High-performance gadolinia-doped ceria-based intermediate-temperature solid oxide fuel cells

Liu, Qinglin

2007

Liu, Q. L. (2007). High-performance gadolinia-doped ceria-based intermediate-temperature solid oxide fuel cells. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/5253>

<https://doi.org/10.32657/10356/5253>

Nanyang Technological University

Downloaded on 26 Apr 2023 17:18:04 SGT

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**HIGH-PERFORMANCE GADOLINIA-DOPED
CERIA-BASED INTERMEDIATE-TEMPERATURE
SOLID OXIDE FUEL CELLS**

**LIU QINGLIN
SCHOOL OF MECHANICAL & AEROSPACE ENGINEERING
2007**

High-Performance Gadolinia-Doped Ceria-Based Intermediate-Temperature Solid Oxide Fuel Cells

Liu Qinglin

School of Mechanical and Aerospace Engineering

A thesis submitted to the Nanyang Technological University
in fulfilment of the requirement for the degree of
Doctor of Philosophy

2007

ABSTRACT

Solid oxide fuel cells (SOFCs) are a highly efficient and environmentally benign device for power generation, which have drawn great attention in recent decades. However, the high operating temperature ($\sim 1000^{\circ}\text{C}$) of conventional SOFCs has imposed stringent materials and processing requirements and this has prevented SOFCs from commercialisation. Therefore, it is quite desirable to operate SOFCs at intermediate temperatures ($500\sim 800^{\circ}\text{C}$). The work presented in this thesis gives an in-depth investigation on the fabrication, characterisation and performance improvement of intermediate temperature SOFCs based on gadolinia-doped ceria (GDC) electrolyte material.

The sintering behaviour and electrical properties of GDC electrolytes were studied using nanosized GDC powder with an average particle size of ~ 5 nm as the raw material. It was found that calcining the raw powder at 750°C would significantly improve the sinterability of the as-received GDC powder. The effect of microstructure on the ionic conductivity of GDC electrolytes was investigated with AC impedance spectroscopy. It was found that the grain interior conductivity is predominantly related to the relative density and insensitive to the grain size of the electrolyte, whereas the grain boundary conductivity is strongly related to both the relative density and the grain size of the electrolyte.

The electrochemical properties of $(\text{La,Sr})(\text{Co,Fe})\text{O}_3$ (LSCF) and LSCF-GDC cathodes on GDC electrolyte were evaluated. It was found that sintering temperature, microstructure and composition have great effects on the cathode performance. After sintering at 900°C for 2 h, the LSCF cathode produced an optimal polarisation resistance of $2.54\ \Omega\text{cm}^2$ at 600°C . The addition of 50 wt.% GDC to LSCF cathode generated a polarisation resistance of $0.26\ \Omega\text{cm}^2$ at 600°C , a reduction by a factor of 9.

A novel spray-copressing process has been developed for fabricating thin film GDC electrolyte. With this process, dense and crack-free GDC films as thin as 10 μm have been successfully obtained. This spray-copressing process is simple, cost-effective and rather flexible. Dilatometric measurements revealed that a proper match between the sintering behaviours of GDC film and NiO-GDC anode substrate is very important to obtain high quality anode-supported GDC films after co-sintering.

Single cells with thin film GDC electrolyte have demonstrated encouraging and impressive output performance in the temperature range of 500-650°C. A single cell, consisting of 22- μm -thick GDC electrolyte, LSCF-GDC composite cathode and Ni-GDC cermet anode, produced maximum power densities of 1004, 595, 316 and 152 mW/cm^2 at 650, 600, 550 and 500°C, respectively. Moreover, with the incorporation of novel $(\text{Ba,Sr})(\text{Co,Fe})\text{O}_3$ (BSCF) cathode, the single cell with a 10 μm GDC electrolyte demonstrated peak power densities of 1329, 863 and 454 mW/cm^2 at 600, 550 and 500°C, respectively, representing the best power outputs ever reported in the literature for ceria-based intermediate temperature SOFCs.

To suppress the electronic conduction in the GDC electrolyte, YSZ film was introduced to the GDC electrolyte cell as an electronic blocking layer. Thin films of YSZ/GDC bilayer electrolyte were successfully fabricated on the anode substrate using a wet ceramic cofiring process. Single cells based on the bilayer electrolyte film produced open-circuit voltages close to the theoretical ones, implying that the electronic conduction in the GDC electrolyte was successfully blocked by the YSZ film. The fuel cell, composed of YSZ(3 μm)/GDC(7 μm) bilayer electrolyte, LSCF-GDC cathode and Ni-YSZ anode, demonstrated high performance in the temperature range of 700-800°C. Maximum power densities of 1321, 938 and 539 mW/cm^2 were measured at 800, 750 and 700°C, respectively.

ACKNOWLEDGEMENTS

The author would like to express his sincere gratitude to his supervisor, Professor Khor Khiam Aik and co-supervisor Associate Professor Chan Siew Hwa for their encouragement, support and valuable guidance throughout the research, which have ensured the completion of this thesis.

The author would also like to extend his sincere appreciation to Associate Professor Jiang San Ping for his valuable advice and enlightenments.

Special thanks go to research fellows, Dr Leng Yongjun, Dr Xia Zetao, and Dr Chen Xiaojun, and research students, Mr Liu Zengcai, Mr Wang Wei and Mr Zheng Yongda, working in the fuel cell research group for their valuable discussion and kind assistance.

Special thanks also go to the technicians in Fuel Cell Lab, Materials Lab, Thermodynamics Lab, AMRC and Energy Conversion Lab for their kind assistance during the research.

Especially, the author would like to express his sincere thanks to his wife and all other family members for their patience, understanding and moral support.

CONTENTS

ABSTRACT	i
ACKNOWLEDGEMENTS.....	iii
CONTENTS.....	iv
LIST OF TABLES.....	viii
LIST OF FIGURES	ix
LIST OF ABBREVIATIONS	xiv
CHAPTER 1 INTRODUCTION.....	1
1.1 Background.....	1
1.2 Objectives	5
1.3 Scope	6
CHAPTER 2 LITERATURE REVIEW	8
2.1 Operation principle of fuel cells	8
2.2 Types of fuel cells	9
2.3 Performance of fuel cells.....	10
2.3.1 Ideal performance of fuel cells	10
2.3.2 Actual performance of fuel cells	11
2.4 Materials for IT-SOFCs	13
2.4.1 Electrolyte materials	15
2.4.2 Cathode materials	27
2.4.3 Anode materials	31
2.4.4 Interconnect materials	34
2.5 Powder synthesis techniques	35
2.5.1 Solid state reaction technique	36
2.5.2 Amorphous citrate process	37
2.5.3 Glycine-nitrate combustion technique	37
2.5.4 Spray pyrolysis technique	38
2.6 Fabrication techniques for SOFC components	39
2.6.1 Chemical vapor deposition	40

2.6.2 Electrochemical vapor deposition	41
2.6.3 Physical vapor deposition	42
2.6.4 Electrophoretic deposition	42
2.6.5 Tape casting	43
2.6.7 Screen printing	44
2.6.8 Slurry coating	44
2.6.9 Dry pressing	45
2.7 Configurations of SOFC stacks	46
CHAPTER 3 EXPERIMENTAL PROCEDURE	49
3.1 Samples preparation	49
3.1.1 sample preparation for electrolyte conductivity measurements	49
3.1.2 Half cell preparation for cathode optimization study	49
3.1.3 Thin film SOFC preparation for performance evaluation	53
3.2 Sample characterization techniques.....	59
3.2.1 X-ray diffractometry	59
3.2.2 Scanning electron microscopy	59
3.2.3 Transmission electron microscopy	59
3.2.4 Particle size analyzer	60
3.2.5 Dilatometry	60
3.2.6 BET analysis	61
3.2.7 Density measurement	61
3.2.8 Grain size determination	62
3.3 Electrochemical characterisation techniques	63
3.3.1 AC impedance spectroscopy	63
3.3.2 DC polarization	67
CHAPTER 4 ELECTRICAL PROPERTIES OF GDC ELECTROLYTES	68
4.1 Introduction	68
4.2 Characteristics of raw powder	69
4.3 Effect of raw powder characteristics on sinterability	73
4.4 Effect of processing and sintering conditions on the ionic conductivity of GDC	

Electrolytes	76
4.4.1 Effect of compaction pressure on ionic conductivity	78
4.4.2 Effect of sintering temperature on ionic conductivity	82
4.4.3 Analysis on grain interior conductivity and grain boundary conductivity.....	85
4.5 Summary	95
 CHAPTER 5 ELECTROCHEMICAL PERFORMANCE OF LSCF AND	
LSCF-GDC CATHODES	97
5.1 Introduction	97
5.2 Optimisation of sintering temperature of LSCF cathodes	100
5.2.1 Impedance behaviour of LSCF cathodes	100
5.2.2 Polarisation resistance of LSCF cathodes as a function of sintering temperature	102
5.2.3 Microstructure of LSCF cathodes.....	104
5.3 Optimisation of composition of LSCF-GDC composite cathodes	110
5.3.1 Polarisation resistance of LSCF-GDC composite cathodes	110
5.3.2 Discussion	113
5.4 Summary	119
 CHAPTER 6 THIN FILM SOFCs WITH GDC ELECTROLYTE	
6.1 Introduction	121
6.2 Fabrication of GDC electrolyte thin films	124
6.2.1 Match of sintering behaviours between electrolyte and anode support ...	124
6.2.2 Effect of powder filling techniques on the microstructure of GDC electrolyte film	130
6.3 Microstructure of the cell	135
6.4 Cell testing	138
6.4.1 Polarisation behaviour of the cells	138
6.4.2 Polarisation resistance of the cells	140
6.4.3 Cell performance	146
6.5 High performance low temperature SOFC with novel BSCF cathode	151
6.5.1 XRD analysis of BSCF powder and microstructure of the cell	152

6.5.2	Open circuit voltage and power density of the cell	154
6.5.3	Polarisation resistance of the cell	158
6.5.4	Repeatability and durability test.....	160
6.6	Summary.....	163
CHAPTER 7 THIN FILM SOFC WITH YSZ/GDC BILAYER ELECTROLYTE ..		165
7.1	Introduction	165
7.2	Bilayer electrolyte cell without additional anode porosity created by pore-former	168
7.2.1	Preparation and microstructure of electrolyte thin films	168
7.2.2	Open circuit voltage of the cell	171
7.2.3	Cell performance and polarisation analysis	172
7.3	Bilayer electrolyte cell with additional porosity created by pore-formers	177
7.3.1	Effect of pore-former addition in the anode substrate on preparation and microstructure of the cell	177
7.3.2	Effect of pore-former addition in the anode substrate on the cell performance	183
7.3.3	Impedance spectra and polarisation analysis of the cell	184
7.3.4	Reaction or interdiffusion between YSZ and GDC	188
7.4	Summary	194
CHAPTER 8 GENERAL DISCUSSION		196
8.1	Minimisation of ohmic polarisation.....	196
8.2	Minimisation of activation polarisation.....	198
8.3	Minimisation of diffusion polarisation.....	200
CHAPTER 9 CONCLUSIONS AND RECOMMENDATIONS		202
9.1	Conclusions	202
9.2	Contributions and achievements.....	206
9.3	Recommendations for future work	207
LIST OF PUBLICATIONS		209
REFERENCES		210
APPENDIX A.....		229

LIST OF TABLES

Table 2-1 Classification and characteristics of fuel cells.....	9
Table 2-2 Requirements and materials for solid oxide fuel cell components.....	14
Table 2-3 Conductivity data for stabilised ZrO ₂ doped with rare earth oxides.....	16
Table 2-4 Ionic conductivity data for doped CeO ₂	17
Table 2-5 Ionic conductivity data for Bi ₂ O ₃ -M ₂ O ₃	23
Table 2-6 Advantages and disadvantages of electrolyte candidates for SOFCs	26
Table 2-7 Synthesised powders and synthesis conditions by solid state reaction	36
Table 2-8 Ceramic processes for SOFC components	40
Table 2-9 Features of planar single cell configurations.....	47
Table 3-1 Compaction and sintering conditions for GDC pellets	50
Table 3-2 Compositions and sintering conditions of cathodes in half cells	52
Table 3-3 Composition of YSZ or GDC suspension for depositing YSZ/GDC bilayer film on anode substrate.....	58
Table 4-1 Particle size of GDC powders	73
Table 4-2 Conductivity data for Gd _{0.1} Ce _{0.9} O _{1.95} electrolyte measured in air	85
Table 5-1 Electronic and ionic conductivities of LSCF and GDC at 700°C	118
Table 5-2 Porosity measurements of various LSCF-GDC composite cathodes.....	118
Table 6-1 Comparison of OCVs and maximum power densities for doped-ceria thin film SOFCs obtained in this study and from references	148
Table 6-2 OCVs and power densities of two BSCF cells.....	162
Table 7-1 Comparison of OCVs for SOFCs with YSZ/doped ceria bilayer electrolyte obtained in this study and from references.....	173

LIST OF FIGURES

Figure 2-1 Schematic diagram of the fuel cell.....	8
Figure 2-2 Ideal and actual fuel cell voltage-current characteristics	11
Figure 2.3 Conductivity (σ) of $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-8}$ in air and humidified air with 6% H_2	22
Figure 2-4 Temperature dependence of electrical conductivity for oxide ion electrolytes ...	26
Figure 2-5 SOFC single cell configurations	47
Figure 2-6 Schematics of four typical SOFC stack designs	48
Figure 3-1 Particle size distribution of LSCF powder.....	50
Figure 3-2 Flowchart for half cell fabrication.....	51
Figure 3-3 Configuration of half cells.....	53
Figure 3-4 Flowchart for the preparation of BSCF powder.....	54
Figure 3-5 Particle size distribution of NiO powder.....	55
Figure 3-6 Flowchart for preparation of GDC electrolyte thin film SOFCs.....	56
Figure 3-7 Configuration of GDC electrolyte thin film SOFCs.....	57
Figure 3-8 SEM micrograph showing typical microstructure of GDC electrolytes after grinding and thermal etching.....	62
Figure 3-9 Typical impedance spectrum showing three arcs.....	63
Figure 3-10 (a) Photo of fuel cell test station and (b) schematic of sample holder	66
Figure 4-1 Particle size distribution of GDC powders	70
Figure 4-2 TEM micrographs of GDC powders	72
Figure 4-3 Cross-sectional morphology of GDC pellets	74
Figure 4-4 An idealized equivalent circuit and its corresponding impedance plot	77
Figure 4-5 Total ionic conductivity as a function of compaction pressure.....	78
Figure 4-6 Grain interior conductivity as a function of compaction pressure.	79
Figure 4-7 Grain boundary conductivity as a function of compaction pressure.	79
Figure 4-8 Relative density and average grain size as a function of compaction pressure....	81
Figure 4-9 Total ionic conductivity as a function of sintering temperature.....	81
Figure 4-10 Grain interior conductivity as a function of sintering temperature.....	83
Figure 4-11 Grain boundary conductivity as a function of sintering temperature	83
Figure 4-12 Relative density and mean grain size as a function of sintering temperature....	84

Figure 4-13 Grain interior conductivity as a function of relative density for GDC electrolytes sintered at 1200°C for 5 h.....	85
Figure 4-14 Grain boundary conductivity as a function of relative density for GDC electrolytes sintered at 1200°C for 5 h.....	88
Figure 4-15 Impedance spectra of GDC electrolytes sintered at various sintering temperatures from 1200-1600°C, measured at 300°C.....	90
Figure 4-16 Schematic diagram of (a) continuous and (b) discontinuous distribution of insulating phase along the grain boundary of electrolytes	91
Figure 4-17 Temperature dependence of grain boundary conductivity for GDC electrolytes densely sintered at 1300°C and 1600°C, respectively.....	91
Figure 4-18 (a) TEM micrograph of GDC electrolyte sintered at 1600°C showing the grain boundary phase at triple junction site. EDX spectra of (b) site A and (c) site B in (a).....	94
Figure 5-1 Impedance spectra measured under open-circuit conditions at various temperatures for a LSCF cathode sintered at 900°C.....	101
Figure 5-2 Polarization resistance versus sintering temperature for LSCF cathodes, tested at 600°C in air.....	103
Figure 5-3 Temperature dependence of polarization resistance for LSCF cathodes sintered at different temperatures, tested in air over temperature range of 500-650°C....	103
Figure 5-4 SEM images of surface morphology of LSCF cathodes sintered at (a) 750°C, (b) 850°C, (c) 900°C, (d) 950°C, and (e) 1100°C for 2 h, respectively.....	108
Figure 5-5 Cross-sectional SEM images of LSCF cathodes on GDC substrates sintered at (a) 750°C, (b) 900°C, and (c) 1100°C for 2 h, respectively.....	109
Figure 5-6 Impedance spectra measured in air at 600°C for LSCF-GDC composite cathodes with various GDC weight fractions.....	111
Figure 5-7 Polarization resistance versus GDC weight fraction in LSCF-GDC composite cathodes, obtained at open circuit and 600°C in air.....	112
Figure 5-8 Temperature dependence of the polarization resistance for pure LSCF and various LSCF-GDC composite cathodes sintered at 900°C for 2 h, measured in air over temperature range of 500-700°C.....	112

Figure 5-9 Schematic illustrations of ionic and electronic pathways and reaction zone in (a) pure LSCF and (b) LSCF-GDC composite cathodes.....	115
Figure 5-10 Ambipolar resistivity at 700°C of porous LSCF-GDC composite cathodes as a function of GDC volume fraction.....	118
Figure 6-1 Surface morphology of GDC film of an electrolyte/anode bilayer.....	125
Figure 6-2 Thermal expansion coefficients of GDC electrolyte and GDC-NiO (35:65 in wt.) anode measured in air.....	126
Figure 6-3 Sintering behaviors of GDC electrolyte and several anodes sintered at 1300°C for 2 h at a heating rate of 5K/min.	126
Figure 6-4 Surface morphology of a 45- μm -thick GDC film of an electrolyte/anode bilayer co-sintered at 1300°C for 2h.....	130
Figure 6-5 Surface morphology of a 20- μm -thick GDC film, prepared by conventional powder filling technique.....	132
Figure 6-6 SEM micrographs of (a) the cross section of a GDC electrolyte/anode bilayer, and (b) the surface of its electrolyte film, prepared by a spray co-pressing process.....	133
Figure 6-7 SEM cross-sectional micrographs of the cells.....	137
Figure 6-8 i -V characteristics of thin film SOFC (a) with a 45- μm -thick GDC electrolyte and (b) with a 22- μm -thick GDC electrolyte tested in air and humidified hydrogen in the temperature range of 500-650°C.....	139
Figure 6-9 Impedance spectra of thin film SOFC with a 45- μm -thick GDC electrolyte measured at open circuit condition and different temperatures, shown in (a) and (b) The total cell resistance, interfacial resistance and ohmic resistance, obtained by Fitting the impedance spectra, are shown in (d). The equivalent circuit used for fitting is shown in (c).....	142
Figure 6-10 Voltage vs. current density curves at various temperatures for a thin film SOFC based on a 45- μm -thick GDC electrolyte, showing the splitting of the voltage loss into ohmic (iR_{Ω}) and electrode ($\eta_a + \eta_c$) components.	144
Figure 6-11 I-V characteristics (solid symbols) and the corresponding power densities (open symbols) for two SOFCs with different GDC electrolyte film thickness measured in humidified hydrogen and air at different operation temperatures.....	147

Figure 6-12 XRD pattern of BSCF powder after calcination at 800°C for 2 h.....	153
Figure 6-13 Cross-sectional SEM micrographs of an anode-supported cell: (a) the entire cell under low magnification and (b) GDC electrolyte, (c) BSCF cathode and (d) Ni-GDC anode under higher magnification.....	153
Figure 6-14 Comparison of OCV values as a function of temperature measured under the same conditions for the three cells with the same Ni-GDC anode but different electrolyte thickness or cathode composition.....	155
Figure 6-15 Voltages (solid symbols) and the corresponding power densities (open symbols) as a function of current density for a SOFC consisting of a novel BSCF cathode, a 10 μm GDC electrolyte and a Ni-GDC anode	156
Figure 6-16 Comparison of maximum power densities of thin-film GDC or SDC electrolyte cells with various cathodes.....	157
Figure 6-17 Impedance spectra of the cell, consisting of 10 μm GDC electrolyte, BSCF cathode and Ni-GDC anode, measured under open-circuit conditions at 500, 550 and 600°C, respectively. The inset shows the Arrhenius plots of the ohmic resistance R_{Ω} and the total interfacial polarisation resistance(R_a+R_c)	159
Figure 6-18 Comparison of the total interfacial resistance (R_a+R_c) of thin-film GDC electrolyte cells with various cathodes	159
Figure 6-19 i -V and corresponding i -P curves of Cell-B measured in the temperature range 450-600°C.....	161
Figure 6-20 Durability test of Cell-B at 500°C under constant voltage of 0.6 V.....	162
Figure 7-1 SEM micrographs of the cross-section of a dense NiO-YSZ anode substrate (a) before and (b) after reduction, (c) surface and (d) cross-section of a YSZ (b) film on a reduced anode substrate, and (e) surface and (f) cross-section (c) of a YSZ/GDC bilayer electrolyte film on a reduced anode substrate.	170
Figure 7-2 Theoretical OCV and measured OCV vs. temperature for single cells with a 10 μm GDC mono-layer electrolyte, a 10 μm YSZ mono-layer electrolyte and a 3 μm YSZ/7 μm GDC bilayer electrolyte, respectively.	171
Figure 7-3 (a) Cell voltage and (b) power density as a function of current density of a YSZ/GDC bilayer electrolyte cell measured between 700 and 800°C.	174
Figure 7-4 Effects of (a) air and (b) hydrogen flow rates and (c) hydrogen concentration on	

the polarisation behaviour of the YSZ/GDC bilayer electrolyte cell without additional anode porosity created by pore-formers.....	176
Figure 7-5 SEM micrographs of the cross section of the anode substrate with the pore-formers burned out (a) before and (b) after reduction. (c) Local enlargement of (b).....	179
Figure 7-6 Defects on the YSZ film directly deposited onto the anode substrate with the pore-formers burned out.....	180
Figure 7-7 Cross-sectional SEM images under (a) low and (b) high magnification of a single cell with YSZ/GDC bilayer electrolyte film deposited onto an anode substrate with an anode interlayer.....	182
Figure 7-8 Cell voltage (solid symbols) and power density (open symbols) as a function of current density of a YSZ/GDC bilayer electrolyte cell with additional porosity in the anode substrate created by pre-formers, measured between 600 and 800°C.....	183
Figure 7-9 Impedance spectra for the YSZ (3µm)/GDC (7µm) bilayer electrolyte cell and a 6 µm YSZ electrolyte cell measured under open-circuit condition between 600 and 800°C.....	185
Figure 7-10 Ohmic resistances as a function of temperature for the YSZ (3µm)/GDC (7µm) bilayer electrolyte cell and a 6 µm YSZ electrolyte cell measured under open-circuit condition between 600 and 800°C.....	186
Figure 7-11 Voltage vs. current density curves for the YSZ/GDC bilayer electrolyte cell at 800 and 700°C, showing the separation of the voltage loss into ohmic (iR_{Ω}) and electrode ($\eta_a + \eta_c$) components.	189
Figure 7-12 EDX line composition analysis of Zr and Ce across the YSZ/GDC bilayer electrolyte film.	190
Figure 7-13 XRD patterns for YSZ-GDC (1:1 by weight) mixture samples before and after heating at 1400°C for 2 h.....	192
Figure 7-14 Electrical conductivity of $(\text{GDC})_x(\text{YSZ})_{1-x}$ system as a function of GDC fraction measured at 800°C in air.....	193

LIST OF ABBREVIATIONS

BET	Brunauer-Emmott-Teller (method for specific surface area measurement)
BSCF	$\text{Ba}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$
BYO	$\text{Bi}_{2-x}\text{Y}_x\text{O}_3$
CVD	Chemical Vapour Deposition
EDX	Energy Dispersive X-ray spectroscopy
EMF	Electro-Motive Force
EVD	Electrochemical Vapour Deposition
GDC	Gadolinia-Doped Ceria ($\text{Gd}_x\text{Ce}_{1-x}\text{O}_{2-\delta}$)
IT-SOFC	Intermediate Temperature Solid Oxide Fuel Cell
LSCF	$\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$
LSGM	$\text{La}_{1-x}\text{Sr}_x\text{Ga}_{1-y}\text{Mg}_y\text{O}_{3-\delta}$
LSM	$\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3-\delta}$
MIEC	Mixed Ionic Electronic Conductor
OCV	Open Circuit Voltage
SDC	Samaria-Doped Ceria ($\text{Sm}_x\text{Ce}_{1-x}\text{O}_{2-\delta}$)
SEM	Scanning Electron Microscope
SOFC	Solid Oxide Fuel Cell
SSC	$\text{Sm}_{1-x}\text{Sr}_x\text{CoO}_3$
TEC	Thermal Expansion Coefficient
TEM	Transmission Electron Microscope
TPB	Tripe Phase Boundary
XRD	X-Ray Diffraction
YSZ	Yttria-Stabilised Zirconia

CHAPTER ONE

INTRODUCTION

1.1 Background

The first fuel cell was built by William Grove in 1839 and operated on pure hydrogen and pure oxygen. Later, Grove built a bank of 50 cells and called it a gaseous voltaic battery. Mond and Langer repeated Grove's work in 1889 and were the first to use the term "fuel cell" for the device (Hall, 1997). They recognized that the fuel cell could be used as an "all-purpose" electric power source and attempted to make it more practical by replacing the oxygen with air and the pure hydrogen fuel with an impure fuel gas derived from coal. However, the technology of fuel cells had experienced a slow development for nearly 100 years until in the late 1950's, when USA put it into practical use as one of the power sources for NASA's space programs, such as the Apollo spaceship. In spite of the successful application in space expeditions, fuel cells had not attracted great interests for terrestrial applications as a result of high cost of fuel cell systems and short life span. Until the early 1970's, when the impacts of energy crisis, global greenhouse effect and environmental pollution mainly due to the conventional power generation through combustion of fossil fuels were felt, people began to divert their attention to fuel cells for their potential applications in terrestrial cases (Perry and Fuller, 2002).

The fuel cell is an electrochemical device that converts chemical energy directly into electricity without intermediate steps which are inevitable in conventional power generation by steam/gas turbines. It does not obey the Carnot cycle principle. On the contrary, the conventional power generation by steam/gas turbines obeys the Carnot

Chapter 1 Introduction

cycle principle, requiring conversion of chemical energy into thermal energy, then thermal energy into mechanical energy, and finally mechanical energy into electrical energy. Therefore, the fuel cell has much higher efficiency in energy conversion than these conventional power generators. This is one of the major advantages of fuel cells. Another crucial advantage of fuel cells is that fuel cells almost have no emission of products that are harmful to the environment we are living in since the product from the electrochemical reaction between hydrogen and oxygen in the operation of fuel cells is pure water. These two major advantages as well as other advantages associated with modularity, sitting flexibility and multi-fuel capability can explain why fuel cell technology has become a very popular and very hot research topic in the past decades.

To date, several kinds of fuel cell systems have been developed (Minh and Takahashi, 1995). In terms of the electrolyte material used, they can be classified into five principal types: proton exchange membrane (polymer) fuel cell (PEMFC), alkaline fuel cell (AFC), phosphoric acid fuel cell (PAFC), molten carbonate fuel cell (MCFC) and solid oxide fuel cell (SOFC). The operating temperature has a big difference from almost room temperature for PEMFC to about 1000°C for SOFC. Among various types of fuel cells, SOFCs are generally thought to be the most promising system for electric utility power generation in both large central power station plants and distributed generation stations since they are capable of achieving power generation efficiency as high as 70% based on a hybrid SOFC/gas turbine generation technology (Chan and Ding, 2004). Furthermore, with the profound research developed and the technological problems solved, SOFCs, in particular the low temperature SOFCs, would also be an important power source candidate for vehicular applications (Nurdin, 2001). The SOFC technology is attracting more and more attention and showing a splendid prospect for a

wide range of industrial applications. In spite of this, there is still a long way to go before commercialisation. Hence, this project will focus on the SOFC and its performance improvement.

