20° to 95° was used for phase identification of the specimens. The single material electrolytes were identified to observe the effects of varying sintering temperature and time.

3.2.3 Microstructure

The specimens of electrolytes were polished using a silicon carbide (SiC) paper and diamond suspension (6μm, 3μm and 1μm) and cleaned using an ultrasonic cleaner (True sweep 2750, Crest Ultrasonics Corp.). The polished specimens were thermally etched at 50°C less than the sintering temperature for 5 minutes. After etching, the specimens were gold sputtered. The microstructure of the specimens was characterized using a scanning electron microscope (JEOL, Model JSM6301F).

The average grain size was estimated using an image analysis method from SEM micrographs.

3.2.4 3-Point Bending Test

Each bar contains 2000 mg of powder and was pressed at 6.89 MPa. The specimens of 6 mm wide (w), 6 mm long (L) and 6 mm thick (h) were sintered at 1450°C, 1500°C, and 1550°C in air for 1 and 2 hours at the heating and cooling rates of 180°C per hour. The variations in surface roughness were observed between batches. To ensure consistency of results, it was necessary to polish all sample surfaces.

The strength of the specimens was measured at room temperature via a three-point bending test as shown in Figure 3.2 using Instron 55R4502 universal testing machine. The maximum flexure stress was calculated from the failure load and the sample geometrical dimensions using equation 3.3.
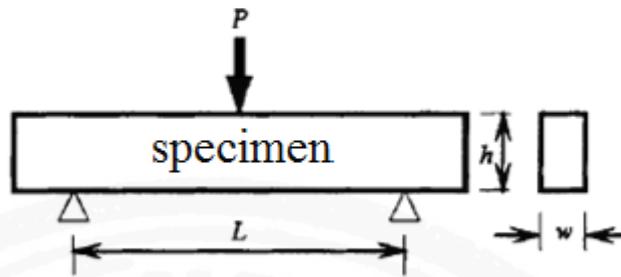
Figure 3.2 Schematic of 3-point bending test.

$$F = \frac{3PL}{2wh^2} \pm S (MPa) \qquad\qquad 3.3$$

where F is the flexure stress, P is the load (N), L is span (10 mm), w is width (mm), h is height (mm), and S is the standard deviation. The loading speed v was 0.50 mm·min^{-1}.

3.2.5 Electrical Properties

The specimens were coated with gold solution on both sides of the pellet and then fired at 800°C for 1 hour. After that, a short circuit, the conduction between both sides of the specimens was measured using a voltmeter before placing them into a specimen holder. The specimen before testing must not be short circuited.

The resistance of the electrolytes was measured using a Solartron 1260 Impedance/Gain-Phase Analyser as shown in Figure 3.3 in the frequency range of 0.05 Hz to 10 MHz from 275 to 600°C. The measured interval range was 25°C with an increase in temperature at the rate of 3°C/min. The measurement results were shown in a Nyquist plot between real number (Z′) in x-axis and imaginary number (-Z″) in y-axis. The resistance of the electrolytes was obtained from the high frequency intercept with the x-axis.
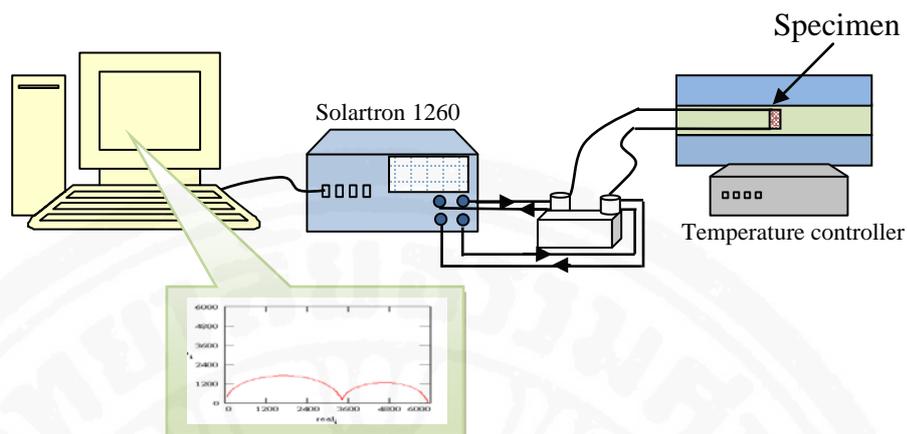
Figure 3.3 Setup of AC-impedance measurement.

The calculation of the ionic conductivity of the electrolyte material is based on Ohm's law;

$$V = IR \qquad\qquad 3.4$$

$$R = \frac{V}{I} \qquad\qquad 3.5$$

And

$$R = \rho \frac{L}{A} \qquad\qquad 3.6$$

$$\rho = \frac{RA}{L} \qquad\qquad 3.7$$

$$\sigma = \frac{1}{\rho} \qquad\qquad 3.8$$

Then

$$\sigma = \frac{L}{RA} \qquad\qquad 3.9$$

Where; V = applied voltage, V,

I = current in Ampare, A,

R = resistance in Ohm, Ω,

ρ = resistivity in Ohm, centimeter, Ω.cm,

σ = conductivity in Siemens/centimeter, S/cm,

L = sample thickness in centimeter, cm, and

A = the cross-sectional area in centimeter square, cm^2

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According to the Arrhenius equation, the conductivity of electrolyte materials can be expressed as;

$$\sigma_T = \left(\frac{A}{T}\right)\exp\left(\frac{-Ea}{RT}\right) \qquad 3.10$$

$$\ln \sigma_T T = -\frac{Ea}{RT} + \ln\left(\frac{A}{T}\right) \qquad 3.11$$

Where; Ea = activation energy for ionic conductivity, J/mol,

T = absolute temperature, K,

R = gas constant, 8.314 J/K mol, and

A = the pre-exponential factor.

From equation 3.11 ln ($\sigma_T T$) versus 1000/T is plotted to determine the activation energy and the electrical conductivity of the electrolyte at 800°C.

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