

**Sirindhorn International Institute of Technology  
Thammasat University**

**Thesis ChE-MS-2009-07**

---

**CHARACTERIZATIONS OF ELECTROLYTES FOR SOLID OXIDE  
FUEL CELL APPLICATION**

**Thitimaporn Duangmanee**

**CHARACTERIZATIONS OF ELECTROLYTES FOR SOLID OXIDE  
FUEL CELL APPLICATION**

A Thesis Presented

by

**Thitimaporn Duangmanee**

Master of Engineering  
Chemical Engineering Program  
Sirindhorn International Institute of Technology  
Thammasat University  
May 2010

**CHARACTERIZATIONS OF ELECTROLYTES FOR SOLID OXIDE  
FUEL CELL APPLICATION**

A Thesis Presented

by

Thitimaporn Duangmanee

Submitted to

Sirindhorn International Institute of Technology

Thammasat University

In partial fulfillment of the requirement for the degree of

MASTER OF ENGINEERING

Approved as to style and comment by

Advisor



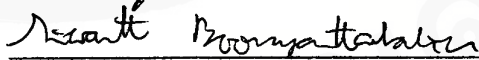
Assoc. Prof. Luckhana Lawtrakul, Dr. rer. nat.

Co-Advisor



Sumittra Charojrochkul, Ph. D.

Committee Member and  
Chairperson of Examination Committee



Siwarutt Boonyarattanakalin, Ph.D.

Committee Member



Asst. Prof. Fakorn Opaprakasit, Ph.D.

External Examiner: Assoc. Prof. Sutin Kuharuangrong, Ph.D.

May 2010

## Acknowledgement

I wish to express my deep gratitude to Dr. Rapeepong Suwanwarangkul, my late advisor, who gave me the opportunity to obtain the continuing scholarship for master's degree studies at Sirindhorn International Institute of Technology (SIIT) by SIIT and National Science and Technology Development Agency (NSTDA). I would like to thank Assoc. Prof. Dr. Luckhana Lawtrakul, my present advisor for her continuous support and for always giving me great encouragement.

I would like to express my profound gratitude and heartfelt thanks to Dr. Sumittra Charojrochkul, the principal researcher at National Metal and Materials Technology Center (MTEC), the author's co-advisor, for her consistent guidance during the conduct of my research work as well as financial help, kindness, encouragement and moral support. Her expertise and knowledge in the field of material science and engineering and in the conduct of good quality research that she has imparted and transferred to me has greatly influenced and encouraged me to apply such skills for my professional development in the future.

I also have a deep sense of appreciation to Asst. Prof. Dr. Pakorn Opaprakasit and Dr. Siwaratt Boonyarattanakalin, the members of my thesis committee for their valuable suggestions. I also would like to offer my gratefulness to Assoc. Prof. Dr. Sutin Kuharuangrong of Suranaree University of Technology for reviewing the thesis and for serving as the external examiner.

I am grateful to Dr. Worawarit Kobsiriphat and Ms Jivaganont Pranuda for their kindness and friendly helps in research of solid oxide fuel cell. I would like to thank the Electrochemical Materials and System (EMS) lab, MTEC, for providing research facilities.

I would like to thank Mr. Joji Ueda, Mr. Yuta Watanabe and Mr. Yoshida Takuya from Nagaoka University of Technology, Japan, Mr. Jason Teoh and Mr. Lee Choon Long from Singapore Polytechnic, Singapore and Mr. Piyachart Kanokhong from Khon Kaen University, Thailand for their help in the experiments. I would like to thank all of my friends in master of Chemical Engineering class at SIIT for their kindness and friendly helps throughout the entire study.

My deepest gratitude is also due to the scholarship provided by SIIT and NSTDA awarded to me and thus enabling me to study and accomplish my master's degree in SIIT and opening a window of wide opportunities. Financial support from Thammasat University Research Fund, 2008 is also gratefully acknowledged.