SOFCs use all solid-state ceramic materials for electrodes, electrolyte and interconnect, while other kinds of fuel cells use liquids as their electrolyte (PEMFC electrolyte has to be humidified). The use of a solid electrolyte in SOFCs eliminates material corrosion and electrolyte management problems and has the advantage of being impervious to gas cross-over from one electrode to the other. Ceramic electrolyte also allows SOFCs to operate under temperatures as high as 1000°C. High operating temperature promotes rapid reaction kinetics, allow reforming of hydrocarbon fuels within the fuel cell, and produce high-quality byproduct heat suitable for use in cogeneration or bottoming cycles. On the other hand, high operating temperature imposes stringent material and processing requirements. Materials problems arising from high operating temperature (~1000°C) required for conventional SOFCs, involve electrode sintering, interfacial diffusion between electrolyte and electrodes, mechanical stresses due to the thermal expansion mismatch and limitations in the selection of materials for interconnects and manifolds. These problems are difficult to be solved in a cost-effective manner and have so far limited the commercial development of SOFCs. Lower operating temperatures, however, would offer a wider choice of materials for interconnects and manifolds, including low cost metallic alloys such as ferritic stainless steels, reduce the stack thermal insulation requirements, signify the design requirements of the balance of plant and increase the system reliability and lifetime because of reduced thermal degradation and thermal cycling stresses (Huijsmans et al., 1998). In addition, for vehicular applications, the high operating temperature of current SOFC

designs would require more time and energy for start-up (Doshi et al., 1999). Therefore, it is quite desirable to operate SOFCs at intermediate temperatures (500-800°C), while still maintaining the power density achieved at high temperatures.

However, there are significant barriers around the following factors to the development of intermediate temperature SOFCs: (1) electrolyte ohmic resistance and (2) electrode polarisation resistance. With a decrease in the operating temperature, electrolyte ohmic resistance and electrode polarisation resistance will dramatically be magnified. Then, reducing the operating temperature and at the same time maintaining satisfactory cell performance become a key issue. At present, research on intermediate temperature SOFCs is based mainly on the approaches as follows:

- To decrease the electrolyte thickness from general 100~200 μm to less than 20 μm by replacing the conventional electrolyte-supported cell configuration with a supported electrolyte cell configuration. By this means the operating temperature of conventional SOFCs with ZrO_2 -based electrolyte might be lowered from 1000°C to about 800°C (Pal and Singhal, 1990; Wang and Barnett, 1993; Souza et al., 1997; Charpentier et al., 2000).
- To employ alternative electrolyte material which exhibits much higher ionic conductivity than the conventional yttria-stabilized zirconia (YSZ). It has been found that ceria-based oxides, lanthanum gallate-based perovskite oxides and stabilized bismuth oxides show excellent ionic conductivity at temperatures below 800°C. Therefore, they may be well served as intermediate or low temperature electrolytes (Godickemeier and Gauckler, 1998; Kuroda et al., 2000; Maric et al., 1999; Zha et al., 2002).

- To improve electrode properties and develop novel electrode materials. It is undoubtedly very important to seek electrode materials with high activity and conductivity as well as good compatibility with intermediate temperature electrolytes in order to arrive at high performance SOFCs operating at reduced temperatures. Strontium-doped lanthanum manganite (LSM) is commonly used in conventional SOFCs. Although addition of a second ionically conducting phase like YSZ or gadolinia-doped ceria (GDC) to form composite cathodes may improve the performance of LSM, it is very difficult to use these cathode materials below 800°C to produce high cell performance. Now the research focus is placed on non-manganese systems, such as $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_3$ (LSCF) and $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ (SSC), which show good compatibility with ceria-based electrolytes (Waller et al., 1996; Murray and Barnett, 2001; Jiang, 2002; Scott et al., 2002; Xia et al., 2002).

1.2 Objectives

In view of the above-mentioned problems with conventional SOFCs due to high operating temperature (~1000°C), intermediate temperature SOFCs (500~800°C) are becoming increasingly attractive. To develop high performance intermediate temperature SOFCs, the above three approaches are integrated in this research.

Earlier work has revealed that GDC is the most promising electrolyte material for intermediate temperature SOFCs since doped lanthanum gallate has high reactivity with conventional Ni-based anode materials and doped bismuth oxide exhibits high reducibility at reducing atmosphere (Steele, 2000; Kharton et al., 2004; Weber and Tiffée, 2004). Therefore, this research focuses on the investigations of intermediate temperature SOFCs based on GDC electrolyte.

The main objectives of this research are:

- To develop a solution/methodology for fabricating high performance GDC-based intermediate temperature SOFCs.
- To investigate the electrochemical properties of the intermediate temperature SOFCs associated with material processing.
- To optimise cell components and use an electronic blocking layer to achieve high performance GDC-based SOFCs in intermediate-temperature range.

1.3 Scope

The scope of this research is outlined below:

- *Investigation of the densification behaviour and electrical properties of GDC electrolytes (Chapter 4).*

In a SOFC, the electrolyte must be highly dense to prevent working gases from crossover. Therefore, densification behaviour of an electrolyte material is of great importance. This part of the work is to investigate the effects of starting powder characteristics and processing conditions (such as compaction pressure and sintering temperature) on the densification behaviour and the electrical properties of GDC electrolytes, thus providing optimum processing parameters for the fabrication of thin film GDC electrolyte for high performance intermediate temperature SOFCs.

- *Investigation of the electrochemical properties of LSCF and LSCF-GDC cathodes (Chapter 5).*

Compared with the anode, the performance of the cathode has a much greater effect on the overall cell performance due to its inherent high polarisation. This part of the work is to study the influence of processing conditions (such as sintering

temperature) and material composition (GDC addition) on the microstructure and electrochemical properties of LSCF cathode, thus achieving optimum cathode performance for the intermediate temperature SOFCs to be developed.

- *Fabrication and evaluation of thin film SOFCs with GDC electrolyte (Chapter 6).*

For successful fabrication of anode-supported thin film electrolyte by cofiring, it is important to ensure a proper match in the sintering behaviour between the anode substrate and the electrolyte film. Dilatometric measurements were conducted to study the sintering behaviours of NiO-GDC anode and GDC electrolyte. To reduce the fabrication cost of electrolyte thin films, the simple and cost-effective dry-pressing technique was first tried out using an ordinary non-porous GDC powder. On this basis, a novel spray-copressing technique is developed for thin film electrolyte fabrication. This part of the research also presents how the thickness of GDC electrolyte film and the use of novel BSCF cathode influence the cell performance.

- *Fabrication and evaluation of thin film SOFCs with YSZ/GDC bilayer electrolyte (Chapter 7)*

The mixed conduction behaviour of GDC electrolyte under SOFC conditions results in losses in the open-circuit voltage of a fuel cell. To suppress the electronic conductivity of GDC electrolyte, thin film SOFCs with YSZ(3 μ m)/GDC(7 μ m) bilayer electrolyte was fabricated for the first time using a wet ceramic cofiring process. This part of the study is to show the electronic blocking effect of YSZ film and the power outputs of thin film SOFCs based on YSZ/GDC bilayer electrolyte as well as the effect of anode substrate porosity on the cell performance. In addition, the influence of interfacial reaction between YSZ and GDC layers on the cell performance is also elucidated.

CHAPTER TWO

LITERATURE REVIEW

2.1 Operation principle of fuel cells

The principle of the fuel cell is very much like conventional batteries. The main difference is that, while the electrical energy produced by batteries is finite, the fuel cell produces electrical energy continuously so long as fuel and oxidant are supplied. Figure 2-1 is a schematic diagram showing the working principle of the fuel cell. Gaseous fuel is fed to the anode side of the cell while the oxidant gas (typically air) is fed to the cathode side of the cell. An electrochemical oxidation of the fuel occurs at the anode side producing positive ions (cations) like proton, while an electrochemical reduction of the oxidant occurs at the cathode side producing negative ions (anions) like oxygen ion. Depending on the type of fuel cells, either anions or cations are conducted through the electrolyte. The potential difference between the cathode and anode causes a current to

Figure 2-1 Schematic diagram of the fuel cell

Table 2-1 Classification and characteristics of fuel cells.

Fuel cell type	AFC	PEMFC	PAFC	MCFC	SOFC
Electrolyte	Potassium hydroxide	Ion Exchange Membrane	Phosphoric Acid	Alkali Carbonates Mixture	Solid Oxide
Operating Temperature	60-120°C	50-100°C	~220°C	~650°C	600-1000°C
Charge Carrier	OH ⁻	H ⁺	H ⁺	CO ₃ ⁻²	O ⁻²
Electrolyte State	Immobilized liquid	Solid but hydrated	Immobilized liquid	Immobilized liquid	Solid
Cell Hardware	Carbon based or metal-based	Carbon based or metal-based	Graphite-based	Stainless Steel	Ceramic
Catalyst	Platinum	Platinum	Platinum	Nickel	Perovskite
Fuel	Pure H ₂	Pure H ₂ (tolerates CO ₂)	Pure H ₂ (tolerates CO ₂ , approx. 1%CO)	H ₂ , CO, CH ₄ , other hydrocarbons (tolerates CO ₂)	H ₂ , CO, CH ₄ , other hydrocarbon (tolerates CO ₂)
Electrical Efficiency	35-55%	35-45%	40%	60%	60%
Cogeneration Heat	Nil	Nil	Low Quality	High	High
References	Cifrain et al., 2004; Gulzow, 1996	Litster et al., 2004; Sishtla et al., 1998	Feret, 1990; Yang et al., 2002;	Ganesan et al., 2003; Daza et al., 2000	Yi et al., 2005; Gardner et al., 2000

flow through the external circuit when connected to a load as shown in Figure 2-1.

Meanwhile, the cations and anions recombine to form the reaction product.

2.2 Types of fuel cells

To date, several kinds of fuel cell systems have been developed (Minh and Takahashi, 1995). In terms of the electrolyte material used, they can be classified into five principal types: proton exchange membrane (polymer) fuel cell (PEMFC), alkaline

fuel cell (AFC), phosphoric acid fuel cell (PAFC), molten carbonate fuel cell (MCFC) and solid oxide fuel cell (SOFC). Table 2-1 gives a comparison of characteristics of these types of fuel cells.

2.3 Performance of fuel cells

2.3.1 Ideal performance of fuel cells

The ideal performance of a fuel cell is defined by its Nernst potential, represented as the cell voltage. For the overall reaction $\text{H}_2 + \frac{1}{2} \text{O}_2 = \text{H}_2\text{O}$, the Nernst equation appears to be:

$$E = E^0 + \frac{RT}{2F} \ln \frac{p_{\text{H}_2} p_{\text{O}_2}^{1/2}}{p_{\text{H}_2\text{O}}} \quad (2-1)$$

where E^0 ---ideal standard potential at standard conditions (one atmosphere and 25°C or 298K), T ---absolute cell temperature (K), p ---partial pressure, R , F ---universal gas constant and Faraday's constant, respectively.

This equation provides a relationship between the ideal standard potential (E^0) for the cell reaction and the ideal equilibrium potential (E) at other temperatures and partial pressures of reactants and products. According to this equation, operating the cell under higher reactant pressures at a given temperature can increase the ideal cell potential. The ideal standard potential E^0 of a H_2/O_2 fuel cell is 1.229V with liquid water as the product. It does not include losses that are found in an operating fuel cell. Thus, it can be regarded as the open circuit voltage (OCV).

The Nernst potential is the electromotive force (EMF) that drives the reversible electrode reactions in equilibrium conditions. The Nernst potential is related to the change in Gibbs free energy by:

$$\Delta G = -2 F E \quad (2-2)$$

The change in Gibbs free energy is the maximum theoretical electrical energy available from the cell operating at a constant temperature and pressure.

2.3.2 Actual performance of fuel cells

Useful work (electrical energy) can be obtained from a fuel cell only when a reasonable current is drawn, but the actual cell potential is decreased from its equilibrium potential because of irreversible losses in the energy conversion process. The losses are often called polarisation, over-potential or over-voltage; they originate primarily from three sources: charge transfer or activation polarisation (η_{act}), resistance or ohmic polarisation (η_{ohm}) and diffusion or concentration polarisation (η_{conc}). These losses result in a cell voltage (V) for a fuel cell that is less than its ideal potential (E), i.e., $V = E - \text{losses}$. Figure 2-2 illustrates the respective losses in the i - V coordinates.

Polarisation cannot be eliminated but can be minimised by material modification and cell design. Temperature, pressure, electrolyte composition, and electrode material

Figure 2-2 Ideal and actual fuel cell voltage-current characteristics.

naturally influence cell polarisation. For example, increasing temperature enhances mass transfer, increases the reaction rate and usually decreases cell resistance, thus reducing cell polarisation and increasing voltage efficiency.

- **Activation polarisation**

Activation polarisation is present when the rate of an electrochemical reaction at an electrode surface is controlled by sluggish electrode kinetics, and it is directly related to the rates of electrochemical reactions. For the electrochemical reaction with $\eta_{act} \geq 50 \sim 100$ mV, η_{act} can be described by the Tafel equation:

$$\eta_{act} = \frac{RT}{\alpha nF} \ln \frac{i}{i_0} \quad (2-3)$$

where α is the electron transfer coefficient of the reaction at the electrode being addressed, i_0 is the exchange current density.

Factors that may contribute to activation polarisation mainly exist in processes involving adsorption of reactant species, transfer of electrons across the double layer, desorption of product species and the nature of the electrode surface.

- **Ohmic polarisation**

Ohmic losses occur because of resistance to the flow of ions in the electrolyte and resistance to flow of electrons through the electrode materials. Decreasing the electrolyte thickness and enhancing the ionic conductivity of the electrolyte can reduce the dominant ohmic losses through the electrolyte. Because both the electrolyte and electrodes obey Ohm's Law, the ohmic loss can be expressed by the equation:

$$\eta_{ohm} = iR \quad (2-4)$$

where i is the current flowing through the cell, and R is the total ohmic cell resistance, which includes electronic, ionic and contact resistance.

- **Concentration polarisation**

When reactants are consumed at the electrodes by an electrochemical reaction, there is a loss of potential due to the inability of the surrounding material to maintain the initial concentration of the bulk fluid. That is, a concentration gradient is formed. Several processes may contribute to concentration polarisation: slow diffusion of the gas phase in the electrode pores, solution/dissolution of reactants/products into/out of electrolyte, or diffusion of reactants/products through the electrode to/from the electrochemical reaction sites. At practical current densities, slow transport of reactants/products to/from the electrochemical reaction sites is a major contributor to the concentration polarisation, which is expressed as:

$$\eta_{conc} = \frac{RT}{nF} \ln \left(1 - \frac{i}{i_L} \right) \quad (2-5)$$

where i is the rate of mass transport to an electrode surface. It can be described by Fick's Law of diffusion: $i = \frac{nFD(C_B - C_S)}{\delta}$, where D is the diffusion coefficient of the reacting species, C_B is its bulk concentration, C_S is its surface concentration, δ is the thickness of diffusion layer. Limiting current i_L is a measure of the maximum rate at which a reactant can be supplied to an electrode, and occurs at $C_S = 0$.

2.4 Materials for IT-SOFCs

The selection of materials for SOFCs is a difficult task. For each component used in SOFCs, involving electrolyte, cathode, anode, interconnect, seal, etc., there are its own particular criteria which have been discussed by many researchers. In general, the factors, such as functionality, compatibility as well as cost should be considered together. The primary function parameters are conductivity, catalytic properties and

Table 2-2 Requirements and materials for SOFC components.

Component	Requirements (In terms of conductivity, stability, compatibility, porosity, thermal expansion, etc.)	Materials	References
Electrolyte	<ul style="list-style-type: none"> ► High ionic conductivity and negligible electronic conductivity; ► Chemical, phase, morphological and dimensional stability under processing and operating conditions; ► No damaging chemical interaction or inter-diffusion with adjoining components; ► No gas permeability; ► Thermal expansion match with adjoining components. 	Y ₂ O ₃ -ZrO ₂ (YSZ) Sc ₂ O ₃ -ZrO ₂ (SSZ) Gd ₂ O ₃ -CeO ₂ (GDC) Sm ₂ O ₃ -CeO ₂ (SDC) (La, Sr)(Ga, Mg)O ₃ (LSGM) (La, Sr)Si ₆ O ₂₄ Ba(Ca, Ce)O ₃	Minh, 1993; Cai et al., 2002; Steele, 2000; Shemilt et al., 2000; Ishihara et al., 1994; Kharton et al., 2004; Iwahara et al., 1995
Cathode	<ul style="list-style-type: none"> ► High electronic and ionic conductivity; ► Chemical, phase, morphological and dimensional stability in high temperature oxidizing environment; ► No damaging chemical interaction or inter-diffusion with adjoining components; ► Sufficient porosity; ► Thermal expansion match with adjoining components. 	(La, Sr)MnO ₃ (La, Sr)CoO ₃ (La, Sr)(Fe, Co)O ₃ (La, Sr)(Fe, Ni)O ₃ (Sm, Sr)CoO ₃ Ag-(Y, Bi) ₂ O ₃ (Ba, Sr)(Fe, Co)O ₃	Jiang and Love, 2003 Endo et al., 2000; Tai et al., 1995 a b; Simner et al., 2002; Xia et al., 2002; Wu and Liu, 1998; Shao and Haile, 2004
Anode	<ul style="list-style-type: none"> ► High electronic and ionic conductivity; ► Chemical, phase, morphological and dimensional stability in high temperature reducing environment; ► No damaging chemical interaction or inter-diffusion with adjoining components; ► Sufficient porosity; ► Thermal expansion match with adjoining components. 	Ni-YSZ cermet Ni-GDC Cu-SDC (La, Sr)(Cr, Mn)O ₃ (La, Sr)TiO ₃ (Zr, Ti, Y)O ₂	Jiang et al., 2000 a; Zha et al., 2004; Park et al., 2000; Tao and Irvine, 2003; Vazquez et al., 2003; Tao and Irvine, 2002
Interconnect	<ul style="list-style-type: none"> ► High electronic conductivity and negligible ionic conductivity; ► Chemical, phase, morphological and dimensional stability in both oxidizing and reducing environment; ► No damaging chemical interaction or inter-diffusion with adjoining components; ► No gas permeability; ► Thermal expansion match with adjoining components. 	(La, Ca)CrO ₃ (La, Sr)(Cr, Ti)O ₃ Cr-5Fe-1Y ₂ O ₃ alloy Fe-16Cr ferritic steel	Fergus, 2004; Mori, 2002; Larring et al., 2003; Kurokawa et al., 2004;

temperatures of stability and sintering. The compatibility of materials, e.g., thermal expansion coefficient, is essential to ensure a long-term stability at elevated temperatures. For the large-scale industrial application, cost effectiveness is also a limiting factor for selecting materials for SOFC systems. Table 2-2 presents a summary of the requirements for the principal components of SOFCs.

The research and development of SOFCs have been promoted since 1960's, and some materials have been found suitable for different components in the SOFCs. High temperature solid oxide fuel cell technology has come to a relatively mature level. High operating temperatures, however, can lead to complex material problems and high fabrication and maintenance cost. Thus, SOFCs are expected to operate at intermediate temperatures. For the reduction in the operating temperature of SOFCs, materials are still the key issue. It is critical to find suitable materials for IT-SOFCs. In the past 40 years, researchers have been striving towards this goal (Steele, 2000). It is of significance to make a review on these efforts.

2.4.1 Electrolyte materials

The main function of the SOFC electrolyte is to conduct oxygen ions from the cathode to the anode. The electrolyte also serves as a separator to prohibit the mixing of the fuel from the oxidant in the fuel cell. Thus, the electrolyte must be stable in both reducing and oxidizing environment, impermeable to the reaction gases and possess sufficient ionic conductivity at the operating conditions. The key requirements for the electrolyte are presented in Table 2-2. Several principal electrolyte materials suitable for use in IT-SOFCs are reviewed with a special emphasis on ceria-based materials which will be investigated in this project.

(1) Zirconia-based electrolyte

Stabilised ZrO_2 has been used almost exclusively as the electrolyte in conventional SOFCs. Among all the stabilised zirconias, the Y_2O_3 stabilised zirconia (YSZ) is the most common. Its ionic conductivity is higher than 0.1 S/cm at 1000°C, and its electronic conductivity is less than 10^{-4} S/cm in the entire oxygen potential region used for the fuel cell operation. However, the ionic conductivity of YSZ decreases rapidly with decreasing temperature. Many researchers have extensively studied the conductivity behaviour of stabilised zirconia. The ionic conductivity behaviour of the material is influenced by several factors such as the type of dopant and the dopant concentration, temperature, atmosphere, grain boundary and time (Sato et al., 1991; Arachi et al., 1999; Yamamoto, 2000). Table 2-3 presents the conductivities for stabilised zirconia doped with different rare earth oxides (Minh and Takahashi, 1995).

As shown in Table 2-3, when zirconia is doped with Sc^{3+} , it exhibits a higher ionic conductivity than those doped with any other rare earth dopant, which could be a potential candidate of electrolyte material for IT-SOFCs. However, it undergoes aging on long-term exposure under high temperatures. The lack of long-term stability of $\text{Sc}_2\text{O}_3\text{-ZrO}_2$ system due to aging is not yet well understood. Aging studies for the $\text{Sc}_2\text{O}_3\text{-}$

Table 2-3 Conductivity data for stabilised ZrO_2 doped with rare earth oxides (Minh and Takahashi, 1995).

Dopant (M_2O_3)	Composition (mol% M_2O_3)	Conductivity (1000°C) (10^{-2} S/cm)	Activation energy (kJ/mol)
Nd_2O_3	15	1.4	104
Sm_2O_3	10	5.8	92
Y_2O_3	8	10.0	96
Yb_2O_3	10	11.0	82
Sc_2O_3	10	25.0	62

ZrO₂ system suggested that samples with 11 or 12 mol% Sc₂O₃ were stable without conductivity degradation upon aging at a high temperature (Yamamoto et al., 1995). It was also found that adding a small amount of second dopant, such as Al₂O₃ and Yb₂O₃, is effective in stabilising the cubic phase with high stable ionic conductivity (Chiba et al., 1996; Ishii et al., 1994). Nevertheless, the availability and cost of Sc remain a concern and may limit future use of this material (Ralph et al., 2001).

(2) Ceria-based electrolyte

Pure CeO₂ has the cubic fluorite structure up to its melting point. Therefore, CeO₂, unlike ZrO₂, does not need any stabilisation. However, pure CeO₂ has n-type electrical conduction and has negligible ionic conductivity. The radius of the Ce⁴⁺ ion in CeO₂ is sufficiently large that a variety of dopants can be incorporated to form solid solutions. CeO₂ doped with a divalent or trivalent oxide shows relatively high oxygen-ion conductivity at elevated temperatures. Table 2-4 lists down some conductivity data for various doped-CeO₂ materials.

Table 2-4 Ionic conductivity for doped CeO₂ (Minh and Takahashi, 1995).

Dopant	Composition (mol%)	Conductivity (800°C) (10 ⁻² S/cm)	Activation energy (kJ/mol)
La ₂ O ₃	10	2.0	-
Y ₂ O ₃	20	5.5	26
Gd ₂ O ₃	20	8.3	44
Sm ₂ O ₃	20	11.7	49
CaO	10	3.5	88
SrO	10	5.0	77

Doped CeO₂ has been considered to be a promising SOFC electrolyte, especially at reduced temperatures, because of its high ionic conductivity at low temperatures. Compared to stabilised ZrO₂, doped CeO₂ shows higher conductivity and a lower conduction activation energy as can be seen from Table 2-4. A large amount of work

has been conducted on this material system (Inaba and Tagawa, 1996; Steele, 2000; Mogensen et al., 2000; Kharton et al., 2004).

Riess et al. (1981) studied the effect of sample preparation on the electrical conductivity of $\text{Ce}_{0.82}\text{Gd}_{0.18}\text{O}_{1.91}$ samples. It was found that the electrical conductivity of the sample obtained from the co-precipitation method with a narrow distribution of powder size was clearly higher than that from the mixing of CeO_2 and Gd_2O_3 with a wide distribution of powder size. In addition, the former showed a lower activation energy than the latter. They regarded that the difference in the electrical conductivity of Gd-doped ceria was due to the inhomogeneity in the Gd distribution and the larger activation energy was interpreted as the cause of the formation of Gd-rich grain boundary. Zhang et al. (2002) also observed the inhomogeneity of the Gd distribution which led to a clear inhomogeneity in grain size since gadolinia has a tendency to suppress the grain growth of CeO_2 .

The effect of density and impurity on electrical conductivity was studied by Gerhardt et al. (1986). The results showed that the effect of density was rather small, but the impurity of Si made the electrical conductivity of grain boundary drastically larger. This effect was interpreted as the cause of the formation of high resistive glassy phase at the grain boundary.

Zhang (2002) conducted detailed investigations on the sinterability of pure ceria and Gd-doped ceria using submicron-sized raw powder by conventional oxide mixing method as well as the effects of various additives (Fe_2O_3 , CoO , CuO , MnO_2 , NiO , etc.) on the sinterability and electrical properties. It was found that a small amount of Fe_2O_3 dopant (<1% in atomic ratio) would promote the densification of CeO_2 powder and reduce the sintering temperature by more than 200°C . Moreover, Fe_2O_3 was identified

Chapter 2 Literature Review

to be a grain boundary scavenger for SiO₂ impurity which accounted for the improvement in the grain boundary conductivity of Si-doped GDC material as a result of the addition of Fe₂O₃.

Doped CeO₂, however, has the tendency to undergo reduction (Ce⁴⁺ ion to Ce³⁺ ion) at low oxygen partial pressures with the consequent introduction of electronic defects. This reduction restricts the range of oxygen partial pressure over which the ionic transference number should remain close to unity. The partial reduction of Ce⁴⁺ to Ce³⁺ at the fuel side of a cell limits the use of ceria-based solid solutions as an electrolyte due to the lower open circuit voltage (OCV) and power loss caused by the electronic conduction through the electrolyte.

Considerable efforts have been made to suppress the electronic conduction in the ceria-based electrolyte and to improve the OCV. First, a bilayered electrolyte structure consisting of a ceria electrolyte layer and a YSZ protective layer was proposed (Yahiro et al., 1988; Inoue et al., 1989). Modelling work demonstrated that the interfacial oxygen partial pressure critical to Ce₂O₃/CeO₂ redox reaction is determined by the thickness ratio of the two layers and, generally, a YSZ film with a few μm in thickness should be good enough to prevent the ceria electrolyte from reduction and to avoid the OCV drop as a result of ceria reduction (Virkar, 1991; Marques and Navarro, 1997; Chan et al., 2003). Using ion plating method, Inoue et al. (1989) deposited a 1.86 μm YSZ film onto a 1.825 mm samaria-doped ceria (SDC) electrolyte, while Eguchi et al. (1992) deposited a 2 μm YSZ film onto a 0.658 mm SDC electrolyte. They successfully obtained an OCV of >1.0 V at 800°C, which is very close to the theoretical value. Other researchers (Mehta et al., 1993 and 1998; Chour et al., 1997; Jang et al., 2002; Kim et al., 2002) did observe the OCV improvement on YSZ/doped ceria bilayer electrolyte

cells where YSZ film was deposited by different methods, such as electrochemical vapor deposition (EVD), metal-organic vapor deposition (MOCVD), and sol-gel coating. However, the measured OCVs still exhibited an obvious deviation from the theoretical electromotive forces (EMF). It seems that the processing parameters have to be optimised so as to obtain a good-quality YSZ film for reduced electronic conduction in the ceria electrolyte. Wachsman et al. (1997) recorded increased OCVs for doped ceria electrolyte coated with a thin layer of doped bismuth oxide at the cathode side. Still, the increased OCVs had a non-negligible deviation from the theoretical OCV. The observed OCV improvement might be partly due to the reduced interfacial polarisation resistance by insertion of a doped bismuth oxide layer since the OCV of a mixed-conducting electrolyte cell is affected by the electrode polarisation resistance under open circuit conditions (Liu and Hu, 1996; Hu and Liu, 1998).

Mishima et al. (1998) developed a composite oxide as an electrolyte in which SDC particles are dispersed in a YSZ matrix. It was found that the electronic conduction caused by reduction of the SDC was effectively blocked by the YSZ matrix and the output voltage was obviously enhanced. The SDC content and the particle size significantly affected the power-generation characteristics of a cell with this biphasic electrolyte. However, this concept does not seem to be not meaningful for cell fabrication because a large size of SDC particles ($>100\text{ }\mu\text{m}$) is necessary so that they are separately dispersed in the YSZ matrix.