Deep affectionate gratitude is acknowledged to my family.



## Abstract

This study is a report on characterizations of electrolytes for solid oxide fuel cells (SOFC). Both zirconia-based electrolytes, 3 mol%  $Y_2O_3$  (Tetragonal Zirconia Polycrystals: TZP) and 8 mol%  $Y_2O_3$  doped  $ZrO_2$  (Yttria Stabilized Zirconia: YSZ) and a ceria-based electrolyte, 10 mol%  $Gd_2O_3$  doped  $CeO_2$  (Gadolinia Doped Ceria: GDC), were studied as single material electrolytes. The main objective in the single material electrolyte study was to compare the changes in mechanical and electrical properties at different sintering temperatures and times using the three-point bending test and AC-impedance spectroscopy, respectively. Moreover, the correlation between the electrical conductivity and microstructure were determined using a Scanning Electron Microscope (SEM).

The mechanical strengths of TZP and YSZ were found to decrease with increasing the sintering temperature and time. Conversely, an increase in sintering temperature and time decreased the mechanical strength of GDC.

In addition, composite electrolytes of TZP/YSZ and GDC/YSZ were investigated; each composition was varied to compare the effect on both mechanical and electrical properties. The TZP/YSZ composite was shown to be a mixed-phase between small and large grains, corresponding to the tetragonal and cubic phases of zirconia, respectively. The mechanical strength of TZP/YSZ electrolytes was found to increase with the ratio of TZP-to-YSZ. The results showed TZP enhances the mechanical strength of the TZP/YSZ composite electrolytes. The GDC/YSZ composite electrolyte is not suitable as an electrolyte of SOFC due to the high porosity when compared with the single material electrolytes of GDC or YSZ.

## Table of Contents

Chapter Title	Page
Signature Page	i
Acknowledgement	ii
Abstract	iv
Table of Contents	v
List of Figures	vii
List of Tables	xii
1. Introduction	1
1.1 Statement of the Problem	1
1.2 Rationale of the Study	3
1.3 Objectives of the Study	4
1.4 Scope of the Study	5
2. Literature Review	6
2.1 Principles of Fuel Cells	6
2.2 Types of Fuel Cell	7
2.3 Advantages/Disadvantages of Fuel Cells	14
2.4 Solid Oxide Fuel Cell Components	16
2.5 Electrical Property of Electrolyte in SOFC	24
3. Methodology	28
3.1 Materials and specimen preparation	28
3.2 Characterization Methods	29
4. Results and Discussion: Single material electrolytes	35
4.1 Characterizations of TZP electrolyte	35
4.2 Characterizations of YSZ electrolyte	45
4.3 Characterizations of GDC electrolyte	55
4.4 Summary	64

## Table of Contents

Chapter Title	Page
5. Results and Discussion: Composite electrolytes	65
5.1 Characterizations of TZP/YSZ electrolyte	65
5.2 Characterization of GDC/YSZ electrolyte	85
5.3 Summary	98
6. Conclusions	100
6.1 Single material electrolytes	100
6.2 Composite electrolytes	101
6.3 Recommendation	102
7. References	103



## List of Figures

Figure	Page
1.1 Advantages (+) and disadvantages (-) of SOFC for different operating temperature ranges, (o) designated states between (+) and (-)	2
2.1 Grove's fuel cell is one of the simplest examples	6
2.2 Proton Exchange Membrane Fuel cells	9
2.3 Alkaline Fuel Cells	10
2.4 Phosphoric Acid Fuel Cells	11
2.5 Molten carbonate fuel cells	12
2.6 Solid Oxide Fuel Cells	13
2.7 Combination the SOFC with a gas turbine engine to improve efficiency	15
2.8 Solid Oxide Fuel Cell designs	16
2.9 Cubic fluorite structure of zirconia	20
2.10 Stabilization of zirconia using yttria, a) pure $ZrO_2$ , and b) YSZ	21
2.11 Phase diagram of $ZrO_2$ - $Y_2O_3$ system	22
2.12 Influence of ionic radii of dopants over the ionic conductivity of $CeO_2$ -based electrolytes	23
2.13 Schematic complex plot and equivalent circuit of polycrystalline	25
2.14 Specific ionic conductivity values for selected oxide electrolytes as a function of reciprocal temperature	27
3.1 Overview of the methodology used in the study	30
3.2 Schematic of 3-point bending test	32
3.3 Setup of AC-impedance measurement	33
4.1 X-ray diffraction patterns all of TZP electrolytes at various sintering Temperatures and times	36
4.2 SEM micrographs of TZP at various sintering temperatures and times	38
4.3 Bending strength of TZP at various sintering temperatures and times	39

## List of Figures

Figure	Page
4.4 Impedance plots of TZP electrolytes after sintering for (a) 1450°C (□, ■), (b) 1500°C (△, ▲) and (c) 1550°C (○, ●) for 1 hour and 2 hours, respectively. All the measurements were taken at 350°C	40-41
4.5 Impedance plots of TZP electrolytes after sintering for (a) 1 hour (□, △, ○) and (b) 2 hours (■, ▲, ●) at 1450°C, 1500°C and 1550°C, respectively. All the measurements were taken at 350°C	42
4.6 Arrhenius plots of the (a) bulk and grain boundary (Gb) and (b) total conductivity for TZP	43
4.7 X-ray diffraction patterns for all YSZ electrolytes at various sintering temperatures and times	46
4.8 SEM micrographs of YSZ at various sintering temperatures and times	48
4.9 Bending strength of YSZ at various sintering temperatures and times	49
4.10 Impedance plots of YSZ electrolytes after sintering for (a) 1450°C (□, ■), (b) 1500°C (△, ▲) and (c) 1550°C (○, ●) for 1 hour and 2 hours, respectively. All the measurements were taken at 350°C	50-51
4.11 Impedance plots of YSZ electrolytes after sintering for (a) 1 hour (□, △, ○) and (b) 2 hours (■, ▲, ●) at 1450°C, 1500°C and 1550°C, respectively. All the measurements were taken at 350°C	52
4.12 Arrhenius plots of the (a) bulk and grain boundary (Gb) and (b) total conductivity for YSZ	53
4.13 X-ray diffraction patterns of GDC electrolytes at various sintering temperatures and times	56
4.14 SEM micrographs of GDC at various sintering temperatures and times	57
4.15 Bending strength of GDC at various sintering temperatures and times	59
4.16 Bending strengths of TZP, YSZ and GDC at various sintering temperatures and times	59