Zhu et al. (1999 and 2003) have reported high ionic conductivity and desirable OCVs at low temperatures for composite electrolytes comprising doped ceria and a molten salt. These materials look interesting, but so far, their properties have not been confirmed by other research groups. Moreover, practical use of such materials seems

Chapter 2 Literature Review

problematic due to possible decomposition of molten salts, and their high corrosion activity under the SOFC operating conditions.

In addition, co-doping approach has been adopted to improve the ionic domain boundary of doped-ceria materials. Maricle et al. (1992) reported that the electrolyte domain boundary could be extended to lower oxygen partial pressure by adding a small amount of Pr to $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$. In order to validate the above finding, Navarro et al. (1997) performed impedance spectroscopic study on the ionic and n-type conductivity in ceria-based electrolytes doped with 2 at.% Pr as a function of oxygen partial pressure down to 10^{-20} atm in the range of 800 to 1000°C. The results of Navarro et al. (1997) also showed favorable improvement of the electrolyte domain boundary by adding small amount of Pr. But they further pointed out that a significant improvement was hardly realised since overall differences between undoped and Pr-doped materials were quite small. Navarro et al. (1997) reported that the exact reason for the improved behaviour was not so clear, but deduced that Pr might act as a trap for electronic defects due to the redox reaction of the $\text{Pr}^{4+}/\text{Pr}^{3+}$. More recently, Lubke et al. (1999) also observed the enhanced electrolyte domain boundary in Gd-doped ceria material with Pr-doping. Using relatively pure samples of Pr-doped $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_2$, however, Steele et al. (2000) were unable to detect any enhanced electrolyte domain boundary. Steele et al. (2000) speculated that the enhanced electrolyte domain boundary observed by Maricle et al. (1992) and Lubke et al. (1999) might be arisen from the grain boundary region since a remarkable improvement in grain boundary behaviour was clearly shown in their work by adding small amount of Pr.

On the other hand, it is interesting to note that the electronic conductivity arisen from the partial reduction of Ce^{4+} to Ce^{3+} became negligible for Gd-doped ceria, as

shown in Figure 2-3, when the temperature was below 500°C. As pointed out by Doshi et al. (1999), to reduce the operating temperature of SOFCs from 800°C to 500°C, however, two major problems must be solved: (1) reduction of the high ohmic resistance without decreasing electrolyte thickness below 5 μm and (2) development of high performance cathode compatible with the electrolyte material.

Figure 2-3 Conductivity of $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$ in air and humidified air with 6% H_2 and values for YSZ shown for comparison.

(3) Bismuth oxide-based electrolyte

Takahashi et al. discovered the high oxide-ion conductivity of Bi_2O_3 and doped bismuth oxides in 1970 (Knauth and Tuller, 2002). Pure Bi_2O_3 has two crystallographic polymorphs: the low temperature semi-conducting α phase with a monoclinic structure and the highly conductive δ phase with a fluorite cubic structure. The phase transition of α - Bi_2O_3 to δ - Bi_2O_3 occurring at 730°C is accompanied by an oxide-ion conductivity jump of almost 3 orders of magnitude. δ - Bi_2O_3 has a disordered fluorite-type structure,

Chapter 2 Literature Review

where a quarter of the oxygen sites are intrinsically empty. Together with the high polarisability of the bismuth cations, this is responsible for the high anion conductivity, 1~2 orders of magnitude larger than that of doped ZrO_2 . However, the limited domain of stability of the δ phase and the mechanical stresses induced by large volume changes during the phase transition decrease the applicability of pure Bi_2O_3 . Takahashi and Iwahara stabilised the δ structure well below the transition temperature by doping with various oxides, including rare earth oxides, such as Y_2O_3 (Knauth and Tuller, 2002).

Among the known oxygen-ion conductors, stabilised Bi_2O_3 shows the highest ionic conductivity at comparable temperatures (Figure 2-4). This greater ionic conductivity of stabilised Bi_2O_3 offers the possibility of its use as an electrolyte in SOFCs at reduced temperatures. Table 2-5 summarizes the conductivity of various Bi_2O_3 - M_2O_3 materials (Minh and Takahashi, 1995). The main drawback of this material is its small oxygen partial pressure range of ionic conduction. Stabilised Bi_2O_3 is easily reduced under low oxygen partial pressures and decomposed into bismuth metal at an oxygen partial pressure of ca. 10^{-13} atm (10^{-8} Pa) at 600°C . Therefore, practical use of stabilised Bi_2O_3 as SOFC electrolyte requires protection of the material from direct exposure to reducing atmospheres (Azad et al., 1994).

Table 2-5 Ionic conductivity data for Bi_2O_3 - M_2O_3 (Minh and Takahashi, 1995).

Dopant	Composition (mol% M_2O_3)	Conductivity (10^{-2} S/cm)	
		500°C	700°C
Dy_2O_3	28.5	0.71	14.4
Er_2O_3	20	0.23	37.0
Y_2O_3	20	0.80	50.0
Gd_2O_3	14	0.11	12.0
Nd_2O_3	10	0.30	85.0
La_2O_3	15	0.20	75.0

High oxide-ion conductivity was evidenced above 570°C in the Aurivillius-type γ phase of $\text{Bi}_4\text{V}_2\text{O}_{11}$. Attempts to stabilise the γ phase to lower temperature led to a new family of so-called BIMEVOX compounds (Abraham et al., 1990), in which vanadium is partially substituted by low-valence cations, such as copper (BICUVOX), nickel (BINIVOX), or cobalt (BICOVOX). These compounds present a large mixed conductivity with a remarkable oxygen-ion conductivity at moderate temperatures. The copper compound, perhaps the most interesting one, has an exceptional oxide-ion conductivity above 200°C, ~ 2 orders of magnitude higher than other oxide-ion conductors at this temperature.

(4) *LaGaO₃-based electrolyte*

High oxygen ion conductivity of LaGaO_3 -based perovskite oxides, doped with Sr on the La site and Mg on the Ga site, was found by Ishihara et al. (1994). The highest ionic conductivity at 800°C (0.17 S/cm) has been reported for the composition $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.83}\text{Mg}_{0.17}\text{O}_{3-\delta}$ (Huang et al., 1998 b). Compared with ceria-based electrolytes, the electrolytic domain of doped LaGaO_3 extends to significantly lower oxygen potentials (Kim and Yoo, 2001). Thus, this type of electrolyte is a very promising material for the fuel cell operating at lower temperatures.

The compatibility of $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{2.85}$ oxide as an electrolyte in SOFCs was investigated by Yamaji et al. (1998). After a long-term operation, the significant migration of the $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{2.85}$ components was observed at both surfaces of the cathode and the anode, which caused fuel cell performance to deteriorate, especially on the anode side. The structure of $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{2.85}$ was studied by Slater et al. (1998). High-resolution powder neutron diffraction has shown that the structure of the $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{2.85}$ is monoclinic at room temperature, rather than orthorhombic

Chapter 2 Literature Review

for the undoped LaGaO_3 phase. These structural differences between doped and undoped LaGaO_3 , and how they vary with temperature are of fundamental importance to the understanding of the high oxide ion conductivity of this material.

The phase relationships and electrical properties of Strontium- and Magnesium-doped LaGaO_3 (LSGM) were studied by Huang et al. (1998 b). Two impurity phases, LaSrGaO_4 and $\text{LaSrGa}_3\text{O}_7$, were identified. The chemical stability of the LSGM electrolyte in a reducing environment was investigated by Yamaji et al. (1999). After annealing at 1273 K, significant changes were observed in the surface morphology of the LSGM electrolyte, and La(OH)_3 , LaSrGaO_4 and some unknown phases were found. The results of inter-diffusion and reaction between NiO and LSGM were investigated by Huang et al. (1999). The inter-diffusion did not significantly affect the oxygen-ion conductivity, because the amount of nickel diffused into the electrolyte is small. However, the interactions between NiO and LSGM, when co-fired at high temperatures, lead to a second LaSrGaNiO_{4-x} -type phase, which increases the interface impedance under anode working conditions and severely affects the fuel cell performance.

To reduce the reaction between LSGM electrolyte and Ni-based anode, several approaches have been used in developing LSGM electrolyte cells, including electrolyte-supporting configuration (Huang et al., 1998 c; Fukui et al., 2002), modified anode composition (Huang et al., 2001), anode-supporting configuration either with protective interlayer of doped ceria (Bi et al., 2004; Huang et al., 2001) or with LSGM thin film deposited on the anode support at low temperatures (Yan et al., 2005; Joseph et al., 2002) and all-perovskite cell configuration (Rambabu et al., 2005). To summarise this section, a comparison of electrical properties of typical electrolyte materials and their advantages and disadvantages is presented in Figure 2-4 and Table 2-6.

Figure 2-4 Temperature dependence of electrical conductivity for oxide ion electrolytes (Yamamoto, 2000).

Table 2-6 Advantages and disadvantages of electrolyte candidates for SOFCs.

Electrolyte	Advantage	Disadvantage
YSZ	Excellent stability in oxidizing and reducing environment; Excellent mechanical stability; Confirmed long-term operation.	Low ionic conductivity; Incompatible with some cathode materials (e.g., LSCF).
ScSZ	High ionic conductivity; Excellent stability in oxidizing and reducing environment.	Availability and price of Sc.
GDC/SDC	High ionic conductivity; Good compatibility with cathode materials; Mixed electronic-ionic conductor at low oxygen partial pressure (application in anode).	Electronic conduction at low oxygen partial pressure, thus reduced OCV and mechanical stability.
LSGM	High ionic conductivity; Good compatibility with cathode materials.	Ga-evaporation at low oxygen partial pressure; Phase stability; Incompatible with NiO; Mechanical stability; Availability and price of Ga.
BYO	Excellent ionic conductivity	Reducibility in reducing atmosphere.

2.4.2 Cathode materials

The main function of the cathode is to provide reaction sites for the electrochemical reduction of the oxidant. In the cathode, oxygen molecules are catalyzed and ionized and then transferred to the electrolyte. Thus, the cathode materials should possess the following features: high electronic conductivity to minimise ohmic loss, sufficient catalytic activity to dissociate oxygen molecules, high chemical, morphological and dimensional stability in the oxidant environment, compatibility with other adjoining components at both the operating temperature and high fabrication temperature, thermal expansion match with other component to avoid cracking and delamination during fabrication and operation and sufficient porosity to allow gas transport to the reaction sites. In addition to these requirements, other desirable properties for the SOFC cathode are high strength and toughness, fabricability and low cost.

Because of the high operating temperature of SOFCs, only noble metals and electronic or mixed conducting oxides can be used as cathode materials. Noble metals such as platinum and palladium are unsuitable for practical applications because of prohibitive cost. So far, the research has been focused on the conductive doped oxides. Some of the perovskite type oxides, ABO_3 , show relatively high electronic conductivity or mixed ionic-electronic conductivity at high temperatures.

(1) Strontium doped lanthanum manganite (LSM)

Doped lanthanum manganite (e.g., $La_{1-x}Sr_xMnO_3$) has been extensively used as cathode material in conventional SOFCs. The selection has been based primarily on three factors: high electrical conductivity in oxidizing atmospheres, adequate compatibility with YSZ electrolyte, and acceptable thermal expansion match with other cell components. However, the oxygen ion conductivity of LSM materials is as low as

10^{-7} S/cm at 900°C, which limits the use of LSM materials as the cathode for intermediate temperature SOFCs (Skinner, 2001).

Two approaches have been taken to improve the performance of LSM cathodes so that they can be used at lower temperatures. The first is to add a second ionically conducting phase, e.g., YSZ, to LSM to extend the surface area over which the oxygen reduction reaction can occur (Jorgensen et al., 2001; Murray and Barnett, 2001; Jiang et al., 2003; Xia et al., 2003). The second approach is to dope LSM with an ion that promotes the formation of oxygen vacancies. For this case, both gallium and aluminum have been doped into B-site to improve the performance of the electrodes (Ralph et al., 2001). While both approaches appear to improve the performance of LSM, it is unlikely that these cathode materials could operate below 800°C. The research now focuses on non-manganese systems, such as $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_3$ and $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$, which show desirable mixed conducting properties and good compatibility with ceria-based electrolytes (Xia et al., 2002; Wang et al., 2003).

(2) Strontium and ferrite doped lanthanum cobaltite (LSCF)

The use of lanthanum cobaltite materials as possible cathodes has been widely explored in recent years (van Doorn and Burggraaf, 2000; Skinner, 2001). Among several kinds of perovskite oxides with the composition of ABO_3 , such as LaCoO_3 , LaFeO_3 , LaMnO_3 and LaCrO_3 , which are known to display high electronic conductivity when alkaline earth metals are doped on the La sites, LaCoO_3 possesses the highest electrocatalytic activity (Takeda et al., 1987). However, LaCoO_3 reacts readily with YSZ electrolyte to form an insulating layer such as LaZr_2O_7 or SrZrO_3 for Sr-doped LaCoO_3 (LSC) at the interface. Thus, LSC material is of no use to YSZ-based SOFCs, in particular, at high temperatures. With the research conducted on reduced temperature

SOFCS where ceria-based materials are widely used as electrolyte, doped LaCoO_3 is seeking its significance and promising applications.

Godickemeier et al. (1996) reported the superior performance of LSC when tested with $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ (SDC) and $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ (GDC) electrolytes compared with LSM. No reaction products have been found between LSC and doped ceria. Even so, LSC has a high thermal expansion coefficient (TEC) ($16\sim 22\times 10^{-6} \text{ K}^{-1}$) compared with doped ceria (ca. $12\times 10^{-6} \text{ K}^{-1}$). The mismatch in thermal expansion between ceria and LSC needs to be resolved.

More recently, $(\text{La}, \text{Sr})(\text{Co}, \text{Fe})\text{O}_3$ (LSCF) has been extensively examined. Doping the Co-site of LSC with Fe has been an effort to reduce the TEC and increase the thermodynamic stability of this mixed conducting material. This material showed a good electrical conductivity at temperatures between 600 and 800°C, high oxygen surface exchange coefficient and high oxygen self-diffusion coefficient. The oxygen self-diffusion coefficient (D^*) of LSCF at 500°C is $2.6 \times 10^{-9} \text{ cm}^2/\text{s}$ compared to that of $10\text{-}12 \text{ cm}^2/\text{s}$ for $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ at 1000°C (Steele, 1996). The LSCF/ $\text{Ce}_{0.9}\text{Sm}_{0.1}\text{O}_{1.95}$ combination exhibits fast electrode kinetics. LSCF does not react with ceria-based electrolytes and has a compatible thermal expansion coefficient (Kharton et al., 2003).

Some important studies on the features of $\text{La}_x\text{Sr}_{1-x}\text{Co}_{1-y}\text{Fe}_y\text{O}_3$ (LSCF) have been carried out by Tai et al. (Tai et al., 1995a; 1995b). This relatively early work characterised the structure of these materials, identifying the rhombohedral/orthorhombic transition at $y=0.8$ for the $x=0.2$ and also studying the effect of this transition on the thermal expansion properties. Several features of interest were noted in the conductivity versus temperature plots, with conductivity decreasing with Fe content while the peak conductivity was observed to shift from 200 to 920°C

Chapter 2 Literature Review

with increasing Fe content. Studying the effect of the La:Sr ratio (Tai et al., 1995a) was also found to have a marked effect on the performance of these materials with peak conductivity of ~ 350 S/cm for $x=0.4$ compared to ~ 160 S /cm for $x = 0.2$. It was also found that the peak conductivity occurred at 550°C which, when combined with the results of the earlier study (Tai et al., 1995b), suggested a composition of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$ as the candidate cathode material.

Variation of the Fe:Co ratio was studied in the $\text{La}_{0.84}\text{Sr}_{0.16}\text{Co}_{1-x}\text{Fe}_x\text{O}_3$ composition and the effect on performance was obtained when used as a cathode on GDC electrolyte (Maguire et al., 2000). The optimum composition was reported to be at Co:Fe=0.7:0.3 with a conductivity of 643 S/cm at 800°C , which steadily increased over the $200\sim 800^\circ\text{C}$ temperature range. These results are in conflict with the results of Tai et al. (1995a; 1995b), as discussed earlier. However, Maguire et al. (2000) have only tested a limited number of materials, but those formed a study of the material in contact with a GDC electrolyte.

Investigation of a different composition of LSCF as a cathode on GDC electrolyte and the effect of thermal treatment on performance was carried out by Waller et al. (1996). A significant improvement in performance was observed with increasing A-site deficiency, which resulted from processing conditions. It was concluded that for LSCF the thermal history of the individual samples was of critical importance since a substantial performance variation was observed when the LSCF/GDC cell was tested.

Further investigation (Kostoglou and Fytikas, 1999) of A-site deficient LSCF has confirmed the performance advantage on increasing A-site deficiency. Although the electrical conductivity was found to decrease slightly as the Sr content decreased, the thermal expansion coefficients were found to be lowest for the compositions with

greatest A-site deficiency, that is $13.8 \times 10^{-6}/\text{K}$ for $\text{La}_{0.6}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ at 700°C . This value is relatively close to that of the common electrolytes, indicating the value of LSCF as a potential cathode material.

2.4.3 Anode materials

The main function of the SOFC anode is to provide reaction sites for the electrochemical oxidation of the fuel. The oxygen oxidizes H_2 , CO , etc., which is electrochemically transported through the electrolyte. Thus, the anode material must be stable in the fuel environment, having sufficient electronic and ionic conductivity and catalytic activity for the fuel gas reaction at the operating temperature and possessing sufficient porosity that allows the reactants to diffuse from bulk materials to the reaction sites inside the anode. Since the SOFC operates at elevated temperatures, the anode also must be chemically and thermally compatible with the other fuel cell components, from room temperature to operating and fabricating temperatures.

(1) Ni-YSZ cermet anode

In conventional SOFCs, Ni-YSZ cermets are widely believed to be the most promising material for the anode because of their high catalytic activity and the low cost of Ni. Ni is stable in contact with YSZ. YSZ is added to make the thermal expansion coefficient of the anode compatible with other cell components, especially with YSZ electrolyte, to inhibit the agglomeration of Ni particles and to transfer the oxygen ions from electrolyte to anode reaction sites which extends the anode reaction zone and reduces the anode overpotential. A network of micro-pores in the anode is required to provide a diffusion path for gaseous reactants and products transport. These functions depend strongly on the microstructural properties of the anode such as Ni and YSZ

particles, YSZ content, sintering conditions and pores distribution (Zhu and Deevi, 2003; Jiang and Chan, 2004)

Studies on anode materials have been focusing on lowering the overpotential, improving the long-term stability and identifying the anodic reaction mechanisms. Itoh et al. (1997) reported that a novel Ni-YSZ cermet anode, with a YSZ frame made of coarse (average size of 27.0 μm) and fine (average size of 0.6 μm) powders to sustain the network of Ni and pores, exhibited high electrical conductivity and more stable microstructure than using homogeneously sized YSZ. Kawada et al. (1990) studied the polarisation characteristics of Ni-YSZ cermets prepared by slurry coating method. It was reported that the interfacial resistance of Ni-YSZ anode on YSZ electrolyte could be reduced by inserting thin interfacial layers of Y_2O_3 -doped CeO_2 (YDC) (Tsai and Barnett, 1997 and 1998; Murray et al., 1999).

(2) CeO_2 -based anode

Ceramics based on CeO_2 exhibit high mixed ionic-electronic conductivity in a reducing environment. The use of the mixed conductors as anode materials results in an enlarged active reaction area of the whole particle surface other than the three-phase boundary of the physical contact points. Hence, CeO_2 -based materials have been evaluated for anode applications in intermediate temperature SOFCs.

CeO_2 -based anode can be divided into three types: (I) pure doped-ceria anode, (II) Ni- CeO_2 (or doped ceria) cermet anode and (III) doped-ceria anode with highly dispersed metal catalyst. Marina et al. (1999) studied $\text{Ce}_{0.6}\text{Gd}_{0.4}\text{O}_{1.8}$ (GDC) as the anode for both H_2 and CH_4 oxidation reactions at 1000°C. At 1000°C and steam ratio of 0.13, the cell produced power output of 470 mW/cm^2 for H_2 and only 80 mW/cm^2 for CH_4 . This indicates that pure GDC has poor electrocatalytic activity for methane oxidation.

Chapter 2 Literature Review

High electrode polarisation resistance of $\sim 11 \Omega\text{cm}^2$ at 800°C was reported for the H_2 oxidation reaction on pure GDC anode. Ni/doped ceria cermet, similar to Ni-YSZ cermet anode, has also been studied by many researchers (Xia and Liu, 2002a; Zha et al., 2004; Jiang et al., 2004). Comparison of anodic overpotentials of Ni-YSZ and Ni-GDC indicates that Ni-GDC anode outperforms Ni-YSZ anode (Joerger and Gauckler, 2001). Experimental results by Livermore et al. (1999) indicate that Ni-GDC cermet exhibits high activity towards methane steam reforming with the onset of methane activation occurring at temperatures as low as 482 K, and no appreciable carbon deposition was observed. Anodes made of doped CeO_2 particles with highly dispersed metal catalysts on the surface have shown significantly improved catalytic activity, especially at reduced temperatures. The effect of various noble metals and SDC particle size of type III anode on anode overpotential was studied by Watanabe et al. (1994). The highest electrocatalytic activity at 800°C was obtained for Ru-dispersed SDC. Highly dispersed Ni in SDC was found to be more effective in promoting the electrocatalytic activity for H_2 oxidation reaction than that of mixed Ni-SDC cermet anodes (Uchida et al., 2003). This was explained by the significant increase in the number of reactive sites at the nano-sized Ni and SDC boundaries.

The competitiveness of ternary component anode consisting of Cu, CeO_2 and YSZ on direct activation of dry hydrocarbons was evaluated by many researchers (Gorte et al., 2000; Craciun et al., 1999; Park et al., 2000). Unlike Ni, copper is inert to hydrogen or hydrocarbon oxidation and has no catalytic activity for the formation of C-C bonds, thus suppressing the carbon deposition. The primary function of copper in the cermet anodes is to provide electronic conduction path. Pure Cu-YSZ anode has very low

electrochemical activity for both H_2 and CH_4 oxidation reactions. Ceria catalyst was added to Cu-YSZ cermet to improve the electrode activity (Atkinson et al., 2004).

2.4.4 Interconnect materials

The function of the SOFC interconnect is to connect the anode of one cell to the cathode of the next cell in electrical series. The interconnect also separates the fuel from the oxidant in adjoining cells of a stack. Thus, the interconnect materials must be stable in both the reducing and oxidizing environment, impermeable to gases and having sufficient electronic conductivity and negligible ionic conductivity at the operating conditions. It also must be chemically and thermally compatible with the other cell components from room temperature to operating and fabricating temperature.

Currently, $LaCrO_3$ is the most commonly used interconnect material for conventional SOFCs. Before $LaCrO_3$ is used as the interconnect material, it must be stabilised by some dopants, such as Sr, Ca, Al, or Co. The substitution of lanthanum and chromium in $LaCrO_3$ with other cations significantly influences the properties of the material (Minh and Takahashi, 1995).

Because of the high cost of the ceramic materials and their low electrical and thermal conductivity at reduced temperatures, some researchers have studied the potential of metallic alloys as the interconnect materials for reduced-temperature operation (Linderroth et al., 1996; Badwal et al., 1997; Brylewski et al., 2001). The primary concerns regarding metallic interconnects are thermal expansion mismatch with other cell components, and long-term instability (oxidation, corrosion) under fuel cell operating conditions. Through a comparison of thermal expansion with YSZ and measurement of the electrical conductivity, Jiang et al. (2000b and 2002) found that $Cr_{94}Fe_5(Y_2O_3)_1$ seemed to be the best candidate for interconnect materials. However, for

Cr-based alloy, evaporation of gaseous Cr species under oxidizing conditions is inevitable. Electrochemical deposition of Cr species at electrode-electrolyte interface would cause degradation of the electrode performance. To overcome the chromium evaporation and related catalyst poisoning problem, protective coatings of lanthanum chromites or lanthanum manganites were deposited on the Cr-based interconnect (Ruchdaschel et al., 1997; Diethelm et al., 1999). Thermally sprayed manganite coatings have led to stable long-term performance lasting about 12,000 h with a degradation rate in cell voltage of less than 1%/1000 h (Diethelm et al., 1999).

For SOFCs with operating temperatures below 800°C, ferritic stainless steels are potential materials for interconnects due to good chemical stability, thermal expansion coefficient close to that of other cell components and much lower material and fabrication cost than doped chromites or chromium-based alloys (Singhal and Kendall, 2003). Much progress has been made in developing ferritic steels that form thin spinel-type corrosion scales with significant electrical conductivity and have well-adhered corrosion scales which reduce the release of volatile Cr species (Abellan et al., 2001).

2.5 Powder synthesis techniques

The characteristics of the starting powder, including particle size, particle shape, size distribution and degree of agglomeration, have a profound influence on the densification and the evolution of the microstructure of the sintered parts. Several kinds of synthesis techniques have been used to prepare ceramic powders for various SOFC components.

2.5.1 Solid-state reaction technique

Solid-state reaction technique is one of the most convenient methods used to synthesise ceramic powders. The standardised powders are mixed in stoichiometric proportions and wet-milled in ethanol to homogenise the mixture. The slurry is then dried and calcined at a certain temperature for several hours. The milling-calcination procedure is then repeated to ensure phase homogeneity. Two major processes are involved in solid-state reactions:

- Breaking and reconstruction of bonds at the contact region, leading to the nucleation of a product phase.
- Transport of substance to the contact region.

The final product is characterised by X-ray diffraction (XRD) technique to ensure a single phase. The drawbacks of this method are large product particle size (generally $>1\ \mu\text{m}$) and inhomogeneity of the product. Some of the synthesised powders by this method are shown in Table 2-7.

Table 2-7 Synthesised powders and synthesis conditions by solid state reaction.

Ceramic powder	Starting materials	Calcination temperature	Holding time	References
$(\text{CeO}_2)_{0.8}(\text{SmO}_{1.5})_{0.2}$	CeO_2 , Sm_2O_3	1300°C	10 h	Milliken et al., 1999
$\text{La}_{1-x}\text{Sr}_x\text{Ga}_{1-y}\text{Mg}_y\text{O}_3$	La_2O_3 , SrCO_3 , MgO , GaO	1000°C	6 h	Yamaji et al., 1998
$(\text{La}_{0.8}\text{Sr}_{0.15})_{0.95}\text{MnO}_3$	La_2O_3 , SrCO_3 , Mn_2O_3	1350°C	10 h	Hayashi et al., 1997
$\text{Ln}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_3$	Ln_2O_3 , SrCO_3 , Co_3O_4 , Fe_2O_3	1000°C	12 h	Qiu et al., 2002
$\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$	La_2O_3 , SrCO_3 , Co_3O_4	1100°C	5 h	Horiata et al., 2001

2.5.2 Amorphous citrate process

The amorphous citrate process is also called Pechini process after its inventor. The process involves dissolving appropriate proportions of salts of desired metal elements in a citric acid/ethylene glycol solution. The solvent is evaporated, and a transparent amorphous resin containing a homogeneous mixture of the metals is formed. The resin is then decomposed by heating to remove the organics and produces the desired oxide. The amorphous citrate or liquid mix process involves two basic chemical reactions: (i) complexation or chelation between metal ions and citric acid, and (ii) polyesterification of complexes with ethylene glycol. The complexation and polyesterification reactions preserve the homogeneity of the metal salt solution in a gel. As a result, powders produced would have high surface area and precise compositional stoichiometry. Polymerisation and decomposition conditions of the amorphous citrate process are often tailored or modified to achieve the desired characteristics of the oxide powder product (Jin et al., 2000). The process has also been modified by changing the citric acid/ethylene glycol ratio of the preparation solution (Huang et al., 1998a).

2.5.3 Glycine-nitrate combustion technique

Several self-sustaining combustion processes were reported to synthesise multi-component composite oxide powders (Chick et al., 1990; Xia and Liu, 2002a; Kim et al., 1997). Metal nitrates and glycine, a low molecular weight amino acid, were dissolved in water. The solution was then boiled to evaporate excess water. The viscous liquid then auto-ignited and underwent self-sustaining combustion, producing an ash composed of the oxide product. These processes have an advantage that oxide powders can be formed directly from the precursor solution without introduction of any intermediate products and can produce high surface area, compositionally homogeneous powders with low

levels of residual carbon. The process uses moderate temperatures to form fine powders rapidly and inexpensively, and the powders are so uniform, which require very little milling. These factors make the process very economical and attractive to industries for manufacturing ceramic-based products. In addition, powder production by this technique makes little impact on the environment.

Xia and Liu (2002a) reported the preparation of highly porous or foam-structured powder of $\text{Gd}_{0.1}\text{Ce}_{0.9}\text{O}_{1.95}$ with extremely low fill density using this glycine-nitrate process. The highly porous structure led to the successful fabrication of a thin and dense electrolyte membrane on the anode substrate by conventional dry-pressing method. Kim et al. (1997) also reported the preparation of ultra-fine $(\text{CeO}_2)_{0.9}(\text{GdO}_{1.5})_{0.1}$ (with specific surface area of 19~23 m^2/g) powders by this powder synthesis method. Chick et al. (1990) prepared $\text{La}_{0.84}\text{Sr}_{0.16}\text{CoO}_3$ (LSC) and $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ (LSM) by glycine-nitrate combustion process. The synthesised powder ashes were composed of very fine (5 to 40 nm in diameter) LSC and LSM particles linked together in chains.

2.5.4 Spray pyrolysis technique

Spray drying differs from spray pyrolysis in that the former provides only drying of the solid or hollow spheres obtained as a result of spraying, while in the latter, the atomised (solid) precursor can also undergo heating to a temperature required for its decomposition and conversion to the desired ceramic powder product. In brief, the process consists of the following steps.

- (a) Atomization (spraying) of the liquid-rich starting material (mostly true solutions, but also colloidal dispersions, emulsions and sols).
- (b) Evaporation of the liquid component, solute condensation with the droplet dried and converted into spherical solid particles composed of the solute.

(c) Pyrolysis (or thermolysis, meaning thermal decomposition) and sintering of the dried precursor spheres.

Spray pyrolysis has been widely used in the preparation of ZrO_2 powders. In a typical process, Dubois et al. (1989) prepared Y_2O_3 -stabilised ZrO_2 powder by the spray pyrolysis technique, using $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and $\text{Y}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ as the source materials. A mist of the mixed solution of Zr^{4+} and Y^{3+} ions within a narrow size distribution range was generated by an ultrasonic atomiser at different frequencies and introduced into a furnace along with a carrier gas below 400°C so as to avoid crystallization of the particles. After the volatile was totally removed, the powders collected with an electro-filter were calcined in air at 410°C for 1 h and then at 700°C for 2 h. The specific surface area of the powder was $30 \text{ m}^2/\text{g}$ with the mean particle size of $0.2\text{--}1.8 \mu\text{m}$. Yoshioka et al. (1992) prepared the composition of 12 mol % $\text{CeO}_2\text{--ZrO}_2$ by the spray pyrolysis of a mixed solution of $\text{ZrO}(\text{NO}_3)_2$ and $\text{Ce}(\text{NO}_3)_3$. The presence of redox compounds, e.g., NH_4NO_3 and NH_2CONH_2 , as additives in the spraying solution helped in the production of fine particles.

2.6 Fabrication techniques for SOFC components

Solid oxide fuel cell (SOFC) is a kind of fuel cells using ceramic materials for its electrolyte, electrodes and interconnect fabrication because of high operating temperature. The properties of the ceramic powders used to fabricate the electrolytes and electrodes are the important elements that affect the performance of the fuel cell, such as operating temperature, stability, tolerance to contamination and so on. However, the material processes affect not only the performance of the SOFC but also the design of the SOFC configuration. The principles of the fabrication processes and their

possible applications on SOFC technology are reviewed in this section. The main fabrication processes for SOFC components are listed in Table 2-8.

2.6.1 Chemical Vapor Deposition (CVD)

Chemical vapor deposition (CVD) is commonly used for fabricating microelectronics, which uses one or more gaseous precursors to form a solid material by means of an activation process. The steps involved are: (1) transport of reactant vapors to surface of substrate where it is then (2) adsorbed, followed by (3) the chemical reaction which leads to a solid product for (4) crystal growth. Film thickness growth

Table 2-8 Ceramic processes for SOFC components.

Category	Sub-category	Process	Application	Reference
Chemical deposition technique	Chemical vapor deposition	Conventional CVD Electrochemical CVD(EVD) Combustion CVD (CCVD) Metal-organic vapor deposition (MOCVD)	Electrolyte Electrolyte Electrode Electrolyte	Will et al., 2000 Young et al., 2000 Liu et al., 2004 Wang et al., 2000
	Liquid precursor route	Sol-gel Spray pyrolysis	Electrolyte Cathode	Chen et al., 1994 Charpentier et al., 2000;
Physical deposition technique	Thermal spray	DC vacuum plasma spray RF vacuum plasma spray Atmosphere plasma spray	Electrode Interconnect Electrolyte	Lang et al., 2001 Henne et al., 1999
	Laser deposition	Pulsed laser deposition Laser spray	Electrolyte	Kokai et al., 1992
	Physical vapor deposition	RF-sputtering Reactive DC magnetron sputtering	Anode Electrolyte	Nakagawa et al., 1989 Wang and Barnett, 1993
Ceramic powder processing technique	Slurry forming	Screen printing Tape casting Tape calendering Slurry coating Electrophoretic deposition (EPD)	Electrode Electrolyte Multi-layer Electrolyte Electrolyte	Sasaki et al., 1994 Ihringer et al., 1997 Minh et al., 1994 Aizawa et al., 1993 Mathews et al., 2000
	Press forming	Dry pressing Extrusion Laminating	Electrolyte Electrolyte Multi-layer	Xia and Liu, 2001a Hatchwell et al., 1999 Ohrui et al., 1998

rates are typically in the range of 1-10 $\mu\text{m/h}$, and are dependent on evaporation rate and substrate temperature. The advantages of CVD include its ability to consistently produce uniform, pure, and adherent films.

In order to fulfill different requirements, several kinds of CVD techniques are available such as electrochemical vapor deposition (EVD) (Young et al., 2000), metal-organic vapor deposition (MOCVD) (Wang et al., 2000), combustion chemical vapor deposition (CCVD) (Liu et al., 2004) and plasma-assisted chemical vapor deposition (PCVD) (Will et al., 2000).

2.6.2 Electrochemical Vapor Deposition (EVD)

EVD is an extended and modified CVD process in which reactor is divided into two chambers by a porous ceramic substrate. One of these chambers is filled with a metal compound reactant while the other with an oxidant source reactor. The process is initialized by a normal CVD type reaction between the metal chloride vapor and the oxidant, which closes the pores in the ceramic substrate. The film growth then proceeds due to the presence of an electrochemical potential gradient across the deposited film. The oxygen ions formed on the oxidant side of the substrate diffuse through the thin deposited layer to the metal chloride side where they react with the metal chloride vapor to form the metal oxide product. For the deposition of YSZ films, a mixture of ZrCl_4 and YCl_3 vapor is used as the metal chloride sources while water vapor is used as the oxidant source. Film growth rates range from 3 to 50 $\mu\text{m/h}$. The EVD process has been used to deposit YSZ films onto the porous cathode in the Siemens Westinghouse sealless tubular SOFCs (Pal and Singal, 1990).

2.6.3 Physical Vapor Deposition (PVD)

Physical Vapor Deposition (PVD) refers to a family of processes in which a material is converted to its vapor phase in a vacuum chamber and condensed onto a substrate surface as a thin film. The synthesis of the coating vapor can be accomplished by any one of the several methods, such as electric resistance heating or ion bombardment, and can be classified into three principal groups, namely vacuum evaporation, sputtering and ion plating. The simplest of these, vacuum evaporation is performed by heating the source material to its evaporation temperature in a vacuum chamber, and then allowing the vapor to condense on the substrate surface. The extremely high sublimation temperatures of ceramic materials make the vacuum evaporation method unsuitable for YSZ deposition. The most commonly used PVD technique for YSZ deposition in the production of SOFCs is radio frequency (RF) sputtering (Nakagawa et al., 1989). The technique involves the generation of high-energy ionized gas particles (such as Ar^+) by means of an electric field to form plasma. The bombardment of the source material (the cathode) by the high-energy particles causes surface atoms to be ejected by momentum transfer. The ejected material, which mostly comprises uncharged atoms, then travels to the substrate (anode) where it condenses to form the desired thin film. YSZ deposition rates for RF sputtering are generally low ($\sim 0.25 \mu\text{m/h}$). Reactive magnetron sputtering is an alternative that allows much higher deposition rates ($\sim 2.5 \mu\text{m/h}$).

2.6.4 Electrophoretic Deposition (EPD)

Electrophoresis is achieved by the motion of charged particles towards an electrode under an applied electric field (Zhitomirsky and Petric, 2000). In the deposition of ceramic films, the ceramic particles must first be electrically charged to permit forming

by EPD. This charge can be imparted by adsorbed inorganic ions or by electrostatically active dispersants. Addition of a binder to the ceramic suspension can also be done to increase the adherence and strength of the green film. However, this adds the requirement of a burnout procedure prior to the sintering of the green film (similar to tape casting). EPD has the advantage of having a short formation time, which can be closely controlled by varying the applied potential. Deposition rates as fast as 1 mm/min can be achieved. The equipment for EPD is relatively simple and low in cost, which makes it a rather promising method for SOFC fabrication (Mathews et al., 2000; Kobayashi et al., 2000). However, the high shrinkage associated with the burnout of organics limits its application to small-scale cells.

2.6.5 Tape casting

Tape casting is one of the most common methods that have been used to fabricate the components of SOFCs. In the tape casting process, ceramic powder and essential additives are dispersed in a solvent to form a slurry, which is then laid onto a carrier by passing it under a doctor blade, or onto a fixed casting surface using a traversing casting head. Other than the ceramic powder, the most important choice is the selection of a binder/plasticizer/dispersant system.

Ihringer et al. (1997) used a water-based tape casting method and produced 0.6~10 μm YSZ layers which were cast on 200~250 μm NiO-YSZ anode substrates and co-sintered at 1350°C. After sintering, the complementary cathode was deposited. The cells exhibited a power density of 580 mW/cm^2 with an OCV of 1.01V at 760°C. Will et al. (2000) produced thin zirconia tapes and laminated them at 50°C with a separately produced green Ni-cermet tape. After sintering of the bilayer, the closed porosity of

zirconia layer was characterised by isolated round holes with diameters of 3~5 μm , which were probably formed due to the high organic content in the green tape.

2.6.6 Screen printing

A highly viscous paste consisting of a mixture of ceramic powder, organic binder and plasticizer is forced through the open meshes of a screen using a squeegee. Parameters such as grain size, grain form, surface properties and packing density of the powder have to be optimised. The screen-printed films are dried and sintered at high temperatures.

Screen printing technique has been widely used to prepare the porous electrodes of SOFCs (Sasaki et al., 1994; Chen et al., 2003). Screen printing technique can also be used to produce dense films. Cassidy (1996) used the screen printing technique as a method to deposit a zirconia layer onto a tape-cast anode support. The green anode-electrolyte bilayer was sintered, resulting in an electrolyte thickness of around 8 μm .

2.6.7 Slurry coating

Thin porous or dense films may be fabricated by the slurry coating method. In the case of a dense electrolyte such as YSZ, stabilised water suspension with a small amount of powder (5% YSZ) is coated onto a substrate by spinning, dipping or spraying method, dried at room temperature, preheated at elevated temperature, and finally sintered. This cycle is normally repeated 5 to 10 times to achieve a desired film thickness. Using an ethanol suspension of YSZ may significantly shorten the drying step. Thin and dense films with no observable cracks were produced by Arai (1989). Aizawa et al. (1993) used the slurry coating technique to deposit a 20~30 μm thick

zirconia film onto tubular cathode substrates. The films were dense and such cells exhibited an OCV close to the theoretical value.

Colloidal deposition is similar to slurry coating. YSZ powder is mixed with isopropanol. To avoid the cracking of YSZ thin film due to the stress, the shrinkage of the substrate is carefully matched to the shrinkage profile of YSZ thin film. The film is under compression rather than tension during sintering (Souza et al., 1997).

2.6.8 Dry pressing

In dry pressing, high pressure is applied to dry powder in a die to form a desired shape. The result of the compaction process is a part with density significantly higher than the starting powder. The green strength of the part is sufficient for handling but far less than that achieved after sintering. Polymeric binders such as polyvinyl alcohol (PVA) or polyvinyl butyral (PVB) are often added to the ceramic powders to improve the green strength. During the application of pressure, the powder is initially repacked into a more efficient arrangement; the pore space is reduced while the number of contacting points between particles is increased. Subsequent increase in pressure causes the particles to plastically deform, further increasing interparticle contact area and reducing pore volume. Since the dry powder will not flow during pressing, the geometry of the part must be relatively simple. The powder distribution in the die cavity must also be as even as possible to avoid a non-uniform pressure distribution in the pressed part. The advantages of dry pressing are simplicity, low cost and high achievable densities. Its disadvantages lie in the difficulty to scale up the process to produce parts with high surface area to thickness ratio. Although dry pressing is a “thick-film” technique, traditionally producing parts no thinner than 500 μm , Xia and Liu (2001a) have successfully developed a method to dry-press ceramic films as thin as

8 μm . A maximum power density of 140 mW/cm^2 at 500°C was reported for SOFCs with thin film ($\sim 15 \mu\text{m}$) electrolytes prepared by dry pressing. The anode, electrolyte and cathode were made from NiO-GDC, GDC and $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ (SSC), respectively.

2.7 Cell configuration and stack design

A SOFC single cell can be configured into various shapes depending on the specific stack design. SOFC cells have been made into tubular, flat-plate or planar, bell-and-spigot, banded, and corrugated structures (Minh and Takahashi, 1995). Each shape results in distinct current paths and requires or incorporates different cell configurations. The configurations in SOFC single cells can be classified into two broad categories: self-supporting and external-supporting. In the self-supporting configuration, one of the cell components (often the thickest layer) acts as the cell structural support. Thus, single cells can be designed as electrolyte-supported, anode-supported, or cathode-supported. In the external-supporting configuration, the single cell is configured as thin layers on the interconnect or a porous substrate. The various cell configurations for SOFCs are schematically shown in Figure 2-5 (Minh, 2004). The key features of each configuration are summarized in Table 2-9 (Singhal and Kendall, 2003).

A SOFC single cell, under typical operating conditions, produces an open circuit voltage of about 1 V. Therefore, it is necessary to connect single fuel cells in series to produce a reasonably high voltage output for practical applications. At present, four common SOFC stack configurations have been proposed and fabricated: the tubular design, the segmented-cell-in-series design, the monolithic design and the flat-plate design. Figure 2-6 shows the schematics of the four designs (Minh and Takahashi, 1995). Among these four designs, the sealless tubular design is the most advanced one. Multi-kilowatt-size tubular stacks have been constructed and tested with a variety of

Figure 2-5 SOFC single cell configurations (C: cathode; E: electrolyte; A: anode).

Table 2-9 Features of planar single-cell configurations.

Cell configuration	Advantage	Disadvantage
Self-supporting Electrolyte-supported	Relatively strong structural support from dense electrolyte; Less susceptible to failure due to anode re-oxidation.	Higher resistance due to low electrolyte conductivity; Higher operating temperatures required to minimise electrolyte ohmic losses.
Anode-supported	Highly conductive anode; Lower operating temperature via use of thin electrolytes.	Potential anode re-oxidation; Mass transport limitation due to thick anodes.
Cathode-supported	No oxidation issues; Lower operating temperature via use of thin electrolyte.	Lower conductivity; Mass transport limitation due to thick cathodes.
External-supporting Interconnect-supported	Thin cell components for lower operating temperature; Strong structures form metallic interconnects.	Interconnect oxidation; Flow-field design limitation due to cell support requirement.
Porous substrate	Thin cell components for lower operating temperature; Potential for use of non-cell material for support to improve properties.	Increased complexity due to addition of new materials; Potential electrical shorts with porous metallic substrate due to uneven surface.

fuels by Siemens Westinghouse (Singhal, 1999; Lundberg et al., 2001). The segmented-cell-in-series design was re-examined in the early 1990s. Their output power is smaller than that of the sealless tubular design. The monolithic design is the latest SOFC stack concept. The design has the potential to achieve high power density because of its compact and lightweight structure. The flat-plate design, common in other types of fuel cell, has received much attention recently (Godfrey et al., 1999; Elangovan et al., 2001; Pham et al., 2001; Tietz et al., 2002). This design offers simple cell geometry and multiple fabrication options so that a lower manufacturing cost can be expected.

Figure 2-6 Schematics of four typical SOFC stack designs: (a) sealless tubular design, (b) segmented-cell-in-series design, (c) monolithic design and (d) flat-plane design.

CHAPTER THREE

EXPERIMENTAL PROCEDURE

3.1 Samples preparation

3.1.1 Samples preparation for electrolyte conductivity measurements

The raw material for the electrolyte in this study was nano-sized $\text{Gd}_{0.1}\text{Ce}_{0.9}\text{O}_{1.95}$ (GDC) powder from Nextech Materials Ltd, USA, which was prepared by hydrothermal process. The influence of calcination at 750°C for 2 h on the powder characteristics and sinterability was determined. GDC pellets for conductivity measurements were made by conventional ceramic processing method, i.e., mixing, pressing and sintering. To minimise impurity levels, no binder was used in the pressing step. In order to study the effect of compaction pressure on the sintering behaviour, GDC pellets were uniaxially pressed using a steel die of 13 mm in diameter under different pressures ranging from 60 to 400 MPa. Green pellets were then sintered in an electric resistance furnace in air with different sintering parameters. Samples information associated with compaction pressures and sintering conditions is shown in Table 3-1.

3.1.2 Half cells preparation for cathode optimisation study

The raw material for the cathode in this study was $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) oxide powder from Thin Film Components, USA. It was synthesized by combustion spray pyrolysis process. The specific surface area of the powder is $4.66 \text{ m}^2/\text{g}$. It has a chemical purity of 99.99% and an average particle size of $1.1 \mu\text{m}$. Figure 3-1 shows the particle size distribution of the LSCF powder. The powder almost displays a Gaussian-

Table 3-1 Compaction and sintering conditions for GDC pellets

Sample code	Compaction pressure (MPa)	Sintering temperature (°C)	Holding time (h)	Heating rate (°C/min)
GDC-1	60	1200	5	5
GDC-2	160	1200	5	5
GDC-3	240	1200	5	5
GDC-4	400	1200	5	5
GDC-5	400	1300	5	5
GDC-6	400	1400	5	5
GDC-7	400	1500	5	5
GDC-8	400	1600	5	5
GDC-9	240	1300	2	5

Figure 3-1 Particle size distribution of LSCF powder.

Chapter 3 Experimental Procedure

type symmetrical distribution in particle size.

The composite cathode materials used in this study were prepared by ball milling the mixture of LSCF powder and GDC powder in isopropanol overnight followed by drying on a hot plate to eliminate the solvent. The GDC powder was calcined at 750°C for 2 h before being mixed with the LSCF powder. The LSCF-GDC compositions were varied from 20 to 60 wt.% GDC, and they are identified as LSCF-GDC20 to LSCF-GDC60 hereafter.

The preparation flowchart of half cells is shown in Figure 3-2. The GDC electrolyte disks were first prepared using the above-mentioned nanosized GDC powder by die pressing and sintering at 1300°C for 2 h to produce a dense structure. After sintering,

Figure 3-2 Flowchart for half cells fabrication.

Chapter 3 Experimental Procedure

the relative density of GDC electrolyte disks was about 97.8% and the dimensions were about 17.4 mm in diameter and 1 mm in thickness. The thickness of GDC disks decreased to ca. 0.8 mm after surface grinding. The LSCF or LSCF-GDC slurry and Ag paste were applied by screen printing to each side of GDC electrolyte disk as the cathode, counter and reference electrodes, respectively. The slurry of the cathode was made by mixing the powder with ~20 wt.% polyethylene glycol 400 using mortar and pestle. Cathodes were first fired at 500°C for 1 h to burn out the organic substances, and then sintered at temperatures ranging from 750 to 1100°C for 2 h at a heating rate of 5°C/min. Table 3-2 tabulates the compositions and sintering conditions of cathodes of half cell samples. The cathode surface area was about 0.5 cm². The distance between counter and reference electrodes is ~3 mm. The symmetrical configuration of half cells is shown in Figure 3-3.

Table 3-2 Compositions and sintering conditions of cathodes of half cells.

Sample code	GDC content in wt. %	Sintering temperature (°C)	Holding time (h)	Heating rate (°C/min)
LSCF-1	0	750	2	5
LSCF-2	0	850	2	5
LSCF-3	0	900	2	5
LSCF-4	0	950	2	5
LSCF-5	0	1100	2	5
LSCF-GDC20	20	900	2	5
LSCF-GDC30	30	900	2	5
LSCF-GDC40	40	900	2	5
LSCF-GDC50	50	900	2	5
LSCF-GDC60	60	900	2	5

Figure 3-3 Configuration of half cells.

3.1.3 Thin film SOFCs preparation for performance evaluation

(1) Synthesis of BSCF powder

Aside from the LSCF, another cathode material used in this study for thin film SOFCs was $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF). The BSCF powder was synthesised using a combined citrate and EDTA complexing method. The preparation procedure of the BSCF material is shown in Figure 3-4. The necessary amount of $\text{Ba}(\text{NO}_3)_2$ was first dissolved in $\text{EDTA-NH}_3\cdot\text{H}_2\text{O}$ solution under heating and stirring, then the calculated amounts of $\text{Sr}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_2$ and $\text{Fe}(\text{NO}_3)_3$ were added to the solution. After stirring

Chapter 3 Experimental Procedure

for a certain time, a proper amount of citric acid was introduced. The molar ratio of EDTA acid:citric acid:total metal ions was controlled to be around 1:1.5:1. Precipitation might occur after the addition of citric acid. $\text{NH}_3\cdot\text{H}_2\text{O}$ was then added to adjust the pH value to around 6, and the solution became transparent. EDTA- NH_3 and citrate formed a buffering solution, so the pH value of the system successfully sustained around 6 during the whole process. With the evaporation of water, a dark purple gel was obtained. The gel was then heated at 130°C for about 12 h to make a primary powder, which was calcined at 800°C for 5 h to obtain the powder with final composition.

Figure 3-4 Flowchart for the preparation of BSCF powder.

Figure 3-5 Particle size distribution of NiO powder.

(2) Preparation of GDC electrolyte thin film SOFCs

The starting materials for the anode of GDC electrolyte thin film SOFCs are NiO powder (J. T. Baker, US) and the above-mentioned GDC powder (Nextech materials, US). Figure 3-5 shows the particle size distribution of NiO powder. Since the Fritsch Analysette 22 Particle Size Analyzer cannot detect the particles smaller than 0.3 μm in size, it is hard to accurately estimate the average particle size. However, the average particle size is smaller than 0.7 μm according to Figure 3-5.

The flowchart for the preparation of GDC electrolyte thin film SOFCs is shown in Figure 3-6. First, the NiO powder was mixed with 35 wt.% of calcined GDC powder by ball milling in isopropanol for overnight, and then the NiO-GDC slurry was dried on a hot plate to remove the solvent. The resulting anode powder was uniaxially pressed under 100 MPa using a 24 mm diameter steel die. To prepare GDC thin film on the anode, GDC powder was added in dry or wet (i.e., dispersed in solvent) form onto the

Chapter 3 Experimental Procedure

pre-pressed green NiO-GDC substrate in the steel die. In the case of wet powder filling, 5 g of GDC powders was dispersed in 40 ml of iso-propanol solvent. After evaporation of solvent, the GDC powder and the substrate were then co-pressed under a pressure of 240 MPa to form a green bilayer. The electrolyte thickness was controlled by the amount of GDC powder added. Green electrolyte/anode bilayers were subsequently cosintered at 1300°C for 2 h at a heating and cooling rate of 5°C/min. An ink prepared

Figure 3-6 Flowchart for preparation of GDC electrolyte thin film SOFCs.

Chapter 3 Experimental Procedure

by mixing LSCF-GDC50 or BSCF powder and proper amount of polyethylene glycol 400 was applied onto the electrolyte film by screen printing technique, followed by sintering at 900°C for 2 h to form a porous cathode with a surface area of 0.5 mm². To minimise the contact resistance between the cathode and the Pt mesh, a porous Pt layer was coated as the current collector by painting Pt paste onto the cathode surface and subsequently sintering at 900°C for 30 min. Figure 3-7 shows the configuration of GDC electrolyte thin film SOFC samples.

Figure 3-7 Configuration of GDC electrolyte thin film SOFCs.

(3) Preparation of YSZ/GDC bilayer electrolyte thin film SOFCs

For YSZ/GDC bilayer electrolyte thin film SOFCs, the anode powder was prepared by homogeneously mixing 60 wt.% NiO powder (J.T. Baker, US) and 40 wt.% YSZ powder (8 mol% Y₂O₃ stabilized ZrO₂, Tosoh, Japan) in isopropanol using ball milling.

Chapter 3 Experimental Procedure

After drying, the NiO-YSZ powder was compacted under an uniaxial pressure to form disks of 24 mm in diameter. To increase the porosity in the anode substrate, part of the NiO-YSZ powder was mixed with 15 wt. % polyvinyl butyral (PVB) powder as pore-former using mortar and pestle. The green anode disks with or without pore-former were then baked at 900°C for 1 h to increase the mechanical strength for handling and/or to remove the pore-former. To form anode-supported YSZ/GDC bilayer electrolyte film, suspensions of YSZ and GDC were applied sequentially onto the baked anode disks using a spray coating method. The composition of YSZ and GDC suspensions is given in Table 3-3. The coated anode disks were subsequently sintered at 1400°C for 2 h to obtain dense YSZ/GDC bilayer electrolyte films supported on anode substrates. The preparation of LSCF-GDC50 composite cathode and Pt current collector is the same as that for GDC electrolyte thin film SOFCs described previously.

Table 3-3 Composition of YSZ or GDC suspension for depositing YSZ/GDC bilayer film on anode substrate.

Composition	Function	Weight (g)
YSZ or GDC	Ceramic powder	1
Isopropanol	Solvent	36
Trichloroethylene	Solvent	4
Corn oil	Despersant	0.1
Benzyl butyl phthalate	Plasticizer	0.1
Polyethylene glycol 6000	Plasticizer	0.1
Polyvinyl butyral	Binder	0.07

3.2 Samples characterisation techniques

3.2.1 X-ray diffractometry (XRD)

A Philips MPD 1880 Diffractometer System (XRD) (Netherlands) was used to study the crystal structure of the synthesised BSCF powder and the interactions between YSZ and GDC during high temperature sintering. X-ray scanning was conducted over a 2θ range of 20-90° at a scan rate of 1.2°/min. Monochromatic Cu $K_{\alpha 1}$ radiation ($\lambda=1.54060$ Å) generated at 40 kV and 30 mA was employed.

3.2.2 Scanning electron microscopy (SEM)

Scanning Electron Microscopy (LEICA S360 SEM, Cambridge, UK, or JSM LV5600 SEM, JEOL, Japan) was used to investigate the microstructures of GDC pellets, half cells, electrolyte/anode bilayers and thin film cells. Since the samples involved in this study were mostly made from ceramic materials normally with poor electrical conductivity at room temperature, the samples were first coated with gold before being placed into the chamber for SEM observation. With energy dispersive and wavelength dispersive spectroscopy attachments, microscopic qualitative and quantitative element analysis can be conducted by the characteristic X-rays emitted from the elements present in the samples. Element analysis techniques like mapping, line scan or spot excitation are often employed to provide information on the inter-reaction and inter-diffusion at the interface between SOFC components during the fabrication and operation procedure.

3.2.3 Transmission electron microscopy (TEM)

The JEOL JEM-2012 (Japan) Transmission Electron Microscope was employed to study the characteristics of the as-received and calcined nanocrystalline GDC powders.

Chapter 3 Experimental Procedure

The powders were ultrasonically dispersed in alcohol for 1 h, and then draw a copper mesh in the suspension to gain some powders on it. To prevent the TEM vacuum chamber from contamination, the copper mesh was placed in another chamber followed by evacuation for 20 min to fully evaporate the solvent and pump away the powders that weakly adhered to the copper mesh. After that, the copper mesh was transferred to the TEM chamber. An accelerating voltage of 200 kV was used for microstructural observation.

3.2.4 Particle size analyzer

The particle size distribution of raw powders was measured by a laser particle size analyzer (Fritsch Analysette 22). He-Ne laser with a wavelength of 0.63 μm is commonly used as the light source. Two sets of data, quantity percentage of individual particles in terms of size in diameter and the distribution density of the particles, were determined. The measurable size range of this equipment is 0.3-300 μm .