## List of Figures

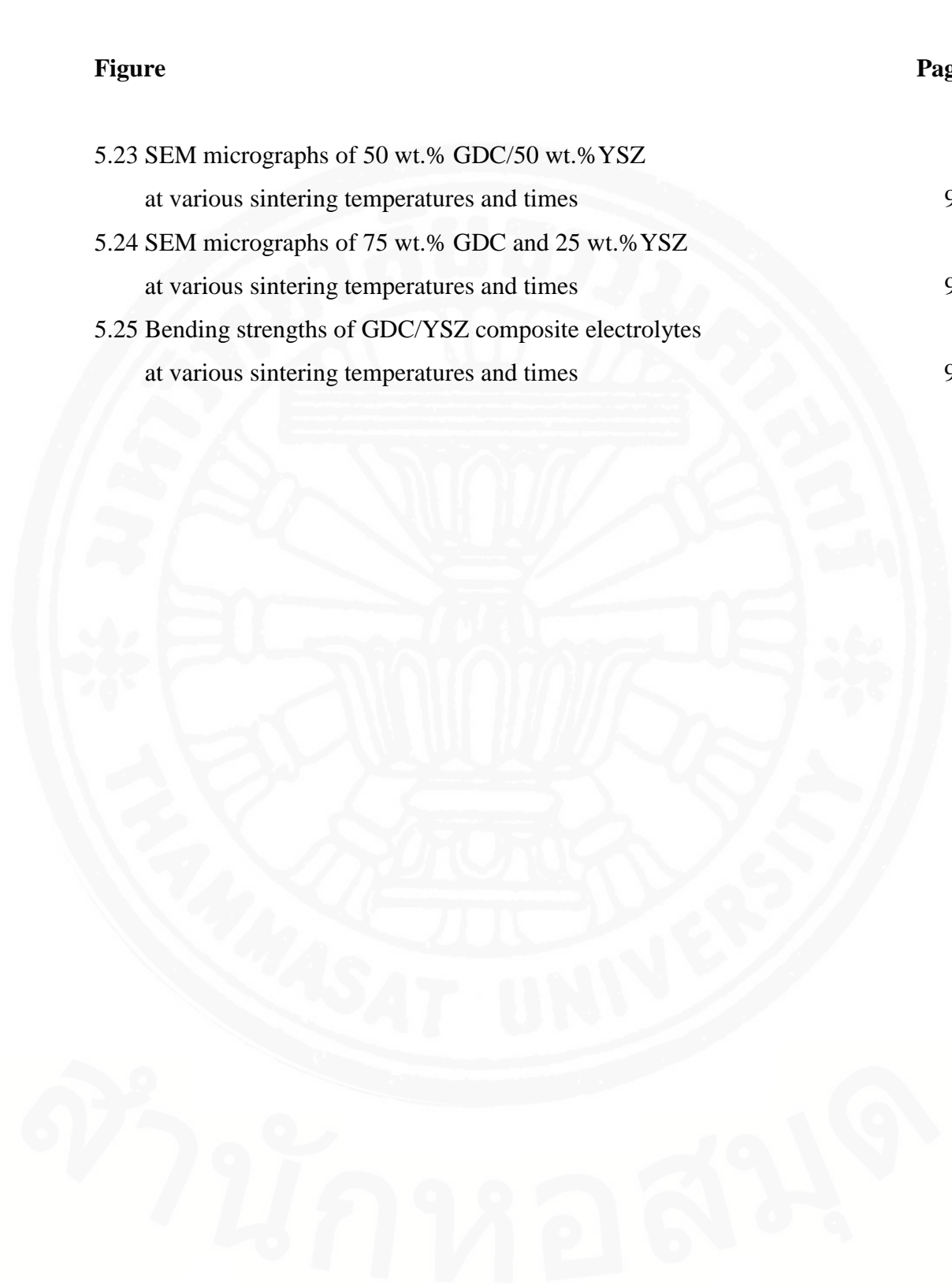
Figure	Page
4.17 Impedance plots of GDC electrolytes after sintering at (a) 1450°C (□, ■), (b) 1500°C (△, ▲) and (c) 1550°C (○, ●) for 1 hour and 2 hours. All the measurements were taken at 250°C	60-61
4.18 Impedance plots of GDC electrolytes after sintering for (a) 1 hour (□, △, ○) and (b) 2 hours (■, ▲, ●) at 1450°C, 1500°C and 1550°C. All the measurements were taken at 250°C	62
4.19 Arrhenius plots of the (a) bulk and grain boundary and (b) total conductivity for GDC	63
5.1 X-ray diffraction patterns of 25 wt.% TZP/75 wt.% YSZ composite electrolytes at various sintering temperatures and times	67
5.2 X-ray diffraction patterns of 50 wt.% TZP/50 wt.% YSZ composite electrolytes at various sintering temperatures and times	68
5.3 X-ray diffraction patterns of 75 wt.% TZP/25 wt.% YSZ composite electrolytes at various sintering temperatures and times	69
5.4 X-ray diffraction patterns of TZP/YSZ composite electrolytes sintered at 1450°C with various composite ratios	70
5.5 X-ray diffraction patterns of TZP/YSZ composite electrolytes sintered at 1500°C with various composite ratios	71
5.6 X-ray diffraction patterns of TZP/YSZ composite electrolytes sintered at 1550°C with various composite ratios	72
5.7 SEM micrographs of 25 wt.% TZP/75 wt.% YSZ at various sintering temperatures and times	74
5.8 SEM micrographs of 50 wt.% TZP/50 wt.% YSZ at various sintering temperatures and times	75
5.9 SEM micrographs of 75 wt.% TZP/25 wt.% YSZ at various sintering temperatures and times	76
5.10 Bending strengths of TZP/YSZ composite electrolytes at various sintering temperatures and times	78