3.2.5 Dilatometry

The shrinkage behaviours of green electrolyte and anode samples were investigated using a Unitherm 1161 dilatometer (Anter, USA) in order to obtain dense, crack-free and continuous electrolyte film on anode substrate after cosintering of electrolyte/anode bilayers. Samples were sintered in the dilatometer furnace at 1300°C for 2 h with a heating rate of 5°C/min and the linear shrinkage of the sample was recorded in a real-time mode by a computer interfaced to the machine. The sintering conditions of samples for dilatometric analysis involving sintering temperature, holding time and heating rate are the same as those for sintering of electrolyte/anode bilayers in a different air furnace.

3.2.6 BET analysis

BET (Brunauer-Emmott-Teller) method was used to measure the specific surface area of the as-received and calcined GDC powders with ASAP 2010 device (Micromeritics, USA). Nitrogen was used as adsorbate in this measurement. For comparison with the results on the average particle size of powders obtained from TEM observation and particle size analyzer, the mean particle size d (nm) was calculated from BET surface area data S_{BET} (m^2/g) and the true density ρ_{T} (g/cm^3) based on the following relationship (Brunauer, 1938).

$$d = 6000 / (\rho_{\text{T}} \cdot S_{\text{BET}}) \quad (3-1)$$

3.2.7 Density/porosity measurement

The density of electrolyte and anode substrate samples was calculated from the geometric dimensions and mass of the samples. After sintering, electrolyte or anode substrate (before and after chemical reduction in hydrogen) samples were ground very carefully using grit papers to obtain smooth surfaces, then the dimensions (diameter and thickness) of the samples were measured using a micrometer. The masses of the samples were measured using a high precision electronic balance with a resolution of 0.1 mg. The relative density of a sample is represented by measured density divided by theoretical density of the sample material. The porosity of a sample is defined as 1 minus relative density.

The porosity of cathode layers was also determined by the dimensions/mass technique. The dimensions of circular cathode layers, especially the thickness, was determined under SEM. The mass of cathode layers was obtained by weighing the electrolyte disk before and after application and sintering of cathode layers.

3.2.8 Grain size determination

The average grain size of sintered GDC electrolytes was determined from SEM micrographs of the samples by the linear intercept technique described by Mendelson (1968). To determine the grain size, sintered electrolytes were polished using diamond pastes and then thermally etched at temperatures $\sim 50^{\circ}\text{C}$ lower than the sintering temperature of the sample for 30 min to clearly reveal the grain boundaries under SEM. Micrographs were taken and lines were drawn on them with at least 250 grains covered. The average grain size, D , was then obtained as follows: $D = 1.56 L$, where L is the average grain-boundary intercept length. For example, for the microstructure shown in Figure 3-8, the average grain size can be determined using the above method as $1.8\ \mu\text{m}$.

Figure 3-8 SEM micrograph showing typical microstructure of GDC electrolytes after grinding and thermal etching.

3.3 Electrochemical characterisation techniques

3.3.1 AC impedance spectroscopy

AC impedance spectroscopy is used extensively in the field of solid-state ionics and electrochemistry to separate bulk and interfacial contributions from the overall alternating-current response of a material. In impedance spectroscopy, a small alternating voltage $V(\omega)$ is applied to a sample, and the induced current $I(\omega)$ is measured. The impedance $V(\omega)/I(\omega)$ is evaluated as a function of the alternating-current frequency (ω). In a complex impedance diagram (Nyquist or Cole–Cole plot), the imaginary part of the impedance Z'' (capacitance) is plotted versus the real part of the impedance Z' (resistance). Figure 3-9 shows a typical impedance spectrum of GDC electrolytes. In this study, AC impedance spectroscopy was employed to characterise the ionic conductivity of GDC electrolytes, cathode impedance and cell impedance under open circuit conditions.

Figure 3-9 Typical impedance spectrum of GDC electrolytes showing three arcs.

(1) Ionic conductivity measurements of GDC electrolytes

The ionic conductivity of GDC pellet samples was measured by a frequency response analyser (FRA, Model 1260, Solartron, UK). The GDC pellets were first coated with a silver paste on both sides to serve as electrodes, and then fired at 850°C for 30 min. Two silver wires were then adhered to each side using silver paste. Upon drying they were fired again at 850°C for 30min. The two wires were connected to the frequency response analyser, one to the counter and reference terminal and the other to the working terminal.

Ionic conductivity measurements of the GDC pellets were carried out over the temperature range of 300°C to 800°C by decreasing the temperature from 800°C. The purpose of the higher testing temperature range from 500°C to 800°C, is to simulate the operating conditions of the SOFC whereas the purpose of the lower temperature range of 300 to 500°C is to distinguish the contribution of the grain interior and grain boundary to the total conductivity of the electrolyte. The impedance measurements were carried out in the frequency range of 1 to 10 MHz with a signal amplitude of 10 mV for the temperature range of 500-800°C and a higher value of 100 mV for the temperature range of 300-500°C to avoid signal perturbation. From high to low frequencies, three semicircles were observed in the impedance spectrum, which represent the respective contributions from the grain interior, grain boundary and the electrodes. However, it is noted that the electrode contribution is more clearly identified at higher temperatures, whereas the grain interior and grain boundary contributions are more prominently identified at lower temperatures.

With the respective measured impedance plots, they are normalised to obtain the resistivity of the samples using the following equation:

$$\rho = \frac{Z' A}{L} \quad (3-2)$$

where ρ is resistivity of sample, A is surface area, L is sample thickness, and Z' is the measured resistance.

The ionic conductivity of the sample can thus be calculated from:

$$\sigma = \frac{1}{\rho} \quad (3-3)$$

The grain interior and grain boundary impedance were obtained by fitting the impedance spectra to the equivalent circuit model using the software program Zview (Version 2.4, Scribner Associates). With the required grain interior and grain boundary impedance from the relevant impedance plots, the grain interior and grain boundary ionic conductivities (σ_{gi} , σ_{gb}) can thus be determined.

(2) Impedance measurements of half cells

Half cells were prepared to study the cathode performance. A symmetrical cell configuration was adopted for half cells, as shown in Figure 3-3. The optimisation of the electrochemical properties of pure LSCF cathode and LSCF-GDC composite cathode was based on this technique.

The impedance measurements of half cells were conducted with an in-house test station including a purpose-built sample holder fitted in a vertical tube furnace and a potentiostat/galvanostat instrument (Autolab PG30/FRA, Eco Chimie, Netherlands). Figure 3-10 shows the photo of the fuel cell test station and the schematic of the sample holder (in the case of thin film SOFC measurement). In this test station, Platinum gauze is used as current collectors. Hence, there is no need to have Ag wire adhered to each electrode of the samples like conductivity measurements of electrolyte pellets mentioned above. Moreover, two platinum wires are connected to each platinum gauze

Chapter 3 Experimental Procedure

Figure 3-10 (a) Photo of Fuel cell test station and (b) schematic of sample holder.

on the anode and the cathode of the cell to serve as separate voltage and current probes. The purpose of using separate voltage and current Pt wires is to eliminate the effect of Pt wire resistance on the measured impedance. For complex impedance measurements of half cells, three-electrode symmetrical configuration, including working, counter and reference electrode, was used. The frequency range was 100 kHz-0.1 Hz with an excitation amplitude of 10 mV. Measurements were taken in air over a temperature range of 500-700°C.

(3) Impedance measurements of thin film SOFCs

The impedance measurement of thin film SOFCs under open-circuit conditions was basically similar to that of half cells described above. Before thin film SOFC is tested, the cell should be sealed properly because different gases are consumed at the cathode side and the anode side of the cell. In this study, the anode side of thin film SOFCs was sealed with a ceramic paste (Ceramabond 668, Aremco Products Inc., USA), while the cathode side was unsealed. To conduct the cell testing, humidified H_2 (3% H_2O) as fuel, entrained by bubbling through water at room temperature, was fed to the anode chamber, while the cathode of the cell was exposed to still air or flowing air as oxidant. Humidified H_2 and air can be supplied at different flow rates controlled by respective mass and rotameter flowmeters. Before electrochemical measurements were performed, the cell was kept at high temperatures for a sufficiently long period to ensure the NiO in the anode was fully reduced to Ni *in situ*. Two-electrode configuration with four-wire connections was used to conduct the impedance measurements of thin film SOFCs. Figure 3-10 b shows the schematic diagram of the sample holder with a thin film SOFC sealed properly.

3.3.2 DC polarisation

DC polarisation technique was employed to characterise the power-generating performance of thin film SOFCs under current loading. Current-voltage (*i*-V) characteristics were recorded on the cell using linear sweep voltammetry at a sweep rate of 1 mV/sec and expressed as a function of flow rate of working gases and operating temperature.

CHAPTER FOUR

ELECTRICAL PROPERTIES OF GDC ELECTROLYTES

4.1 Introduction

Recently, an intensive investigation was being done to reduce the operating temperature of conventional SOFCs from 1000°C to 500-800°C. One of the effective approaches is to develop a new electrolyte material which can offer high oxygen ionic conductivity at reduced temperatures. Ceria-based oxides have been found to possess this ability (Inaba and Tagawa, 1996; Steele, 2000). According to Steele (2000), doped ceria ceramics, especially Gd-doped CeO_2 , are the most promising electrolyte material for intermediate temperature SOFCs operating at 500~700°C. However, it is well known that CeO_2 -based materials are difficult to densify below 1500°C (Zhang, 2002). This makes it difficult for the manufacture of ceria-based electrolytes for the SOFC system, because the ceria-based electrolyte and other cell components, i.e., the cathode and/or the anode, have to be cosintered below 1500°C in the case of electrode-supported cells. To promote the densification of CeO_2 -based materials at lower temperatures, two methods, either preparing ultrafine CeO_2 -based powders (Torrens et al., 1998) or using sintering promoters (Zhang, 2002), have been exploited. In this study, commercial ultrafine nanosized powder of $\text{Gd}_{0.1}\text{Ce}_{0.9}\text{O}_{1.95}$ (GDC) was selected as the raw material for the fabrication of thin film electrolyte as an essential component of anode-supported SOFCs or thin film SOFCs.

Since the electrical properties of the electrolyte are very important in determining the performance of SOFCs, much work has been carried out on the electrical properties of GDC electrolyte and related affecting factors (Inaba and Tagawa, 1996; Steele, 2000;

Chapter 4 Electrical Properties of GDC Electrolytes

Zhou et al., 2002). Apart from the chemical compositions and operating conditions, sintering conditions also have an important influence on the ionic conductivity of the sintered electrolytes. Different sintering conditions will result in diverse characteristics in the microstructure of the electrolyte, such as the grain size, grain boundary phases and relative density. Interpretation of the microstructure's influence on the ionic conductivity of the electrolyte can help one to optimise the sintering conditions and further improve the electrical properties of the electrolyte.

The investigation on the sinterability of commercial nanosized $\text{Gd}_{0.1}\text{Ce}_{0.9}\text{O}_{1.95}$ (GDC) powder and its electrical properties is presented in this chapter. Focus is placed on the relationship of the processing and sintering conditions with the microstructures so as to optimise the processing and sintering conditions for obtaining the best electrical properties. The optimised processing and sintering conditions will be adopted for the preparation of thin film electrolyte, which forms an important basis for the fabrication of GDC electrolyte thin film SOFCs.

4.2 Characteristics of raw powder

Figure 4-1 shows the particle size distribution curves of as-received and calcined $\text{Gd}_{0.10}\text{Ce}_{0.90}\text{O}_{1.95}$ (GDC) powders, measured by a Particle Size Analyzer. The calcination treatment was conducted at 750°C for 2 h. The particle size and size distribution of GDC powders before and after the calcination are significantly different. The as-received GDC powder presents a broad size distribution of ~0.3-65 μm with about one-third of fine particles (< 4 μm) and two-thirds of coarse particles (4~65 μm), while the powder exhibits almost a Gaussian type and narrow distribution after calcination in spite

Chapter 4 Electrical Properties of GDC Electrolytes

Figure 4-1 Particle size distribution of (a) as-received GDC powder and (b) calcined GDC powder at 750°C for 2 h, measured by a Particle Size Analyser.

Chapter 4 Electrical Properties of GDC Electrolytes

of the lack of information on the particles smaller than 0.3 μm . From the size distribution, the average particle size was estimated to be $\sim 8 \mu\text{m}$ and $\sim 1 \mu\text{m}$ for the as-received and calcined GDC powders, respectively. The particle size and size distribution determined by the particle size analyzer seem to be abnormal because the particle size of powders normally increases with the high temperature calcination. Under the transmission electron microscope (TEM) analysis, however, the powders exhibit much smaller particle size, as shown in Figure 4-2. From the TEM micrographs, the average particle size is estimated as $\sim 5 \text{ nm}$ for the as-received GDC powder and it increases to 20-40 nm for that after calcination at 750°C for 2 h. The big difference in the particle sizes obtained from the particle size analyzer and TEM is because the former measures the size distribution of agglomerates of powders due to an incomplete dispersion of individual particles while the latter would indicate the size of individual particles. The same trend was also found for NiO powder by Jiang et al. (2000a). Hence, it is not hard to understand that the particle size analyzer revealed a larger average particle size for the as-received GDC powder compared with that for the calcined GDC powder because the former with $\sim 5 \text{ nm}$ particles may have a larger specific surface area and thus stronger inter-particle attraction force, leading to increased tendency of particle agglomeration. BET measurements proved this point. The as-received GDC powder has a specific surface area of $157.8 \text{ m}^2/\text{g}$ but it is decreased dramatically to $23.4 \text{ m}^2/\text{g}$ after the calcination. In addition, the TEM micrographs also revealed reduced particle agglomeration degree for the calcined GDC powder. Table 4-1 lists the average particle sizes of the as-received and the calcined powders evaluated by the particle size analyzer and TEM and calculated by Equation (3-1) using the BET data. The particle sizes obtained by TEM and BET method are fairly close to each other, as shown in Table 4-1.

Figure 4-2 TEM micrographs of (a) as-received GDC powder and (b) calcined GDC powder at 750°C for 2 h.

Table 4-1 Particle size of GDC powders

Evaluation method	Particle size	
	As-received GDC powder	Calcined GDC powder at 750°C for 2 h
Particle size analyzer	8 μm	1 μm
TEM	~ 5 nm	20-40 nm
BET	5.3 nm	35.5 nm

4.3 Effect of raw powder characteristics on sinterability

Initial sintering experiments were conducted using the as-received GDC powder. However, a series of sintering experiments revealed that it was quite difficult to obtain a densely sintered GDC pellet with the as-received powder even with a sintering temperature of as high as 1500°C, which is normally required for sintering the micron- or submicron-sized CeO_2 -based powder (Zhang, 2002). After the powder was calcined at 750°C for 2 h, however, almost fully dense GDC pellets could be achieved at a much lower sintering temperature. Figure 4-3 shows the cross-sectional SEM micrographs of sintered GDC pellets made from the as-received powder and the calcined powder.

Many pores can be seen in the microstructure of the pellet made from the as-received powder, while the number and size of pores are greatly reduced in the microstructure of the pellet made from the calcined powder even though the sintering temperature for the latter was reduced by 300°C. The density measurements showed that the former pellet obtained a relative density of 91.3% while the latter had a relative density as high as 97.5%. Therefore, the calcination of the powder played a significant role in the sinterability improvement of this GDC powder.

Chapter 4 Electrical Properties of GDC Electrolytes

Figure 4-3 Cross-sectional morphology of GDC pellets (a) made from as-received powder and sintered at 1500°C for 5 h and (b) made from calcined powder and sintered at 1200°C for 5 h.

Chapter 4 Electrical Properties of GDC Electrolytes

There might be two reasons for the improved sinterability of nanosized GDC powder induced by the calcination. On the one hand, the calcination substantially increases the green density of GDC pellets, which has an important impact on the sintering behavior (Leng et al., 2003). The higher the green density of the compact, the easier it is to obtain a densely sintered part. BET measurements have revealed that the as-received GDC powder has a very large specific surface area. This makes preparing complete high-green-density pellets very difficult. In pellet-pressing stage, when demolding the green pellet from the die, the pellet always strongly adhered to the steel plates due to a high compaction pressure applied, and complete green pellets were hard to obtain. Consequently, a relatively low compaction pressure of ~60 MPa was used for green pellet pressing, which produced a green relative density of ~31.5%. However, a green relative density as high as 54.6% was reached under the same compaction pressure after the powder was calcined at 750°C for 2 h. On the other hand, the calcination greatly reduces the tendency of powder agglomeration. The presence of agglomerates is one common characteristic of fine powders and it is generally well known that the smaller the particles, the greater the extent of agglomeration. The extent of agglomeration in the powders has a marked influence on sintering behaviour, because they can densify more rapidly than the surrounding matrix. Therefore, the agglomerates can cause large gaps and stresses in the structure which are hard to be removed during sintering. The smaller the agglomerates, the smaller the remaining flaws. Therefore, powder calcination is often adopted in practice to improve the sinterability of powders and the quality of sintered parts (Zhou et al., 2002).

Based on the sinterability investigation described above, later in this chapter, all GDC pellets for electrical conductivity study were prepared from the powder after

calcination at 750°C for 2 h so as to fully reveal the relationship of the processing and sintering conditions with the electrical properties of GDC electrolytes.

4.4 Effect of processing and sintering conditions on the ionic conductivity of GDC electrolytes

The ionic conductivity of GDC electrolytes was measured by means of AC impedance spectroscopy. The interpretation of impedance spectra for polycrystalline materials has been well documented (Macdonald, 1987). In general, the AC impedance of an ionic conductor contains contributions from grain interior, grain boundary and electrode/electrolyte interface, which are reflected in a complex plane by three successive arcs as shown in Figure 4-4b. The frequency increases from the right to the left across the plot. The arc at the high frequency end of the spectrum represents the grain interior resistivity; the arc at the middle of the spectrum is a consequence of grain boundary effect and the low frequency arc is attributed to the electrode response. An idealized equivalent circuit for ceramic oxides corresponding to the impedance plot (Figure 4-4b) is shown in Figure 4-4a. In a practical case, however, not all these arcs can be observed, depending on the nature of the sample and measurement conditions. In this study, three arcs can be identified clearly at lower temperatures (usually $\leq 350^\circ\text{C}$). With increasing temperatures the first arc representing grain interior effect at high frequency region disappears gradually, which is due to very short relaxation time of charge conduction in grain interior. An example of measured impedance spectrum of GDC electrolytes is given in Figure 4-4c. Ionic conductivities (i.e., grain interior (σ_{gi}), grain boundary (σ_{gb}) and total (σ_{t}) conductivity) of GDC electrolytes can be obtained by fitting the measured impedance plot to the equivalent circuit using the software package.

Chapter 4 Electrical Properties of GDC Electrolytes

Figure 4-4 (a) An idealised equivalent circuit and (b) its corresponding impedance plot. (c) An example of practical impedance spectrum of GDC electrolytes measured at 350°C. R_{gi} and C_{gi} , R_{gb} and C_{gb} , and R_{el} and C_{el} represent resistances and capacitances for grain interior, grain boundary, and electrode responses, respectively.

Figure 4-5 Total ionic conductivity as a function of compaction pressure. All GDC pellets were sintered at 1200°C for 5 h.

4.4.1 Effect of compaction pressure on the ionic conductivity of GDC electrolytes

Compaction pressure means the pressure under which green GDC pellets were formed by die-pressing. Figure 4-5 shows the total ionic conductivity results of GDC pellets prepared under different compaction pressures and subsequently sintered at 1200°C for 5 h. When the electrolyte operates at 400°C, the total ionic conductivity increases rapidly as the compaction pressure increases from 60 to 240 MPa, and then increases rather slowly with further increase of the compaction pressure from 240 MPa to 400 MPa. The same trend was also observed at other measuring temperatures. In order to understand these trends, the effects of the compaction pressure on the ionic conductivity of grain interior and grain boundary were studied and the results are shown in Figure 4-6 and Figure 4-7, respectively. For the grain interior conductivity, it seems to have the same trend with the increase of compaction pressure as the total ionic

Chapter 4 Electrical Properties of GDC Electrolytes

Figure 4-6 Grain interior conductivity as a function of compaction pressure. All GDC pellets were sintered at 1200°C for 5 h.

Figure 4-7 Grain boundary conductivity as a function of compaction pressure. All GDC pellets were sintered at 1200°C for 5 h.

Chapter 4 Electrical Properties of GDC Electrolytes

conductivity, whereas the grain boundary conductivity always increases steeply as the compaction pressure increases from 60 to 400 MPa. This implies that the grain boundary conductivity is more sensitive than the grain interior conductivity to the compaction pressure in the range of 240-400 MPa.

The results of the conductivity of grain interior and grain boundary as a function of compaction pressure indicate that both grain interior conductivity and grain boundary conductivity contribute to the increase of the total ionic conductivity in the compaction pressure range of 60-400 MPa. These conductivity trends may be due to the different microstructures of sintered electrolytes. Density measurements exhibit a big difference in the relative density of the GDC pellets pressed under different compaction pressures after sintering at 1200°C for 5 h, while the grain size has no obvious difference due to the same sintering conditions applied, as shown in Figure 4-8. This clearly indicates that both the grain interior conductivity and the grain boundary conductivity are related to the relative density of sintered GDC electrolytes. As the relative density increases, both the grain interior conductivity and the grain boundary conductivity increase, leading to an enhanced total ionic conductivity for the GDC electrolyte. This also confirms that a fully dense electrolyte microstructure is desirable to obtain a high ionic conductivity electrolyte. However, when the relative density of the electrolyte increases to a certain value, the enhancement of the total ionic conductivity is less obvious as the relative density increases further, especially at high temperatures where the grain interior resistivity dominates the total resistivity.

Chapter 4 Electrical Properties of GDC Electrolytes

Figure 4-8 Relative density and average grain size as a function of compaction pressure. All GDC electrolyte pellets were sintered at 1200°C for 5 h.

Figure 4-9 Total ionic conductivity as a function of sintering temperature.

4.4.2 Effect of sintering temperature on the ionic conductivity of GDC electrolytes

Figure 4-9 shows the total ionic conductivity as a function of sintering temperature for the GDC pellets formed by die-pressing under 400 MPa. When the electrolyte operates at 400°C, the total ionic conductivity does not change apparently as the sintering temperature increases from 1200°C to 1400°C. However, when the sintering temperature increases further to 1500°C or even higher, the total ionic conductivity begins to decline substantially. Similar trends can also be observed for other measuring temperatures. Likewise, to better understand the contribution of the grain interior and the grain boundary conductivity to the total ionic conductivity, the relationships of the grain interior conductivity and the grain boundary conductivity as a function of sintering temperature were studied and the results are shown in Figure 4-10 and Figure 4-11, respectively. The grain interior conductivity keeps almost constant for various sintering temperatures, while the grain boundary conductivity seems to have the same trend as the total ionic conductivity with the sintering temperature, implying that the variation in the total ionic conductivity is induced principally by the grain boundary conductivity and has little to do with the grain interior conductivity. These trends can also be correlated with the microstructures of the GDC electrolytes. As shown in Figure 4-12, all the GDC electrolytes have a very dense structure with a relative density of >97% after sintering at different temperatures. Results show that the grains in the electrolytes grow significantly with the increase of sintering temperature. This indicates that the grain size in the electrolytes has no influence on the grain interior conductivity, but is closely related to the grain boundary conductivity.

Chapter 4 Electrical Properties of GDC Electrolytes

Figure 4-10 Grain interior conductivity as a function of sintering temperature.

Figure 4-11 Grain boundary conductivity as a function of sintering temperature.

Figure 4-12 Relative density and average grain size as a function of sintering temperature.

It is noted that there is no obvious change in the grain boundary conductivity for the grain size smaller than $\sim 1 \mu\text{m}$; however, for grain size above $1.0 \mu\text{m}$, the grain boundary conductivity drops significantly, thus leading to a clear drop in the total ionic conductivity. Therefore, a high ionic conductivity can be achieved with the GDC electrolytes densely sintered at a temperature below 1400°C . Table 4-2 compares some conductivity results obtained in this study with some data from references (Steele, 2000; Xia and Liu, 2002a; Zhou et al., 2002). Except data reported in the reference (Steele, 2000) where highly pure raw powder was used, the conductivity results for $\text{Gd}_{0.1}\text{Ce}_{0.9}\text{O}_{1.95}$ electrolyte in air obtained in this study are basically close to those in most references.

Chapter 4 Electrical Properties of GDC Electrolytes

Table 4-2 Conductivity data for $\text{Gd}_{0.1}\text{Ce}_{0.9}\text{O}_{1.95}$ electrolyte measured in air.

σ_t , 500°C (S/cm)	σ_t , 600°C (S/cm)	σ_t , 700°C (S/cm)	Sources
0.0095	0.0253	0.0544	(Steele, 2000)
0.0063	0.0167	-	(Xia and Liu, 2002a)
0.0053	0.0169	0.0396	This study
-	0.013	-	(Zhou et al., 2002)

Figure 4-13 Grain interior conductivity as a function of relative density for GDC electrolytes sintered at 1200°C for 5 h.**4.4.3 Analysis on grain interior conductivity and grain boundary conductivity**

From the present results, it is known that both grain interior conductivity and grain boundary conductivity are affected by the relative density of GDC electrolytes. Figure 4-13 shows the relative density dependence of grain interior conductivity. The grain interior conductivity increases linearly with increasing relative density. The linear

Chapter 4 Electrical Properties of GDC Electrolytes

correlation between grain interior conductivity and porosity was also reported by Gibson (1998). To explain the experimental results, the following study is conducted.

The normalized apparent grain interior conductivity σ_g of the electrolyte with cross-sectional area A and thickness L can be obtained from the following equation (Chen et al, 2002):

$$\sigma_g = \frac{L}{R_g A} \quad (4-1)$$

where R_g is the grain interior resistance obtained from the impedance spectrum.

The specific grain interior conductivity $\sigma_{g,sp}$ which is based on the microstructure, is given by (Chen et al., 2002):

$$\sigma_{g,sp} = \frac{L}{R_g A_g} \quad (4-2)$$

Where A_g is the total grain area across which the oxygen ions can transport in the electrolyte.

Since the grain interior resistance R_g is known, combining Equations (4-1) and (4-2) gives the following expression:

$$\sigma_g = \frac{\sigma_{g,sp} A_g}{A} \quad (4-3)$$

Assuming that the pores are well distributed within the electrolyte, thus the relative density ξ can be simply expressed by:

$$\xi = \frac{A_g}{A} \quad (4-4)$$

Substituting Equation (4-4) into Equation (4-3), the apparent grain interior conductivity as a function of relative density can be obtained.

$$\sigma_g = \xi \sigma_{g,sp} \quad (4-5)$$

Chapter 4 *Electrical Properties of GDC Electrolytes*

Equation (4-5) can well explain the linear relationship between the grain interior conductivity and the relative density for GDC electrolytes, as shown in Figure 4-13. In addition, it also gives a reasonable explanation for the finding that the grain interior conductivity almost does not change with the grain size or sintering temperature when the electrolytes have similar dense structures, as can be seen from Figure 4-10 and Figure 4-12.

Similarly, the relationship between the grain boundary conductivity and the microstructure can be determined. The normalized apparent grain boundary conductivity σ_{gb} of the electrolyte with cross sectional area A and thickness L can be obtained from the following equation:

$$\sigma_{gb} = \frac{L}{R_{gb} A} \quad (4-6)$$

The specific grain boundary conductivity $\sigma_{gb,sp}$ is given by

$$\sigma_{gb,sp} = \frac{N \delta_{gb}}{R_{gb} A_{gb}} \quad (4-7)$$

where A_{gb} is the total grain boundary area across the ion transport path, N is the number of grains across the electrodes and δ_{gb} is the grain boundary thickness.

Since the grain boundary resistance R_{gb} is known, combining Equations (4-6) and (4-7) gives the following expression:

$$\sigma_{gb} = \frac{L A_{gb} \sigma_{gb,sp}}{N A \delta_{gb}} \quad (4-8)$$

Since the average grain size, d_g can be defined as:

$$d_g = \frac{L}{N} \quad (4-9)$$

Thus Equation (4-9) becomes

Chapter 4 Electrical Properties of GDC Electrolytes

$$\sigma_{gb} = \frac{d_g A_{gb} \sigma_{gb,sp}}{A \delta_{gb}} \quad (4-10)$$

Equation (4-10) describes the relation between the grain boundary conductivity and the microstructure of the electrolyte.

The change of the grain boundary area and grain growth in the electrolyte during sintering is a complex process. Initially, particle necking causes an increase in the total grain boundary area at initial stage and intermediate stage of the sintering process. But, later in final sintering stage grain growth acts to reduce the grain boundary area. Assuming the grain boundary thickness and specific grain boundary conductivity keep constant during the sintering, the apparent grain boundary conductivity is strongly related to the product of grain size and total grain boundary area, i.e., $d_g \times A_{gb}$. For the GDC electrolytes sintered under same conditions of 1200°C for 5 h, the grain size is

Figure 4-14 Grain boundary conductivity as a function of relative density for GDC electrolytes sintered at 1200°C for 5 h.

Chapter 4 Electrical Properties of GDC Electrolytes

very close to each other, as shown in Figure 4-8. Then the grain boundary conductivity depends mainly upon the total grain boundary area. As the relative density of the electrolyte increases, the grain boundary area will increase. Accordingly, the grain boundary conductivity will increase with increasing relative density of the electrolyte. Figure 4-14 shows the effect of relative density on the grain boundary conductivity of GDC electrolytes. Equation (4-10) can well explain the large increase of the grain boundary conductivity with reducing porosity in the electrolyte. Since pores are always observed at grain boundaries, it is reasonable to state that the grain boundary conductivity is more sensitive to the porosity than the grain interior conductivity, which was also confirmed by Gibson (1998). For the GDC electrolytes densely sintered at sintering temperatures from 1200°C to 1600°C, increasing the sintering temperature causes further grain growth and hence the reduction of the grain boundary area, which counteracts their effects on the grain boundary conductivity, thus leading to a relatively unchanged grain boundary conductivity for sintering temperatures below 1400°C. However, Equation (4-10) seems difficult to explain the sharp increase of the grain boundary resistivity when the sintering temperature increases from 1400°C to 1500°C. Figure 4-15 shows the impedance spectra of the GDC electrolytes densely sintered at temperatures from 1200°C to 1600°C. It can be seen that the grain boundary semicircle becomes significantly larger when the sintering temperature increases to 1500°C and further to 1600°C. This phenomenon is generally attributed to the segregation of insulating impurities at grain boundaries (Gerhardt et al., 1986; Appel and Bonanos, 1999).

Chapter 4 Electrical Properties of GDC Electrolytes

Figure 4-15 Impedance spectra of GDC electrolytes sintered at various sintering temperatures from 1200-1600°C, measured at 300°C in air.

Figure 4-16 Schematic diagram of (a) continuous and (b) discontinuous distribution of insulating phase along the grain boundary of the electrolyte.

Figure 4-17 Temperature dependence of grain boundary conductivity for GDC electrolytes densely sintered at 1300°C and 1600°C, respectively. The slope represents the activation energy of grain boundary conduction.

Chapter 4 Electrical Properties of GDC Electrolytes

It is widely accepted that the predominant constituent of the grain boundary impurities in ceria-based solutions is silica, and silica contamination results mainly from precursor chemicals and sample preparation (Steele, 2000). When an amorphous thin siliceous film forms continuously between grains during sintering (see Figure 4-16a), the blocking of the movement of oxygen ions through the grain boundary leads to reduced grain boundary conductivity. In this case, it is obvious that oxygen ions must transport across the grain boundary phase to maintain an ionic current. Thus the activation energy for grain boundary conductivity, by rights, should change with the grain boundary phase. However, comparison between the activation energies for grain boundary conduction in GDC electrolytes sintered at different temperatures cannot provide evidence for an obvious change in the chemical composition at the grain boundaries. As shown in Figure 4-17, the grain boundary activation energy for oxygen ion conduction is 1.03 eV and 1.00 eV for GDC electrolytes sintered at 1300°C and 1600°C, respectively. They are almost the same. Therefore, it was proposed that the grain boundary impurity phase is not distributed continuously along the grain boundary, but present at some local boundary sites like triple junction points, as illustrated in Figure 4-16 b (Badwal et al., 1990; Gremillard et al., 2000). Thus, oxygen ions may transport across the grain boundaries in two ways. One through the “clean” grain-to-grain contact and the other through the grain boundary impurity phase. Because of insulating effects of the grain boundary impurity phase, oxygen ions tend to transport across grain boundaries through the “clean” grain-to-grain contact, thus causing a constant activation energy for the grain boundary conduction. To find physical evidence of discontinuous distribution of the grain boundary phase, thin film samples were prepared by grinding and ion milling for TEM observation on the GDC electrolyte

Chapter 4 Electrical Properties of GDC Electrolytes

sintered at 1600°C. The TEM micrograph in Figure 4-18a clearly indicates the presence of grain boundary phase at triple junction sites. EDX analysis was employed to reveal the compositional difference between the grain boundary phase (A site) and grain interior (B site). The EDX spectra of site A and site B are given in Figures 4-18 b and c, which clearly indicate that Si impurities segregate at the grain boundary, whereas Si is not detectable in the grain interior. The Cu peaks in the spectra are most likely due to contaminations from the Cu ring in the ion milling process of the thin film sample. The Cu ring is used to support the thin film sample. Silica has been confirmed to be very detrimental to the ionic conductivity of doped ceria electrolytes (Steele, 2000; Zhang et al, 2004). Hence, the TEM observation and the EDX analysis results well explain the large grain boundary impedance arc shown in Figure 4-15.

It is noted that, on one hand, the impurity level has significant effects on the grain boundary conductivity. Clearly, the higher the resistive impurity level, the greater the detrimental effects on the grain boundary conductivity. On the other hand, the segregation of impurities at grain boundaries is highly dependent on the sintering temperature. Sintering temperature affects the segregation degree of impurities by changing the amount of grain boundaries and the wetting properties of the impurity phase. As shown in Figure 4-12, at low sintering temperatures ($\leq 1400^\circ\text{C}$), the grain size of the electrolytes is still very small and trace levels of resistive impurities are diluted by the high-density grain boundaries. Thus the grain boundary conductivity shows no obvious difference. As the sintering temperature increases ($> 1400^\circ\text{C}$), grains grow rapidly and thus significantly reduce the amount of grain boundaries. Moreover, the wetting properties of the impurity phase may be significantly enhanced at high sintering temperatures (Badwal, 1992), promoting the propagation of the impurity phase along

Chapter 4 Electrical Properties of GDC Electrolytes

Figure 4-18 (a) TEM micrograph of GDC electrolyte sintered at 1600°C showing the grain boundary phase at triple junction site. EDX spectra of (b) site A and (c) site B in (a).

Chapter 4 Electrical Properties of GDC Electrolytes

the grain boundaries. Both factors result in a significant increase in the grain boundary coverage fraction, thus substantially increasing the grain boundary resistance. To minimize the grain boundary resistivity for high performance ionic conductors, two approaches can be considered, i.e., reduction of impurity level in raw materials and decrease of processing temperatures by synthesizing nano-scale powders and/or using sintering aids (Torrens et al., 1998; Zhang, 2002).

4.5 Summary

The calcination of the as-received nanosized GDC powder at 750°C for 2 h significantly changed the powder characteristics by reducing the specific surface area from 157.8 m²/g to 23.4 m²/g and lessening the particle agglomeration, thus improving the sinterability of the raw powders. It was found that the compaction pressure for green pellet preparation with the current GDC powder has a great effect on the relative density of sintered electrolytes. With a high compaction pressure of 400 MPa, dense GDC electrolytes can be obtained at relatively low sintering temperatures. The GDC electrolyte, with a relative density of 97.5% after sintering at 1200°C for 5 h, exhibits fairly good electrical properties. The ionic conductivities were registered as 0.0396, 0.0169 and 0.0053 S/cm at 700°C, 600°C and 500°C, respectively.

The ionic conductivity measurements were correlated with the microstructural characteristics (such as porosity and grain size) of the GDC electrolytes. It was found that the grain interior conductivity is predominantly related to the relative density and insensitive to the grain size of the electrolyte, whereas, the grain boundary conductivity is strongly related to both the relative density and the grain size of the electrolyte. Microstructures with high density and small grain size are of great significance for a

Chapter 4 Electrical Properties of GDC Electrolytes

high-conductivity GDC electrolyte. With sintering temperature below 1400°C for the current GDC powder, the densely sintered GDC electrolytes exhibit similar electrical properties. When the sintering temperature reaches 1500°C, the ionic conductivity of the electrolyte will be deteriorated significantly due to decreased grain boundary conductivity. TEM observations indicate the presence of the grain boundary phase, which contains much Si impurities as revealed by EDX analysis.

CHAPTER FIVE

ELECTROCHEMICAL PERFORMANCE OF LSCF AND LSCF-GDC CATHODES

5.1 Introduction

In efforts to cut costs in every aspect of SOFCs for broad-based commercialisation, the main research focus has shifted in recent years towards reducing operating temperatures. To reduce the operating temperature, cell resistance must be minimised in terms of electrolyte resistance and electrode reaction resistance at the electrode/electrolyte interface (Doshi et al., 1999). The electrolyte resistance can be significantly reduced by preparing a thin electrolyte on a porous electrode support, or by using new electrolyte materials, such as GDC, which have higher oxygen ionic conductivity at reduced temperatures than the conventional YSZ electrolyte (Pal and Singal, 1990; Murray et al., 1999; Leng et al., 2004). In Chapter 4, an ionic conductivity of 0.0169 S/cm was obtained for $\text{Gd}_{0.1}\text{Ce}_{0.9}\text{O}_{1.95}$ (GDC) at 600°C, while the corresponding value for YSZ is only 0.0032 S/cm (Murray and Barnett, 2001). The conductivity of the former is 5 times greater than the latter. With regard to the electrode reaction resistance, the cathode reaction (oxygen reduction) resistance generally shows much larger values compared with the anode reaction resistance (Horita et al., 2001). Therefore, it is desirable to develop a higher performance cathode material than the conventional LSM oxide for reduced temperature operation.

The mixed ionic-electronic conductor (MIEC) $(\text{La}, \text{Sr})(\text{Co}, \text{Fe})\text{O}_3$ (LSCF) is regarded as one of the most promising cathode materials for intermediate temperature SOFCs. Impedance spectroscopy data for porous LSCF electrodes on YSZ and doped-

Chapter 5 Electrochemical Performance of LSCF and LSCF-GDC Cathodes

ceria electrolytes have shown much lower interfacial resistance than that of conventional LSM electrodes. The high electrocatalytic activity of LSCF electrodes is promoted by the rapid surface exchange kinetics, high oxygen vacancy concentration, and especially, the mixed conducting behaviour of the material (Murray et al., 2002). A drawback of the Co-based cathodes is their tendency to react with zirconia to form resistive zirconate compounds. For this reason, LSCF has been proposed primarily as a cathode material for use with ceria electrolytes, where there are no known reactions (Qiu et al., 2002).

To improve the cathode performance, one commonly used approach is to add an ionically conducting secondary phase, typically YSZ, to the electronically conducting electrode material, typically LSM, forming a composite cathode. It is well known that electrochemical reactions generally take place at the triple phase boundary (TPB) between the gas pore, electrolyte and catalyst where the catalyst transports electrons, the electrolyte material transports oxygen ion species, and the pore allows gaseous reactants to transport to the reaction sites. In a composite cathode, the TPB extends from the cathode/electrolyte interface into the cathode, thus greatly improving the cathode performance. While LSM is a poor ionic conductor and the oxygen reduction reactions are limited to the TPB region, LSCF is a MIEC with appreciable ionic conductivity, thus the exchange of oxygen occurs at the mixed conductor surface with diffusion of oxygen ions through the mixed conductor bulk. However, the work by Dusastre and Kilner (1999) and Murray et al. (2002) clearly indicates that the addition of GDC to LSCF cathodes has a significant influence on the improvement of cathode performance over the temperature range of 500-750°C. It was found by Dusastre and Kilner (1999) that the lowest polarisation resistance was obtained when 36 vol.% $\text{Gd}_{0.1}\text{Ce}_{0.9}\text{O}_{1.95}$ was

Chapter 5 Electrochemical Performance of LSCF and LSCF-GDC Cathodes

added to LSCF, a reduction by a factor of 4 compared with that of a pure LSCF cathode. Murray et al. (2002) discovered that the addition of 50 wt.% $\text{Gd}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ to $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ cathodes on YSZ electrolytes produced a factor of ~10 reduction in the low-current interfacial resistance. Therefore, it can be confirmed that the high ionic conductivity of GDC plays a key role in greatly expanding the electrochemical reaction zone from the vicinity of the cathode/electrolyte interface.

In order to develop high performance GDC-based IT-SOFCs, LSCF oxide was selected as the cathode base material to match with the GDC electrolytes in this study. To further improve the electrochemical performance of pure LSCF, preparation of LSCF-GDC composite cathodes seems to be a promising approach.

The work in this chapter is first to optimise the sintering temperature of LSCF cathodes due to different characteristics of starting materials used. Then the optimised sintering temperature will be used for sintering of LSCF-GDC composite cathodes. Since there are still inconsistencies in the literature in the volume percentage of GDC content used in LSCF-GDC composite cathodes for optimal electrochemical performance, a wide range of LSCF-GDC composite cathodes with different compositions were fabricated via screen printing and characterised electrochemically so as to determine the optimum composition for LSCF-GDC system. The optimised LSCF-GDC composition will be used in the fabrication of high performance GDC-based IT-SOFCs.

5.2 Optimisation of sintering temperature of LSCF cathodes

5.2.1 Impedance behaviour of LSCF cathodes

Various temperatures from 750 to 1100°C were chosen to sinter LSCF cathodes fabricated onto the GDC electrolyte by an identical screen printing process. After sintering, all the half-cell samples were evaluated by electrochemical impedance spectroscopy (EIS). Figure 5-1 shows the impedance spectra of a LSCF cathode sintered at 900°C, measured at open-circuit conditions in the air from 650 to 500°C. It can be observed from Figure 5-1 that each spectrum is composed of two depressed arcs, signifying the presence of at least two reaction steps involved in the oxygen reduction on the LSCF electrode. According to the reaction mechanism study of oxygen reduction on porous LSCF cathode (Adler et al., 1996), the arc at high frequencies (left side) is attributed to the charge transfer of oxygen ions between electrode and electrolyte and the low frequency arc (right side) is due to the polarisation caused by surface exchange and diffusion of oxygen species to the electrode/electrolyte interface. It can also be clearly seen that the total cathode interfacial (polarisation) resistance, indicated by the difference between the high frequency and low frequency intercepts with the real axis, increases with the decrease of the operating temperature. This is because the electrocatalytic activity decreases with the decrease of temperature. In addition, by comparing the diameter of the high frequency arc and the low frequency arc, it is easy to find out that the low frequency arc becomes more dominant with decreasing temperature, which means that the primary rate-limiting mechanism is exchange and diffusion related.

Chapter 5 Electrochemical Performance of LSCF and LSCF-GDC Cathodes

Figure 5-1 Impedance spectra measured under open-circuit conditions at various temperatures for a LSCF cathode sintered at 900°C.

5.2.2 Polarisation resistance of LSCF cathodes as a function of sintering temperature

Polarisation resistance (R_p) values were obtained for LSCF cathodes sintered at different temperatures by fitting the impedance plots to a LR(RQ)(RQ) equivalent circuit. An inductive component is included in the equivalent circuit since the test station shows a strong inductance, which is characterised by the portion of the impedance spectra with the imaginary component $-Z'' < 0$.

Figure 5-2 shows the polarisation resistance versus sintering temperature for LSCF cathodes, tested at open circuit and 600°C in air. As the sintering temperature increases, the polarisation resistance significantly decreases from 7.75 Ωcm^2 for 750°C to 2.54 Ωcm^2 for 900°C. However, further increasing the sintering temperature results in a dramatic increase in the polarisation resistance. For the LSCF cathode sintered at 1100°C, a R_p value of 10.21 Ωcm^2 was obtained. Consequently, the best electrochemical activity is reached for the LSCF cathode sintered at 900°C. For other sintering temperature around 900°C, such as 850°C and 950°C, the polarisation resistance is slightly higher than that of 900°C.

For other testing temperatures, similar trend can be seen for the change of polarisation resistance with sintering temperature, as shown in Figure 5-3, which gives the temperature dependence of the polarisation resistance of LSCF cathodes. Therefore, the optimised sintering conditions for the LSCF material used in this study seem to be 900°C for 2 h, yielding the lowest polarisation resistance.

In addition, the slopes of the $\log R_p$ versus $1/T$ plots in Figure 5-3, represent the activation energy for oxygen reduction on the porous LSCF cathodes. It can be seen that

Chapter 5 Electrochemical Performance of LSCF and LSCF-GDC Cathodes

Figure 5-2 Polarisation resistance versus sintering temperature for LSCF cathodes, tested in air at 600°C and open circuit condition.

Figure 5-3 Temperature dependence of the polarisation resistance for LSCF cathodes sintered at different temperatures, tested in air over the temperature range of 500-650°C.

Chapter 5 Electrochemical Performance of LSCF and LSCF-GDC Cathodes

the slopes of the $\log R_p$ versus $1/T$ plots are nearly the same for all sintering temperatures studied, yielding an activation energy of 1.63 ± 0.04 eV. This activation energy is in good agreement with prior studies of LSCF cathodes where activation energies of ~ 1.6 eV were reported (Murray et al, 2002; Dusastre and Kilner, 1999). Similar activation energies for different sintering temperatures are reasonable since the activation energy is mainly determined by the electrode composition and intrinsic properties of electrode materials, and not much affected by the microstructural variation due to the sintering temperature.

5.2.3 Microstructure of LSCF cathodes

The electrochemical performance of a porous cathode depends not only upon its intrinsic properties, such as oxygen surface exchange coefficient, oxygen self-diffusion coefficient and mixed ionic electronic conductivity, but also upon its extrinsic characteristics, especially the microstructural features, involving particle size, particle agglomeration degree, surface area, porosity, particle-to-particle connection, cathode/electrolyte bonding, and even cathode/electrolyte inter-reaction or inter-diffusion, etc. The intrinsic properties of electrodes are fixed by the choice of materials, however, the microstructural variables can be controlled by processing. In general, fine particle size, large surface area, adequate porosity, good connection between particles and good adhesion between cathode and electrolyte are essential to achieve high cathode performance. The cathode polarisation resistance trend, as shown in Figure 5-3, can also be correlated with the microstructural change with sintering temperature. Figure 5-4 shows the SEM images of surface morphology of LSCF cathodes after sintering at various temperatures from 750 to 1100°C. For the LSCF cathodes sintered at around 900°C, including 850°C, 900°C and 950°C, the morphologies appear to be

Chapter 5 Electrochemical Performance of LSCF and LSCF-GDC Cathodes

similar with very fine particle size of $\sim 0.2 \mu\text{m}$, adequate porosity and good necking connections between particles. As a result, these cathodes produced comparatively close polarisation resistances, 3.59, 2.54 and $4.27 \Omega\text{cm}^2$ for sintering temperature of 850°C , 900°C and 950°C , respectively, as shown in Figure 5-2. The slight difference in the cathode microstructures with the sintering temperature increased from 850°C to 950°C produced a relatively low polarisation resistance at sintering temperature of 900°C . However, the morphologies of the LSCF cathodes sintered at 750°C and 1100°C seem to be quite different from those of the cathodes sintered at around 900°C . For sintering temperature of 750°C , the cathode has very fine particles, but no obvious necking features can be observed between particles, implying that this sintering temperature is not high enough and the particle-to-particle connections are rather weak. The weak connections between particles will increase the resistance for oxygen species diffusion and electron transfer through the porous cathode. Moreover, the bonding between the cathode particles and the electrolyte also has an influence on the cathode performance. Good bonding between the cathode and the electrolyte is important for oxygen ions to efficiently transport through the cathode/electrolyte interface. Figure 5-5 shows the cross-sectional morphologies of LSCF cathodes sintered at various temperatures. The LSCF cathode sintered at 1100°C shows much better interfacial bonding between the cathode and electrolyte than those sintered at 900°C and 750°C . It is reasonable to deduce that the interfacial bonding is improved with increasing sintering temperature of the cathode, although the microstructural evidence is weak for the cathodes sintered from 750 - 900°C . Therefore, weak connections between LSCF particles and weak bonding at the LSCF/GDC interface due to the low sintering temperature of 750°C may be the main reason for the high polarisation resistance or low electrochemical activity of

Chapter 5 Electrochemical Performance of LSCF and LSCF-GDC Cathodes

the cathode. Thus, the sintering temperature has to be increased to enable the formation of good connections between LSCF particles and good bonding at the LSCF/GDC interface so as to enhance the cathode reaction activity. As shown in Figure 5-4 b, c and d, when the sintering temperature is increased to around 900°C, good necking connections are generated between the particles while the microstructure remains in the form of fine particles and high porosity. For the cathode sintered at 1100°C, however, the grain size becomes larger, ~0.45 μm , and this excessively high sintering temperature causes the formation of local dense domains, which greatly reduces the surface area and porosity of the cathode, as can be observed from Figure 5-3 e, implying that the sintering temperature of 1100°C is too high to consider. As a result, a significantly increased cathode polarisation resistance was obtained.

Since the sintering condition of 900°C for 2 h for LSCF cathodes used in this study can provide the optimum electrochemical reaction activity, it will be adopted for the sintering of LSCF-GDC composite cathodes to optimise the composition of LSCF-GDC system so as to achieve further improved cathode performance.

Chapter 5 Electrochemical Performance of LSCF and LSCF-GDC Cathodes

Chapter 5 Electrochemical Performance of LSCF and LSCF-GDC Cathodes

Figure 5-4 SEM images of surface morphology of LSCF cathodes sintered at (a) 750°C, (b) 850°C, (c) 900°C, (d) 950°C, and (e) 1100°C for 2 h, respectively.

Chapter 5 Electrochemical Performance of LSCF and LSCF-GDC Cathodes

Figure 5-5 Cross-sectional SEM images of LSCF cathodes on GDC electrolytes sintered at (a) 750°C, (b) 900°C, and (c) 1100°C for 2 h, respectively.

5.3 Optimisation of composition of LSCF-GDC composite cathodes

5.3.1 Polarisation resistance of LSCF-GDC composite cathodes

Figure 5-6 shows the impedance spectra of LSCF-GDC composite cathodes with various GDC weight fractions, measured at open-circuit condition and 600°C in air. Compared with those of pure LSCF cathodes as shown in Figure 5-1, the impedance spectra of LSCF-GDC composite cathodes display significant overlapping between high frequency and low frequency arcs, giving the appearance of a single depressed arc. Attempts were made to fit the impedance arcs of LSCF-GDC composite cathodes. However, overlapping of the arcs made it difficult to deconvolute the impedance spectra with reasonable accuracy. Therefore, R_p values for LSCF-GDC composite cathodes were determined directly from the arc diameter, viz, the difference between the real axis intercepts of the impedance plot. Figure 5-7 shows the polarisation resistance versus GDC weight fraction in LSCF-GDC composite cathodes measured at open circuit and 600°C in air. For pure LSCF cathode, i.e., the cathode with zero GDC weight fraction, the R_p is 2.54 Ω/cm^2 . As the GDC weight fraction increases, R_p decreases continuously at first. When the GDC fraction increases to 50 wt.%, R_p exhibits the lowest value, i.e., 0.26 Ω/cm^2 . The effect of GDC addition to LSCF is remarkable, with R_p for the LSCF-GDC50 cathode being ~9 times lower than that for the pure LSCF cathode. With further increase of GDC content from 50 wt.% to 60 wt.%, R_p drastically increases to 2.63 Ω/cm^2 , close to that of the pure LSCF cathode.

For other testing temperatures, similar trend can be observed for the polarisation resistance varying with LSCF-GDC composite composition. Figure 5-8 shows the temperature dependence of the polarisation resistance of various LSCF-GDC composite

Chapter 5 Electrochemical Performance of LSCF and LSCF-GDC Cathodes

Figure 5-6 Impedance spectra measured in air at 600°C for LSCF-GDC composite cathodes with various GDC weight fractions.

Chapter 5 Electrochemical Performance of LSCF and LSCF-GDC Cathodes

Figure 5-7 Polarisation resistance versus GDC weight fraction in LSCF-GDC composite cathodes, obtained at open circuit and 600°C in air.

Figure 5-8 Temperature dependence of the polarisation resistance for pure LSCF and various LSCF-GDC composite cathodes sintered at 900°C for 2 h, measured in air over the temperature range of 500-700°C.

Chapter 5 Electrochemical Performance of LSCF and LSCF-GDC Cathodes

cathodes, measured in air over the temperature range of 500-700°C. It seems that the addition of 50 wt.% GDC to LSCF offers the optimal electrochemical reaction activity for oxygen reduction within the temperature range under study.

In addition, the change of cathode composition due to GDC addition results in a change of the activation energy for oxygen reduction, as can be observed from the slopes of the $\log R_p$ versus $1/T$ plots for different composition LSCF-GDC composite cathodes. The activation energies are also summarised in Figure 5-8. It can be seen that for pure LSCF cathode, the activation energy is 1.60 eV, whereas it decreases to 1.14 eV for LSCF-GDC60 composite cathode. Generally, the activation energy decreases with the increase of GDC content added to LSCF. This is probably because the GDC component has a lower activation energy for the oxygen ion conduction process. For the GDC material used in this study, the activation energy for the total ionic conductivity within the temperature range of 500-700°C is ~0.70 eV. Consequently, as the GDC fraction increases, the oxygen reduction process on the LSCF-GDC composite cathodes is increasingly affected by the GDC phase, especially when the GDC content is over 60 wt.%.

5.3.2 Discussion

The oxygen reduction reaction occurring on a SOFC electrode is expressed as:

Clearly, three pathways are involved for effective transport of electrons, oxygen ions and oxygen gases to and/or away from reaction sites. To realize a high performance electrode for the oxygen reduction, therefore, a mixed conductor with both high ionic and electronic conductivities is expected in addition to a reasonable porosity for gas diffusion. With mixed conductivities, mixed ionic and electronic conductor (MIEC)

Chapter 5 Electrochemical Performance of LSCF and LSCF-GDC Cathodes

electrodes have extended active reaction sites where oxygen ions and electrons are available or can be easily moved away. Thus, the electrode reaction can be significantly accelerated. It is well known that LSCF materials have mixed conductivities, which make it much better in the electrochemical performance for the oxygen reduction than conventional LSM, a typical electronic conductor with extremely low ionic conductivity, for example, 1.1×10^{-7} S/cm at 900°C (Yasuda et al., 1996) and 5.9×10^{-8} S/cm at 800°C (Endo et al., 1996). It is noted, however, that the activation enthalpy for the oxygen self-diffusion in LSCF is high at 186 ± 5 kJ/mol (Dusastre and Kilner, 1999) and thus the ionic conductivity drops rapidly with decreasing temperature. Kharton et al. (2003) obtained a close activation energy of ~ 200 kJ/mol for ionic transport in $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$, a composition exactly the same as that employed in this study. For the composition of $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$, the ionic conductivity is 0.005 S/cm at 900°C, and it decreases to ~ 0.0007 S/cm at 800°C (Kharton et al., 2003), which is much lower than that of GDC. At 800°C, ionic conductivity of 0.068 S/cm was obtained for the GDC electrolyte in this study. As the operating temperature decreases further, the difference between the ionic conductivities of LSCF and GDC will be further widened. Hence, the ionic conductivity of the LSCF cathode should by right be enhanced by adding GDC. The addition of GDC phase can create an effective pathway for oxygen ions transport involved in the oxygen reduction reaction. Figure 5-9 schematically illustrates the transport pathways for oxygen ions and electrons in porous LSCF and LSCF-GDC composite electrodes. In LSCF-GDC composite electrodes, electrons transport through LSCF which has overwhelming electronic conductivities, and oxygen ions transport via the GDC which has much higher ionic conductivities than the LSCF.

Figure 5-9 Schematic illustrations of ionic and electronic pathways and reaction zone in (a) pure LSCF and (b) LSCF-GDC composite cathodes.

With effective transport of oxygen ions and electrons, the reaction sites, i.e. the TPB, for the oxygen reduction on composite cathodes extend from the electrolyte/electrode interface to the whole electrode. The reaction kinetics can thus be substantially enhanced. This well explains the present experimental results. Adding 50 wt.% GDC to LSCF produced a reduction by a factor of 9 in the polarisation resistance. The

Chapter 5 Electrochemical Performance of LSCF and LSCF-GDC Cathodes

significant enhancement of the electrochemical activity of the LSCF cathode due to the addition of GDC provides strong evidence that the TPB plays an important role in the electrochemical properties observed for the LSCF-GDC composite cathodes in the temperature range studied. This is in agreement with the findings reported by Liu and Wu (1998).