## List of Figures

Figure	Page
5.11 Impedance plots of TZP/YSZ composite electrolytes for (a) 25 wt.%TZP/75 wt.%YSZ, (b) 50 wt.%TZP/50 wt.%YSZ and (c) 75 wt.%TZP/25 wt.%YSZ at various sintering temperatures and times. All the measurements were taken at 350°C	79-80
5.12 Arrhenius plots of the (a) bulk and grain boundary (Gb) and (b) total conductivity for 25 wt.%TZP/75 wt.%YSZ composite electrolytes	81
5.13 Arrhenius plots of the (a) bulk and grain boundary (Gb) and (b) total conductivity for 50 wt.%TZP/50 wt.%YSZ composite electrolytes	82
5.14 Arrhenius plots of the (a) bulk and grain boundary (gb) and (b) total conductivity for 75 wt.%TZP/25 wt.%YSZ composite electrolytes	83
5.15 Arrhenius plots of the highest conductivity of each proportion of TZP/YSZ composite electrolyte.	85
5.16 X-ray diffraction patterns of 25 wt.%GDC/75 wt.%YSZ composite electrolytes at various sintering temperatures and times	87
5.17 X-ray diffraction patterns of 50 wt.%GDC/50 wt.%YSZ composite electrolytes at various sintering temperatures and times	88
5.18 X-ray diffraction patterns of 75 wt.%TZP/25 wt.%YSZ composite electrolytes at various sintering temperatures and times	89
5.19 X-ray diffraction patterns of GDC/YSZ composite electrolytes sintered at 1450°C with various composite ratios	90
5.20 X-ray diffraction patterns of GDC/YSZ composite electrolytes sintered at 1500°C with various composite ratios	91
5.21 X-ray diffraction patterns of GDC/YSZ composite electrolytes sintered at 1550°C with various composite ratios	93
5.22 SEM micrographs of 25 wt.% GDC/75 wt.%YSZ at various sintering temperatures and times	94

## List of Figures

Figure	Page
5.23 SEM micrographs of 50 wt.% GDC/50 wt.% YSZ at various sintering temperatures and times	95
5.24 SEM micrographs of 75 wt.% GDC and 25 wt.% YSZ at various sintering temperatures and times	97
5.25 Bending strengths of GDC/YSZ composite electrolytes at various sintering temperatures and times	96



## List of Tables

Table	Page
2.1 Different types of fuel cells	8
2.2 Ionic Conductivity of Doped CeO <sub>2</sub>	24
4.1 Densities and average grain sizes of all TZP electrolytes at various sintering temperatures and times	37
4.2 Activation energies and conductivities of TZP electrolytes	44
4.3 Densities and average grain sizes of all YSZ electrolytes at various sintering temperatures and times	47
4.4 Activation energies and conductivities of YSZ electrolytes	54
4.5 Densities and average grain size of all GDC electrolytes varied sintering temperatures and sintering times	55
4.6 Activation energies and conductivities of GDC electrolytes	64
5.1 Densities of TZP/YSZ composite electrolytes at various sintering temperatures, times and composite ratios	72
5.2 Activation energies and conductivities of TZP/YSZ composite electrolytes	83
5.3 Densities of GDC/YSZ composite electrolytes at various sintering temperatures, times and composite ratios	91