The transport properties in a composite, such as electrical conductivity, are especially sensitive not only to the percentage of each phase, but also to how phases are connected. Percolation theory is extensively employed to shed light on the electrical transport behaviour in a two or more phase composite in which phases possess different electrical conduction behaviour (Martin, 1992; Wu and Liu, 1997). What follows is the analysis of polarisation resistance dependence on GDC fraction in the LSCF-GDC system prepared in this study, based on the most widely used effective medium percolation theory (EMPT) and the concept of ambipolar conductivity.

To apply the EMPT, the LSCF-GDC composite cathode can be viewed as a mixed conductor on the macroscopic scale. The pores in the composite cathode to facilitate gas transport and increase reaction sites can be considered as a third phase in the composite. The effective conductivity of a mixture consisting of three randomly distributed phases is given by (Wu and Liu, 1997):

$$\frac{\sigma_m - \sigma_1}{2\sigma_m + \sigma_1} p_1 + \frac{\sigma_m - \sigma_2}{2\sigma_m + \sigma_2} p_2 + \frac{\sigma_m - \sigma_3}{2\sigma_m + \sigma_3} p_3 = 0 \quad (5-2)$$

$$p_1 + p_2 + p_3 = 1 \quad (5-3)$$

where σ_m represents the effective conductivity of a porous mixture, σ_1 , σ_2 and σ_3 represent the conductivity of each constituent phase, and p_1 , p_2 and p_3 are the volume fraction of each phase.

Chapter 5 Electrochemical Performance of LSCF and LSCF-GDC Cathodes

The ambipolar conductivity is an important parameter, which characterises the simultaneous transport properties of both electronic and ionic species in a mixed conductor. In order to predict the ambipolar transport properties of the solid component in the composite, the effective electronic and ionic conductivities are considered separately. If the interaction between the ionic and the electronic charge carriers is negligible, the ambipolar conductivity of the solid phase composite conductor can be approximated as (Wu and Liu, 1997):

$$\sigma_{amb} = \frac{\sigma^e \sigma^i}{\sigma^e + \sigma^i} . \quad (5-4)$$

Although the actual role of pores in a porous electrode is rather complicated, for the sake of simplicity, the conductivities of the pores are assumed to be zero, i.e., $\sigma_3=0$. Then the effective electronic, σ^e , and ionic σ^i , conductivity of the porous mixed conductor of LSCF-GDC composites can be calculated based on Equations (5-2) and (5-3) using experimental values of electronic and ionic conductivities for the pure components (see Table 5-1) at 700°C. Based on Equation (5-4), the ambipolar conductivity, σ_{amb} , and the corresponding ambipolar resistivity, $\rho_{amb} = 1/\sigma_{amb}$, can be easily obtained as a function of volume fraction of GDC in LSCF-GDC composites for different values of porosity. Figure 5-10 shows the calculated results. A noticeable feature is the characteristic minima in the ambipolar resistivity or the consequent maxima in the ambipolar conductivity which occurs when the percolation limit of the ionically conductive GDC phase is achieved. It is also clear that the percolation limit becomes smaller as the composite electrode porosity increases. For the composite with a porosity of 30%, the model predicts that the electrode containing 53 vol% GDC exhibits

Chapter 5 Electrochemical Performance of LSCF and LSCF-GDC Cathodes

Table 5-1 Electronic and ionic conductivities of LSCF and GDC at 700°C.

Material	$\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$	$\text{Gd}_{0.1}\text{Ce}_{0.9}\text{O}_{1.95}$
σ_e (S/cm)	170 (Kharton et al., 2003)	1×10^{-6} (Dusastre and Kilner, 1999)
σ_i (S/cm)	6.6×10^{-5} (Kharton et al., 2003)	0.0396 (Present study)

Table 5-2 Porosity measurements of various LSCF-GDC composite cathodes

Cathode Composition	LSCF	LSCF-GDC20	LSCF-GDC30	LSCF-GDC40	LSCF-GDC50	LSCF-GDC60
Porosity (%)	33.2 ± 0.9	31.5 ± 1.1	34.1 ± 1.3	31.6 ± 0.7	30.4 ± 1.1	28.9 ± 1.4

Figure 5-10 Ambipolar resistivity at 700°C of porous LSCF-GDC composites as a function of GDC volume fraction.

Chapter 5 Electrochemical Performance of LSCF and LSCF-GDC Cathodes

the lowest ambipolar resistivity. The porosities of the composite cathodes prepared in this study were measured by dimensions/mass method. The measurements are given in Table 5-2. Since the porosities are very close to 30%, the predicted result is in good agreement with the experimental data where the LSCF-GDC composite cathode with 50 wt.% (equivalent to 55 vol.%) GDC produced the lowest polarisation resistance (see Figure 5-8). Then it is conceivable that, firstly, this composite electrode has a high density of triple phase boundary (TPB) with very fine and sufficiently porous microstructure, and secondly, the optimum distribution and connection between these two materials LSCF and GDC in this composite offer continuous and the most convenient pathways for efficient electron and ion transport involved in the oxygen reduction process on the composite electrode where the LSCF is regarded mainly as the electron transport media while the GDC as oxygen ion transport components.

5.4 Summary

LSCF cathodes were prepared on GDC electrolytes using screen printing method and subsequently sintered at temperatures 750-1100°C for 2 h. The electrochemical impedance spectroscopy revealed that sintering conditions have a significant influence on the electrochemical properties of LSCF cathodes. The optimal sintering temperature is 900°C for the LSCF on the GDC electrolyte, which produced the lowest interfacial resistance, $2.54 \Omega\text{cm}^2$ at 600°C. SEM observations showed that the performance of LSCF cathodes can be well correlated with the microstructure. Appropriate sintering temperature can provide fine grain size, large surface area, proper porosity, good

Chapter 5 Electrochemical Performance of LSCF and LSCF-GDC Cathodes

connections between cathode particles and good bonding between cathode and electrolyte, thus leading to the optimal cathode performance.

Various LSCF-GDC composite cathodes with varying GDC content were sintered at 900°C for 2 h and then also evaluated by the electrochemical impedance spectroscopy. The measurement results showed that the addition of GDC phase to LSCF cathodes on GDC electrolytes substantially improves the electrochemical properties. The lowest polarisation resistance, a reduction by a factor of 9 was achieved as a result of 50 wt.% GDC addition to LSCF. This optimum GDC fraction is consistent with the prediction by the effective medium percolation theory.

Although LSCF is a MIEC with high electronic and appreciable ionic conductivity, its ionic conductivity is much lower compared with GDC material, and also rapidly decreases with operating temperature. The significant enhancement of the electrochemical properties of LSCF due to the addition of GDC phase indicates that the triple phase boundary (TPB) has a great contribution to the electrochemical performance of LSCF-GDC composite cathodes.

CHAPTER SIX

THIN FILM SOFC WITH GDC ELECTROLYTE

6.1 Introduction

Solid oxide fuel cells (SOFC) have great potential to be the clean, more efficient, and versatile technologies than other energy conversion methods. While the existing SOFC technology has demonstrated much higher energy efficiency with minimal pollutant emission over conventional energy technologies, the cost of current SOFC systems is still prohibitive for wide commercial applications (Minh and Takahashi, 1995). To be economically competitive, the cost of materials and fabrication must be dramatically reduced. One effective approach to cost reduction is to reduce the operating temperature so that interconnects, heat exchangers, and structural components can be fabricated from relatively inexpensive metals. Recently, considerable efforts have been directed to reduced-temperature SOFCs (Pal and Singal, 1990; Souza et al., 1997; Steele, 2000). The operating temperature can be reduced by decreasing the electrolyte thickness, by using electrolytes of high ionic conductivity at lower temperatures or by reducing electrode/electrolyte interfacial resistances.

Doped-ceria ceramics show much better oxygen ionic conductivity at temperatures below 800°C than the conventional YSZ electrolyte (Inaba and Tagawa, 1996; Steele, 2000). In Chapter 4, the author showed that high oxygen ionic conductivity has been obtained for sintered pellets prepared from the nanosized gadolinia-doped ceria (GDC) powder. The microstructure of the GDC electrolytes has been well correlated with the processing and sintering conditions. Chapter 5 has shown improved interfacial

Chapter 6 Thin Film SOFC with GDC electrolyte

properties of LSCF cathode on the GDC electrolyte at reduced temperatures compared with LSM cathode commonly used in conventional high temperature SOFCs. Moreover, it was found that the addition of GDC to LSCF has greatly increased the electrochemical properties, and the optimization of the composition of composite cathodes consisting of GDC and LSCF has been conducted. On the basis of the above-mentioned work, this chapter presents the incorporation of the previous work into complete single cells which would expect to offer high performance when operating at reduced temperatures.

For a complete single cell, there are three integral components: cathode, electrolyte and anode. Since satisfactory materials for electrolyte and cathode components have been chosen, good performance anode material should also be studied to acquire a high performance cell. Considering that ohmic loss and cathode overpotential are often the main factors limiting SOFC performance, and the anode polarisation only accounts for a very small fraction of the overall cell polarisation (Doshi, 1999; Xia and Liu, 2001b), conventional Ni-based material, which has a good electrocatalytic activity for hydrogen oxidation (Jiang et al., 2000a), was selected as anode for the single cell in this study. To further improve the anode performance, some amount of GDC was added to the Ni anode to increase the ionic conductivity of the electrode. Based on the related work presented in the literature (Xia and Liu, 2001b; Xia and Liu, 2002a), a mass ratio of 35:65 for GDC to NiO was adopted to form the Ni-GDC cermet anode such that complete GDC-based SOFCs were assembled and evaluated.

To develop high performance cells, a thin film electrolyte supported by an electrode is often used to reduce the electrolyte-contributed resistance. So far, various thin film deposition techniques have been explored for preparation of dense electrolyte

Chapter 6 Thin Film SOFC with GDC electrolyte

films on porous electrode substrates, which have been reviewed in Chapter 2. These thin film deposition techniques include a variety of atomic-scale physical and chemical vapor deposition, sol-gel process, electrochemical vapor deposition, combustion chemical vapor deposition, and more traditional particle deposition techniques (Will et al., 2000). The atomic-scale deposition techniques involving a vapor phase or a solution, often face difficulties either in stoichiometry control or in preventing the gas or the solution from filtration into the porous substrates. On the other hand, the particle deposition techniques such as electrophoretic deposition (EPD), slurry coating (or colloidal coating), screen printing, tape casting and tape calendering often have high requirements with relation to the powder characteristics, including particle shape, size, size distribution, etc., and also have difficulties in achieving required sintered density or desired film thickness (Will et al., 2000; Singhal, 2000). Further and in particular, many of these film deposition techniques are complex to control and expensive, whereas dry-pressing technique, known as a conventional ceramic processing technique, seems to be simple, reproducible and very cost-effective.

Dry-pressing technique has been widely used in the laboratory and industry to make parts normally thicker than 0.5 mm. Xia and Liu (2001a), however, successfully employed dry-pressing technique to obtain GDC electrolyte film as thin as 8 μm on porous substrates. They reported that the key point was the use of a highly porous or foam-structured powder with extremely low fill density, which was synthesised by glycine-nitrate combustion method. Except this work, no other reference so far has reported thin film electrolyte preparation using dry-pressing technique. To evaluate the applicability and to broaden the application of dry-pressing technique for thin film

Chapter 6 Thin Film SOFC with GDC electrolyte

electrolyte preparation, attempts were made to use this technique for preparing thin film GDC electrolytes from ordinary non-porous GDC powders.

In addition, due to the difference between the highly porous powder synthesised by Xia and Liu (2001a) and the non-porous powder used in this study, the conventional powder filling technique commonly used in laboratories can not satisfy the requirements for preparing GDC films with a thickness of around 20 μm . As a result, a spray-copressing process, which is a combination of suspension spray as a novel powder filling technique and dry pressing technique, has been explored for the thin film electrolyte fabrication. In this chapter, single cells based on GDC electrolyte films were assembled and tested. The recorded cell performance indicates a significant progress in the development of intermediate-temperature SOFCs based on GDC electrolyte.

6.2 Fabrication of GDC electrolyte thin films

6.2.1 Match of sintering behaviours between electrolyte and anode support

For thin film SOFCs, generally, the bilayer of thin electrolyte film on the porous anode support/substrate is co-sintered under the same sintering conditions. Thus it is quite critical for the two layers to possess similar sintering and thermal expansion behaviours. It is well known that, the compacted parts undergo a big shrinkage during the heating and holding steps of the sintering process, and they also experience cooling shrinkage during the cooling step. Any large difference in shrinkage of two bonded layers may cause high mechanical stresses in the bilayer part. When the stress is above the mechanical strength of either layer of the part, cracking will inevitably take place. For a bilayer ceramic structure, it is important but not enough for the two layers to have the final shrinkage match after sintering, which helps to produce a flat bilayer sample.

Figure 6-1 Surface morphology of GDC film of an electrolyte/anode bilayer, prepared by dry-pressing process and cosintering at 1300°C for 2 h, where the electrolyte was prepared from GDC powder after calcination at 750°C for 2 h, and the anode from GDC-NiO (35:65 in weight) mixture with the GDC powder also calcined at 750°C for 2h.

More importantly, there should be a good shrinkage match between the two layers at any temperature during the cosintering process, which may minimize the possibility of cracking of the sintered bilayer part during the fabrication stage.

Figure 6-1 shows the cracks on the GDC electrolyte surface of a sintered bilayer sample prepared by a dry pressing process and cosintering at 1300°C for 2 h, where the electrolyte was prepared from the GDC powder after calcination at 750°C for 2 h, and the anode from the GDC-NiO (35:65 in weight) mixture with the GDC powder also calcined at 750°C for 2h. In spite of the initial separate sintering experiments which revealed a close final shrinkage for the GDC electrolyte and the anode, cracking still happened after they were copressed to form a bilayer followed by cosintering. This suggests that there might be a big mismatch between thermal expansion coefficients (TEC) and /or the real-time shrinkages of the two layers during cosintering and cooling

Figure 6-2 Thermal expansion coefficients of GDC electrolyte and GDC-NiO (35:65 in wt.) anode measured in air.

Figure 6-3 Sintering behaviours of GDC electrolyte and several anodes sintered at 1300°C for 2 h at a heating rate of 5 K/min. Electrolyte was prepared from GDC powder after calcination at 750°C for 2 h; Anode-1, Anode-2 and Anode-3 from GDC-NiO (35:65 in weight) mixture with the GDC powder calcined at 750°C, 650°C, and 550°C for 2 h, respectively.

Chapter 6 Thin Film SOFC with GDC electrolyte

steps. In addition, cracks were observed only on the GDC electrolyte side, implying that the GDC layer was subjected to a tensile stress arising from the shrinkage mismatch between the two layers. This is also due to the fact that the GDC layer is far thinner than the anode support layer, $\sim 45\ \mu\text{m}$ and $\sim 0.8\ \text{mm}$ thick, respectively.

To check whether or not the observed cracks in the electrolyte film were caused by the TEC differences, TEC measurements were first conducted on sintered electrolyte and anode pellets. The results are given in Figure 6-2. It can be seen that both materials basically exhibit a linear expansion behaviour in the measuring temperature range of 30-900°C. The average TEC is $12.1 \times 10^{-6}\ \text{K}^{-1}$ for the electrolyte and $12.5 \times 10^{-6}\ \text{K}^{-1}$ for the anode. The similar TEC values of the electrolyte and anode suggest that the TEC is unlikely to be responsible for the cracks in the electrolyte film as shown in Figure 6-1. Then the real-time shrinkage is most likely the reason for the above cracks. To ensure a close real-time shrinkage of the GDC electrolyte film and the anode substrate during co-sintering, dilatometric measurements have been conducted for green electrolyte and anode pellets individually. As shown in Figure 6-3, a big difference exists between the sintering behaviours of GDC electrolyte and Anode-1 although they have a close final shrinkage after sintering, i.e., 12.3% and 11.2% respectively. The starting temperatures for the densification of GDC electrolyte and Anode-1 are $\sim 800^\circ\text{C}$ and $\sim 980^\circ\text{C}$, respectively. It can be seen that the GDC electrolyte has experienced a linear shrinkage of $\sim 5\%$ when Anode-1 begins to shrink, and also, the maximum deviation between the real-time linear shrinkage of the GDC electrolyte and Anode-1 comes up to 7.5% at around 1100°C . This big shrinkage deviation would give rise to a high mechanical stress in the bilayer. Such mechanical stress exerting on the GDC film should be of tensile nature considering that the real-time shrinkage of the GDC electrolyte is always larger

Chapter 6 Thin Film SOFC with GDC electrolyte

than that of Anode-1. This well explains the cracks developed in the bilayer sample with GDC electrolyte film on Anode-1 support, as shown in Figure 6-1. The presence of microcracks across the electrolyte will lead to a lower ionic conductivity of electrolyte, and also, the diffusion of hydrogen from the anode side to the cathode side through the cracks may greatly decrease the open-circuit voltage (OCV) and thus deteriorates the performance of the cell.

To ensure crack-free in the electrolyte of the bilayer, the sintering behaviours of the two layers must be carefully adjusted to provide a good match. To achieve this, several ways can be used, including the adjustment of the sintering behaviours of the electrolyte, the anode, or both. In this study, the sintering behaviour of the anode was adjusted to match with that of the GDC electrolyte prepared from raw powders after calcining at 750°C for 2 h.

The sintering behaviour is closely dependent on the composition and the characteristics of raw powders used. Since the starting temperature for the densification of GDC electrolyte is 800°C while that is 980°C for Anode-1, the sintering behaviour of the anode should be adjusted to achieve a lower starting densification temperature. With the anode composition (35:65 for GDC:NiO ratio in wt.%) kept constant and the same NiO powder, the effect of the calcination of raw nanocrystalline GDC powder at different temperatures on the sintering behaviour of GDC-NiO composite anode was investigated. Figure 6-3 shows the shrinkage behaviours of three kinds of anodes with the GDC powder calcined at different temperatures. It can be observed that the starting densification temperature decreases with decreasing calcination temperature of the GDC powder in the composite anode. The Anode-2, with GDC powder calcined at 650°C for 2 h, seems to have the best matching in shrinkage behaviour with the electrolyte made

Chapter 6 Thin Film SOFC with GDC electrolyte

of GDC powder calcined at 750°C for 2 h. Although a difference (~2%) still exists in the real-time shrinkage between the Anode-2 and the electrolyte, and the electrolyte layer seems to be subjected to a tensile stress in the medium temperature range during the cosintering process, it would not cause any cracking developed in the electrolyte film. Figure 6-4 shows the micrograph of the electrolyte surface of a bilayer sample co-sintered at 1300°C for 2 h, of which the thin electrolyte layer was prepared from GDC powder calcined at 750°C for 2 h, and the anode substrate from the NiO-GDC mixture with the GDC powder calcined at 650°C for 2 h. No apparent cracks were seen on the electrolyte surface. It is reasonable to deduce that the dense and crack-free electrolyte layer will be effective in preventing the cross-over of hydrogen gas from the anode to the cathode. In addition, as a consequence of the final shrinkage of the electrolyte, 12.3%, which is close to that of Anode-2, 14.2%, flat bilayers with electrolyte film supported on Anode-2 have been obtained. It should be noted that flat bilayers are helpful in preparing cathodes by screen printing to form a complete cell. From here, all bilayers were prepared from the powders under these conditions unless otherwise stated.

With regard to the combination of the electrolyte with the Anode-3, as can be observed from Figure 6-3, the shrinkage of the Anode-3 remains smaller than that of the electrolyte till the end of sintering. As a result, the electrolyte layer will always be in a compressive stress, thus eliminating the cracking of the electrolyte layer. In fact, no cracks were observed under SEM on the bilayer with GDC film supported on Anode-3. Such a combination, however, could not provide a flat bilayer sample. In fact, the bilayer was badly warped and appeared to be convex towards the electrolyte side due to a much larger final shrinkage of the Anode-3, 17.0%, in comparison with that of the electrolyte, 12.3%.

Figure 6-4 Surface morphology of a 45- μm -thick GDC film of an electrolyte/anode bilayer co-sintered at 1300°C for 2h, where the electrolyte was prepared from GDC powder calcined at 750°C for 2 h, and the anode from GDC-NiO (35:65 in wt.%) mixture with the GDC powder calcined at 650°C for 2 h.

6.2.2 Effect of powder filling techniques on the microstructure of GDC electrolyte film

Dry-pressing technique is commonly used to make a part thicker than 0.5 mm. However, for fabrication of high quality thin films by dry-pressing technique, there are two important factors to be considered with respect to the raw powders: fill density and flow behaviour (Xia and Liu, 2001a). In general, the lower the fill density and the more favorable the flow behaviour of the powder, the easier it is to make the loose powder uniformly distributed at the time of powder filling.

Xia and Liu (2001a) used highly porous or foam GDC powder with an extremely low fill density to prepare a thin film electrolyte onto the anode substrate by dry-pressing technique. A 26- μm -thick GDC film with a relative density of 92% was

Chapter 6 Thin Film SOFC with GDC electrolyte

obtained after sintering, while the relative density was only 80% for an 8- μm -thick GDC film. They attributed the reduced sintered density of GDC film with decreasing film thickness to the poor flow behaviour of the foam powder. The poor flow behaviour inevitably resulted in a non-uniform distribution of loose powders and consequent low packing density.

In this study, an ordinary non-porous nanocrystalline GDC powder was used, instead. Its characteristics have been presented in Chapter 4. The fill density is much higher than the foam powder used by Xia and Liu (2001a), and the powder also has a very poor flow behaviour compared with those powders exhibiting nearly spherical shape and smooth particle surface. However, a bilayer with a 45- μm -thick GDC film on the anode substrate was successfully prepared by dry-pressing process. Figure 6-4 shows the surface morphology of such a GDC film. Almost no cracks or pores can be observed on the GDC film. A single SOFC was assembled based on this bilayer sample and its performance is presented in Section 6.4. Considering this film is not thin enough to reduce the electrolyte resistance, attempts were made to further reduce the film thickness from 45 μm to 20 μm using less amount of powder during the dry-pressing process. However, the result was not desirable. Figure 6-5 shows the surface morphology of a 20- μm -thick GDC film on the anode substrate prepared by the dry-pressing process using a conventional powder filling technique, which means that the dry powders are directly spread onto the anode substrate in a steel die. Many pores can be seen on the film surface and low OCV and performance of the cell based on this GDC film can be expected. The presence of the porous microstructure in this thinner electrolyte film may be due to the fact that the conventional powder filling technique is hard to make a uniform distribution of ordinary non-foam powder when the film

Figure 6-5 Surface morphology of a 20-μm-thick GDC film, prepared by conventional powder filling technique, in an electrolyte/anode bilayer after co-sintering at 1300°C for 2 h. The powder conditions are the same as presented in Figure 6-4.

thickness is reduced to a very low value. Non-uniform distribution of powders will result in a relatively low packing density and thus a low density after sintering.

To reduce the porosity in the electrolyte film, two approaches can be used, i.e., either improving the flow behaviour of the powder or improving the powder filling technique, to achieve a uniform and reproducible filling. It is rather difficult to achieve the former with the current powder. The latter was considered in this study. A novel powder filling technique, suspension spray, has been explored to replace the conventional powder filling technique commonly used in laboratories. Suspension spray process involves dispersing raw powders in a solvent, spraying the suspension onto the substrate, and volatilizing the solvent. The spraying process can be repeated for several times depending upon the powder content in the suspension and the film thickness required. Since the agglomeration degree of powders in the suspension is significantly reduced by ultrasonic treatment and thermal movement of solvent molecules, the

Figure 6-6 SEM micrographs of (a) the cross section of a GDC electrolyte/anode bilayer, and (b) the surface of its electrolyte film, prepared by spray-copressing process, a combination of suspension spray powder filling technique and dry-pressing technique.

Chapter 6 Thin Film SOFC with GDC electrolyte

uniform distribution of powders on the substrate can be greatly improved by this powder filling technique. As a result, dense GDC electrolyte films with a thickness of $\sim 20\text{ }\mu\text{m}$ on the anode substrate were successfully obtained after co-sintering at 1300°C for 2 h. Moreover, the thickness homogeneity of the film has also been much improved. Figure 6-6 shows the cross sectional view of an electrolyte/anode bilayer and the top view of its GDC film prepared by the combination of suspension spray filling technique and dry-pressing technique, termed as spray-copressing technique hereafter. The GDC film is about $20\text{ }\mu\text{m}$ thick and displays a very dense microstructure. In fact, a number of tests have confirmed that with this spray-copressing technique, thin, uniform and dense electrolyte films can be easily and successfully prepared from ordinary non-porous powders.

6.3 Microstructure of the cells

Figure 6-7 a through d show the cross-sectional SEM micrographs of a whole single cell and its components after electrochemical testing. The electrolyte layer is about 45 μm thick. An enlargement of the electrolyte film displays an almost fully dense structure except a few isolated microvoids. The cathode layer, consisting of very fine grains of $\sim 0.2 \mu\text{m}$ in size, has a thickness of $\sim 70 \mu\text{m}$. It has been proven that a thickness of 10 μm is sufficient for a mixed-conducting cathode since the oxygen reduction reaction takes place mainly within such a thickness range (Mogensen and Skaarup, 1996; Adler et al., 1996). A thicker cathode layer may produce large gas diffusion resistance at high current densities. On top of the cathode is a porous platinum layer ($\sim 10 \mu\text{m}$ thick) used as a current collector to minimise the contact resistance between the composite cathode and the platinum mesh probe. The thickness of the porous anode was about 0.8 mm, and the porosity of the anode was about 7.8% and 33.4%, respectively, before and after the reduction of NiO to Ni in the composite anode. From Figure 6-7a, good adhesion can be seen at both the electrolyte/cathode interface and the electrolyte/anode interface, which is also essential for the cell to achieve high power outputs.

To examine the effect of electrolyte film thickness on the cell performance, another single cell based on a 22- μm -thick GDC electrolyte prepared by the spray-copressing method was also assembled and tested. Figure 6-7e shows the cross-sectional micrograph of this cell. Since it was prepared under the same processing conditions, the cell showed almost the same microstructure as the previous one except for the different electrolyte film thickness.

Chapter 6 Thin Film SOFC with GDC electrolyte

Figure 6-7 SEM cross-sectional micrographs of (a) a SOFC consisting of a 45-μm-thick GDC electrolyte, a Ni-GDC cermet anode and a LSCF-GDC composite cathode, (b) local enlargement of the electrolyte, (c) local enlargement of the cathode, and (d) local enlargement of the anode. (e) Cross-sectional micrograph of a cell with a 22-μm-thick GDC electrolyte and the same Ni-GDC cermet anode and LSCF-GDC composite cathode as in the previous cell.

6.4 Cell testing

6.4.1 Polarisation behaviour of the cells

Figure 6-8a shows the results of voltage (V) versus current density (i) measurements for a thin film electrolyte SOFC consisting of a 45- μm -thick GDC electrolyte, a LSCF-GDC composite cathode and a Ni-GDC cermet anode, obtained in humidified hydrogen and air at temperatures from 500 to 650°C. For the lower measuring temperatures, the slope ($-dV/di$) of i -V curve is larger near $i=0$ but decreases rapidly with increasing i , and then tends to be constant, indicating a change in the dominant polarisation mechanism of the cell. In fact, at low current densities, it is activation polarisation that dominates the total cell polarisation, which is generally featured by an upward bending behaviour in the i -V curve of a cell. Activation polarisation is mainly associated with the electrocatalytic activity of electrodes. The better the electrocatalytic activity of electrodes, the lower the activation polarisation contribution will be. With the increase of the current density, ohmic polarisation contributes more and more to the total cell polarisation. Since the ohmic polarisation is proportional to the ohmic resistance of the cell, which basically does not change at a constant temperature, i -V characteristics appear in linear regression at high current densities. As the temperature is increased, the electrocatalytic activity of the electrodes is much improved, and the activation polarisation arising from the electrochemical reactions contributes less; thus the cell i -V characteristics become more linear. When the temperature is increased to 650°C, the i -V curve displays a totally linear manner, implying that the ohmic polarisation dominates the cell performance within the range of the current densities under study.

Figure 6-8 *i*-V characteristics of thin film SOFCs (a) with a 45-μm-thick GDC electrolyte and (b) with a 22-μm-thick GDC electrolyte tested in air and humidified hydrogen in the temperature range of 500-650°C.

Chapter 6 Thin Film SOFC with GDC electrolyte

For the single cell with a 22- μm -thick GDC film and the same cathode and anode, as shown in Figure 6-8b, the i -V curves demonstrate a similar trend to those of the previous cell at temperatures below 650°C, i.e., the cell voltage drops rapidly at low current densities and then tend to drop slowly at a constant rate with increasing current density until a short-circuit current density is reached when the cell voltage drops to zero. At 650°C, however, the cell displays a different polarisation behaviour compared with that of the previous cell. At high current densities, the polarisation curve shows a downward bending behaviour, i.e., the cell voltage again drops rapidly with increasing current density. This is a typical diffusion polarisation behaviour incurred by limited mass transport to the reaction sites. When the reactants involved in either cathodic or anodic reaction are insufficiently supplied, the diffusion polarisation will be encountered.

6.4.2 Polarisation resistance of the cells

AC impedance spectra of the cell with a 45 μm GDC electrolyte were measured under open-circuit conditions in the temperature range of 400-650°C using a four-probe configuration, and plotted in Figures 6-9 a and b. The intercept of the impedance plot with the real axis at high frequency (left side) represents the ohmic resistance (R_{Ω}) through the cell, whereas the difference between the high- and low-frequency (right side) intercepts corresponds to the total resistance of the two interfaces: the cathode/electrolyte interface (R_c) and the anode/electrolyte interface (R_a). The ohmic resistance includes the electronic and ionic resistance of the electrodes and electrolyte and the contact resistance between the electrodes and the electrolyte and between the cell and the current collectors. The interfacial resistance (R_c+R_a) mainly reflects the polarisation resistance of the electrodes in the electrochemical processes involving

Chapter 6 Thin Film SOFC with GDC electrolyte

oxygen reduction on the cathode and hydrogen oxidation on the anode. Because the electrochemical test station used in this study involves a considerable inductance, as reflected by the portion of the impedance spectra with the imaginary component $-Z'' < 0$, which apparently affects the high frequency intercept, an equivalent circuit including an inductor component, as shown in Figure 6-9 c, was thus employed to fit the impedance spectra. As a result, the interfacial resistance and the ohmic resistance of the cell are resolved distinctively from the total cell resistance, and are shown in Figure 6-9 d as a function of operating temperature.

As can be seen from Figure 6-9 d, the total cell resistance, the ohmic resistance and the interfacial resistance all increase with decreasing temperature, in which the interfacial resistance increases more rapidly than the ohmic resistance. From the slope of Arrhenius plots, activation energies can be determined. For the interfacial resistance of the cell, the activation energy is calculated to be 127.1 kJ/mol (equivalent to 1.32 eV), which is very close to 1.36 eV, the activation energy for the interfacial resistance

Figure 6-9 Impedance spectra of thin film SOFC with a 45- μ m-thick GDC electrolyte measured at open-circuit condition and different temperatures, shown in (a) and (b). The total cell resistance, interfacial resistance and ohmic resistance, obtained by fitting the impedance spectra, are shown in (d). The equivalent circuit used for fitting is shown in (c).

Chapter 6 Thin Film SOFC with GDC electrolyte

of LSCF-GDC (50:50 by weight) composite cathode on GDC electrolyte shown in Chapter 5. It seems that the total interfacial resistance of the cell is dominated by the electrochemical property of the cathode or the cathode/electrolyte interfacial resistance. From Figure 6-9d, it can also be seen that the ohmic resistance and the interfacial resistance of the cell at 650°C are almost the same. At lower temperatures, the interfacial resistance is much higher than the ohmic resistance and is dominant in the total cell resistance. This implies that below 650°C the interfacial resistance determines the cell performance. This, however, is the case only at open-circuit condition or at near-zero cell current. As the cell current is increased, the ohmic resistance rapidly becomes the main factor limiting the cell performance, especially at higher temperatures (Tsai et al., 1997). This is because ohmic resistance does not change with the cell current while the interfacial resistance depends strongly on the DC bias. Therefore, to accurately assess the contributions of ohmic resistance and electrode interface to the power density of a fuel cell, polarisation overpotentials under high current densities have to be used for comparative study. Figure 6-10 shows the i - V curves measured at various temperatures. The voltage loss is split into the ohmic drop (iR_{Ω}) and the electrode overpotential ($\eta_a + \eta_c$), which includes the cathode overpotential (η_c) and the anode overpotential (η_a). For the cell voltage and the voltage losses, this relationship is valid: $V_{\text{cell}} = \text{OCV} - iR_{\Omega} - (\eta_a + \eta_c)$. The percentage values marked in the figure represent the contributions of iR_{Ω} and $(\eta_a + \eta_c)$ to the total voltage loss at a cell voltage of 0.4V where the maximum power density is generally reached. By comparing iR_{Ω} and $(\eta_a + \eta_c)$, it is clear to see that above 550°C the cell performance is dominated by the ohmic drop. This implies that the ohmic resistance must be reduced to further improve the cell performance at temperatures higher than 550°C. Because the ohmic resistance of the

Chapter 6 Thin Film SOFC with GDC electrolyte

Figure 6-10 Voltage vs. current density curves at various temperatures for a thin film SOFC based on a 45-μm-thick GDC electrolyte, showing the splitting of the voltage loss into ohmic (iR_{Ω}) and electrode ($\eta_a + \eta_c$) components. R_{Ω} values for iR_{Ω} calculation were taken from Figure 6-9d. Percentages represent the contribution of (iR_{Ω}) or ($\eta_a + \eta_c$) to the total voltage loss.

Chapter 6 Thin Film SOFC with GDC electrolyte

cell is mainly represented by the electrolyte resistance, the ohmic resistance can be significantly reduced by reducing the electrolyte thickness. If the electrolyte thickness is reduced to about 20 μm from the present 45 μm , one may expect to produce much higher power outputs at corresponding temperatures. The performance measurements of the cell with a 22 μm GDC film, which are presented in Section 6.4.3, have confirmed that a significant increase in power density can be achieved at temperatures above 550°C by reducing the electrolyte thickness.

In contrast, it can also be seen from Figure 6-10 that below 550°C, the electrode overpotential component dominates the total voltage loss and is in agreement with the trend revealed in Figure 6-9d. This implies that improving electrode performance should be considered in the first place so as to further enhance the cell performance at temperatures lower than 550°C. Since previous studies (Doshi et al., 1999; Xia and Liu, 2001b) reported that the interfacial resistance is dominated by the cathode/electrolyte interface and the resistance from the anode/electrolyte interface is comparatively negligible, the performance improvement of the cells operating at low temperatures depends mainly on the advancement of electro-catalytically active cathodes. A novel cathode material $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF), which exhibits excellent electrochemical activity for oxygen reduction reaction at low temperatures (Shao and Haile, 2004), has been synthesized and incorporated into GDC-based fuel cells. Due to substantial improvement in the cathode performance, the cell with a BSCF cathode has generated highly impressive power densities at low temperatures that are presented in Section 6.5.

6.4.3 Cell performance

To examine the effect of the thickness of GDC electrolyte film on the cell performance, two single cells with different electrolyte film thickness (45 μm and 22 μm) have been assembled with the same Ni-GDC cermet anode and LSCF-GDC composite cathode and tested using humidified hydrogen and air. Figure 6-10 shows the voltages and the corresponding power densities of the two single cells as functions of current density and operating temperature. Characteristic parameters involved in Figure 6-11, including the measured cell OCVs and maximum power densities at different operating temperatures, are summarized in Table 6-1, together with the theoretical OCVs and typical literature data associated with doped-ceria electrolyte film. As can be seen from Table 6-1, compared to the data reported in the literature, the power outputs obtained in this study are very encouraging, which represent a significant progress in the development of intermediate/low temperature SOFCs. Furthermore, for the cell with a 45 μm GDC film prepared in this study, the maximum power densities are 581, 377, 227, 120 mW/cm^2 at 650, 600, 550 and 500°C, respectively. With the electrolyte film reduced from 45 μm to 22 μm , the cell performance has been greatly enhanced, and maximum power densities of 1004, 595, 316, 152 mW/cm^2 were obtained at 650, 600, 550 and 500°C, respectively. Accordingly, the corresponding increase in maximum power density is estimated to be 72.8% (650°C), 57.8% (600°C), 39.2% (550°C) and 26.7% (500°C). Obviously, the increase in maximum power density drops rapidly with decreasing operating temperature. The increase in maximum power density achieved at 650°C is much higher than that at 500°C. This is because at high temperatures the ohmic drop dominates the cell performance; while at lower temperatures the cell performance is essentially controlled by the electrode overpotentials, as demonstrated in

Chapter 6 Thin Film SOFC with GDC electrolyte

Figure 6-11 i -V characteristics (solid symbols) and the corresponding power densities (open symbols) for two SOFCs with different GDC electrolyte film thickness measured in humidified hydrogen and air at different operating temperatures.

Chapter 6 Thin Film SOFC with GDC electrolyte

Table 6-1 Comparison of OCVs and peak power densities for doped-ceria-based thin film SOFCs obtained in this study and from references.

Operating temperature (°C)	Nernst potential (V)	This study		This study		Peng et al. (2002)		Xia and Liu (2001b)		Doshi et al. (1999)		Zheng et al. (1996)		Liu et al. (2004)	
		OCV (V)	$P_{\max}$ (mW/cm ²)	OCV (V)	$P_{\max}$ (mW/cm ²)	OCV (V)	$P_{\max}$ (mW/cm ²)	OCV (V)	$P_{\max}$ (mW/cm ²)	OCV (V)	$P_{\max}$ (mW/cm ²)	OCV (V)	$P_{\max}$ (mW/cm ²)	OCV (V)	$P_{\max}$ (mW/cm ²)
650	1.130	0.864	581	0.856	1004	0.85	360	----	330	----	----	0.676	125	0.80	481
600	1.138	0.903	377	0.896	595	----	230	0.85	270	----	----	----	----	0.84	375
550	1.147	0.941	227	0.930	316	----	136	----	205	----	----	----	----	0.87	286
500	1.155	0.982	120	0.961	152	----	78	0.92	145	0.98	140	----	----	0.90	204
450	1.165	1.012	58	----	----	----	----	----	62	----	----	----	----	----	----
400	1.178	1.041	25	----	----	----	----	1.01	30	----	----	----	----	----	----
Cell description		Cathode: LSCF-GDC Anode: Ni-GDC Electrolyte: GDC, 45 μ m, by dry-pressing		Cathode: LSCF-GDC Anode: Ni-GDC Electrolyte: GDC, 22 μ m, by spray-copressing		Cathode: SSC Anode: Ni-YDC Electrolyte: YDC, 15 μ m, by screen printing		Cathode: SSC-GDC Anode: Ni-GDC Electrolyte: GDC, 26 μ m, by dry-pressing		Cathode: ANLC-1 Anode: Ni-GDC Electrolyte: GDC, 30 μ m, by multilayer tape casting		Cathode: LSCF Anode: Ni-YSZ Electrolyte: GDC, 5~10 μ m, by tape casting		Cathode: SSC-GDC Anode: Ni-GDC Electrolyte: GDC, 20 μ m, by dry-pressing	

Chapter 6 Thin Film SOFC with GDC electrolyte

Section 6.4.2. Since the electrodes (both the anode and cathode) in the two cells are the same, the increase in power density is inevitably very limited at lower temperatures through the reduction of electrolyte thickness. Therefore, alternative electrode materials, especially cathode materials, with higher electrochemical performance, have to be developed in order to improve the cell power outputs at these lower temperatures.

With reference to the measured OCVs of a fuel cell, it is generally related to the density of the electrolyte as well as operating conditions. Under fixed operating conditions such as temperature and composition and pressure of working gases, the OCV value depends on the density of the electrolyte. Open pores and cracks in the electrolyte will lead to gas crossover and hence lower OCV values than the theoretical ones. To prevent gas crossover through the electrolyte, a relative density of >94% is generally required to eliminate the open porosity in the electrolyte. Since the electrolyte films prepared in this study were almost fully dense and no cross-film cracks or pinholes were observed under SEM (Figure 6-7 b), the hydrogen permeation through the electrolyte should have been blocked. Also, cell sealing was carefully performed to ensure no hydrogen leaking through the seals. Nevertheless, an apparent difference between the measured OCVs and the theoretical OCV values can be seen from Table 6-1, which is not seen on YSZ electrolyte cells. Moreover, the difference increases with increasing temperature. This OCV loss is attributed to the electronic conductivity of doped ceria electrolytes incurred by reduction of Ce^{4+} to Ce^{3+} in reducing atmospheres (Figueiredo et al., 1999; Steele, 2000). Therefore, the problem with the phase stability in reducing environments restricts the doped-ceria materials to applications as SOFC electrolyte at relatively low temperatures. In order to utilize the attractive ionic conductivity of doped-ceria ceramics at higher temperatures but still within 800°C,

Chapter 6 Thin Film SOFC with GDC electrolyte

where metallic alloys can be considered for interconnects and manifolds to reduce the stack cost, some researchers (Inoue et al., 1989; Virkar, 1991; Marques and Navarro, 1996 and 1997; Chan et al., 2003) have proposed the use of a bilayer electrolyte, typically with a very thin YSZ layer (1~2 μm) deposited on a doped-ceria layer. With the introduction of a YSZ film, one can expect to avoid the significant OCV drop for the ceria-based electrolyte cell since YSZ is highly stable under practical operating conditions of SOFCs. Some references reported the simulation results on the performance of bilayer electrolyte cells (Marques and Navarro, 1996 and 1997; Horita et al., 1997; Chan et al., 2003), which demonstrate that the stability of doped-ceria electrolyte in reducing atmosphere can be greatly enhanced and the bilayer electrolyte is a promising candidate for IT-SOFCs based on doped ceria material. However, limited experimental work has been reported on this so far (Inoue et al., 1989; Jang et al., 2002). As an important part of this project, the investigation of YSZ/GDC bilayer electrolyte cells with YSZ film as an electronic blocking layer has been conducted and will be presented in Chapter 7.

6.5 High performance low temperature SOFC with novel BSCF cathode

As has been demonstrated earlier, when the operating temperature is lowered to around 500°C, the electrode overpotentials, mainly the cathode overpotential, dominate the overall cell performance. At such low temperatures, reducing the electrolyte thickness would not provide any significant improvement in cell performance. Consequently, efforts have to be directed to the improvement of cathode performance and development of novel cathode materials in order to achieve satisfactory power densities at low temperatures (Xia and Liu, 2002b; Liu et al., 2004).

Recently, Shao and Haile (2004) reported a new cathode material, $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF), for low-temperature SOFCs, which has been extensively investigated as oxygen permeation membrane material for oxygen generation (Shao et al., 2000; Shao et al., 2001; Veen et al., 2003). With this BSCF cathode, outstanding performance has been obtained at low temperatures from a single SOFC based on a 20- μm -thick $\text{Sm}_{0.15}\text{Ce}_{0.85}\text{O}_{1.925}$ (SDC) electrolyte film. Maximum power densities, 1,010 mW/cm^2 and 402 mW/cm^2 were produced at 600°C and 500°C, respectively. Apart from this, no other publication is available on the BSCF cathode. As this material is a potential candidate for low temperature SOFC development, extensive and detailed studies on BSCF cathodes are necessary in terms of oxygen reduction reaction mechanism, phase stability, compatibility with other doped- CeO_2 or doped- LaGaO_3 materials, as well as the long-term performance stability under practical SOFC operating environments. According to Steele (2000), Gd_2O_3 is the preferred dopant for CeO_2 oxide compared to Sm_2O_3 and Y_2O_3 because $(\text{Gd}'_{\text{Ce}} - \text{V}_{\text{O}}^-)$ complexes exhibit the lowest association enthalpy and Gd_2O_3 -doped CeO_2 shows a much better ionic

conductivity at low temperatures. Therefore, it is of importance and significance to examine the performance of the BSCF/GDC system.

6.5.1 XRD analysis of BSCF powder and Microstructure of the cell

Figure 6-12 shows the X-ray diffraction (XRD) pattern of the as-synthesized BSCF powder after being calcined at 800°C for 2 h. All the peaks in the XRD pattern can be well indexed as a cubic perovskite structure, and sharp lines reflect a well-developed crystallization, indicating that a single crystalline phase of BSCF oxide was successfully obtained after calcination.

To minimise the electrolyte resistance at low-temperature operation, great efforts have been made to fabricate GDC-based anode-supported cells by spray-copressing method, as described earlier. Figure 6-13 shows the cross-sectional SEM micrographs after electrochemical testing of a single anode-supported cell, consisting of a GDC electrolyte, a BSCF cathode and a Ni-GDC cermet anode. It can be observed from Figure 6-13a that the GDC electrolyte film is about 10 μm thick, sandwiched by a porous cathode (top layer) and a porous anode (bottom layer). Good adhesion can also be seen both at the cathode/electrolyte and anode/electrolyte interface, which has been produced by high-temperature firing. Figure 6-13b clearly shows a dense structure of the electrolyte film. The GDC film seems almost fully dense except a few isolated voids, and no cross-film cracks or pinholes were observed under SEM, suggesting that the 10- μm -thick GDC electrolyte film has been successfully fabricated onto the anode substrate by this spray-copressing method developed in-house. In contrast to the dense electrolyte film, both the cathode (Figure 6-13c) and the anode (Figure 6-13d) are highly porous. Sufficient porosity is important for electrodes, which allows rapid transport of gaseous reactants and provides abundant sites for electrochemical reactions

Figure 6-12 XRD pattern of the BSCF powder after calcination at 800°C for 2 h.

Figure 6-13 Cross-sectional SEM micrographs of an anode-supported cell: (a) the entire cell under low magnification (top layer: cathode; middle layer: electrolyte; bottom layer: anode support) and (b) GDC electrolyte, (c) BSCF cathode and (d) Ni-GDC anode under higher magnification.

in properly designed electrodes. It is noted that the BSCF cathode shows a much coarser structure than the Ni-GDC anode, though the former was sintered at a much lower temperature than the latter (950°C vs. 1300°C), indicating that the BSCF powder exhibits a much higher sinterability than the NiO-GDC powder. It is reasonably believed that refining and optimizing the cathode microstructure would likely improve the electrochemical activity of the BSCF electrode.

6.5.2 Open circuit voltage and power density of the cell

Figure 6-14 gives a direct comparison of measured OCV values as a function of temperature for three cells with different GDC electrolyte thickness or composition of cathode. All the three cells had the same Ni-GDC cermet anode and measured under the same humidified hydrogen/air conditions. Three aspects can be summarized as follows. Firstly, all the OCVs of the three cells decrease with increasing temperature. This tallies with the theoretical analysis based on thermodynamic equilibrium (Zha et al., 2001; Matsui et al., 2005). Secondly, for cells with the same LSCF-GDC (50:50 by weight) composite cathode, the OCVs decrease with decreasing electrolyte thickness (Riess et al., 1996; Matsui et al., 2005). In addition, the cells with the same electrolyte thickness but different cathode materials (one with LSCF-GDC, the other with BSCF), display an obvious difference in OCV values. Within the investigated temperature range, the cell with BSCF cathode developed in this study shows 30-40 mV higher OCVs than that with LSCF-GDC composite cathode reported by Leng et al. (2004), indicating that electrode materials have a great influence on the OCV of cells based on doped-ceria electrolyte (Riess, 1996; Zha et al., 2003). The OCV values of the BSCF cell are quite close to those of the cell with LSCF-GDC cathode and thicker GDC film of 45 μm . The observed OCV variations with electrolyte thickness and electrode material are resulted

Figure 6-14 Comparison of OCV values as a function of temperature measured under the same conditions for three cells with the same Ni-GDC anode but different electrolyte thickness or cathode composition.

from the mixed-conducting property of the doped-ceria electrolyte, which are not observed on YSZ electrolyte cells because YSZ is almost a pure ionic conductor in a wide range of reducing and oxidizing atmospheres.

An OCV of 0.903 V was recorded at 600°C for the present BSCF cell, displaying a large deviation from the theoretical value, i.e., 1.138 V at 600°C, which is due to the electronic conductivity of doped-ceria materials incurred by the reduction of Ce^{4+} to Ce^{3+} at reducing atmospheres, as mentioned earlier. This OCV loss can be partly alleviated as the temperature decreases. At 500 and 400°C, the cell produced an OCV of 0.984 and 1.032 V, respectively, which are much closer to the theoretical values, implying that the electronic conductivity of GDC electrolyte is insignificant at these low temperatures. This implicitly indicates that GDC is a very promising candidate used as an electrolyte in SOFCs, in particular, operating at around 500°C (Steele, 2000).

Figure 6-15 Voltages (solid symbols) and the corresponding power densities (open symbols) as a function of current density for a SOFC consisting of a novel BSCF cathode, a 10 μm GDC electrolyte and a Ni-GDC anode, measured in humidified hydrogen and air at different temperatures.

Figure 6-15 shows the voltages and the corresponding power densities expressed as a function of current density for the BSCF cell (as in Figure 6-13), measured in humidified hydrogen and air at temperatures from 400 to 600°C. The cell has generated maximum power densities of 1329, 863, 454, 208 and 83 mW/cm^2 at temperatures from 600 down to 400°C with intervals of 50°C. These performance characteristics are extremely impressive and, to the best of our knowledge, represent the best performance ever reported in the literature for low-temperature SOFCs. For comparison, the maximum power densities at different temperatures in this study are plotted against other results obtained from the literature with different cathode materials and shown in Figure 6-16. It can be seen that the cells with BSCF cathode present much higher power outputs than those with other cathode materials, including LSCF-GDC (Leng et al., 2004), SSC-GDC (Xia and Liu, 2001b), ANLC-1 (Doshi et al., 1999) and Ag-BICUVOX

Figure 6-16 Comparison of maximum power densities of thin-film GDC or SDC electrolyte cells with various cathodes.

(Xia and Liu, 2002b). For example, at 500°C, the maximum power density is 454 mW/cm² for the cell with BSCF cathode attained in this study, which is about three times of that for the cells with cathodes of LSCF-GDC, SSC-GDC and ANLC-1 (i.e., 167, 145 and 140 mW/cm², respectively); this maximum power density is almost double the performance of the cell with a novel Ag-BICUVOX cathode (Xia and Liu, 2002b), i.e., 231 mW/cm². Hence, with the introduction of BSCF cathode, significant improvement in power output has been achieved from doped-ceria electrolyte cells operating at low temperatures. It is noted that the cell based on 10 μm GDC thin-film electrolyte and BSCF cathode prepared in this study has produced greater power densities at low temperatures than that based on the same BSCF cathode but with a thicker SDC electrolyte film of 20 μm (Shao and Haile, 2004). The maximum power density of the former is 1329 mW/cm², which is much higher than 1010 mW/cm² of the

latter at 600°C. The improved power output is most likely attributed to the thinner electrolyte used.

6.5.3 Polarisation resistance of the cell

Shown in Figure 6-17 are the impedance spectra of the fuel cell with a two-electrode configuration measured at 500, 550 and 600°C under open-circuit conditions. The ohmic resistance R_{Ω} and the total interfacial polarisation resistance ($R_a + R_c$), including the anode/electrolyte interfacial polarisation resistance R_a and the cathode/electrolyte interfacial polarisation resistance R_c , of the cell were extracted by fitting the impedance spectra to the equivalent circuit with a configuration of $LR_{\Omega}(RQ)(RQ)$ (as in Figure 6-9 c). The extracted results are shown as an inset in Figure 6-16 in the form of Arrhenius plots. Obviously, at temperatures above 500°C, the ohmic resistance dominates the total cell resistance, below which, the interfacial polarisation resistance of the electrodes controls the total cell resistance. From the slopes of the Arrhenius plots, respective apparent activation energies of 120.3 and 61.9 kJ/mol for the ohmic resistance and the total interfacial polarisation resistance were determined. The activation energy for the total interfacial polarisation resistance of the cell is very close to 116 kJ/mol, which is the activation energy for the interfacial polarisation resistance of BSCF cathode on SDC electrolyte as reported by Shao and Haile (2004). It seems that the cathode/electrolyte interfacial polarisation resistance dominates the total interfacial polarisation resistance of the cell within the range of temperatures under investigation.

Figure 6-17 Impedance spectra of the cell, consisting of a 10 μm GDC electrolyte, a BSCF cathode and a Ni-GDC anode, measured under open-circuit conditions at 500, 550 and 600°C, respectively. The inset shows the Arrhenius plots of the ohmic resistance R_Ω and the total interfacial polarisation resistance ($R_a + R_c$).

Figure 6-18 Comparison of the total interfacial resistance ($R_a + R_c$) of thin-film GDC electrolyte cells with various cathodes.

Chapter 6 Thin Film SOFC with GDC electrolyte

Figure 6-18 shows the total interfacial polarisation resistance ($R_a + R_c$) of the GDC electrolyte cells with different cathodes, including the BSCF cell developed in this study and those obtained from the literature. It is clear that the BSCF cell developed in this study displays much lower interfacial resistances than those with other cathode materials. For example, at 500°C, the total interfacial resistance is 5.1, 0.76, ~0.6, 0.55 and 0.26 Ωcm^2 for the SOFCs with LSCF-GDC (Leng et al., 2004), SSC-GDC (Xia and Liu, 2001b), ANLC-1 (Doshi et al., 1999), Ag-BICUVOX (Xia and Liu, 2002b) and BSCF cathodes, respectively. Considering that the anodes of the five cells are basically the same, and the fact that the anode/electrolyte interfacial polarisation resistance is negligible (Doshi et al., 1999; Xia and Liu, 2001b), the difference between the total interfacial polarisation resistance values of the five cells should be attributed to the use of different cathode materials. Among these five GDC-based cells, the cell with BSCF cathode developed in this study exhibits the lowest total interfacial polarisation resistance, which well explains the excellent cell performance shown in Figure 6-16.

6.5.4 Repeatability and durability test

To examine the performance repeatability, one more similar single cell with BSCF (denoted as Cell-B) cathode was tested under identical conditions. The previously presented BSCF cell is denoted as Cell-A. Figure 6-19 shows the i - V and corresponding i - P curves of Cell-B measured in the temperature range of 450-600°C. For comparison, the OCV and maximum power densities are summarized in Table 6-2. It can be seen from Table 6-2 that the OCVs repeat very well for the two cells with a very small relative error of 1.2% in the temperature range studied. This also indicates that the GDC electrolyte films prepared by the spray-copressing process are good and stable in quality. The maximum power densities of the two cells are also close with a maximum

Figure 6-19 *i*-V and corresponding *i*-P curves of Cell-B measured in the temperature range of 450-600°C.

error of 8.4% in the temperature range of investigation, showing an acceptable performance repeatability.

The observed performance results have demonstrated a very promising cathode material for low temperature SOFC. For industrial applications, however, long-term stability of the material needs to be seriously examined under operating conditions. Figure 6-20 shows the initial durability test of Cell-B for a period of 33 h. The cell was operated under a constant voltage of 0.6 V at 500°C. The test was interrupted for 2 times at 10 h and 21 h, respectively. During the first 10 h period, the current density decreases from 643 mA/cm² to 584 mA/cm². The performance degradation is about 9.2%. During the subsequent 11 h period, the cell performance shows some improvement. After the second interruption, the cell performance looks quite stable and the current density

Chapter 6 Thin Film SOFC with GDC electrolyte

keeps at around 610 mA/cm². As a whole, the cell demonstrates a good performance stability while much longer operation needs to be done.

Table 6-2 OCV and power densities of two BSCF cells.

Temperature (°C)		600	550	500	450
Cell-A	OCV (V)	0.903	0.948	0.984	1.013
	P _{max} (mW/cm ²)	1329	863	454	208
Cell-B	OCV (V)	0.892	0.952	0.988	1.022
	P _{max} (mW/cm ²)	1217	803	424	199
OCV error (%)		1.2	0.4	0.4	0.9
P _{max} error (%)		8.4	7.0	6.6	4.3

Figure 6-20 Durability test of Cell-B at 500°C under constant voltage of 0.6 V.

6.6 Summary

GDC films were successfully fabricated from ordinary non-porous powders on anode substrates by a simple, reproducible and cost-effective dry-pressing process. Dilatometric measurements were carried out to study the sintering behaviour of NiO-GDC anode substrate so as to provide insights for shrinkage matching with the GDC electrolyte film during cosintering. With the conventional dry-powder filling method, dense and crack-free electrolyte films of $\sim 45\text{ }\mu\text{m}$ in thickness were obtained after the green electrolyte/anode bilayers were co-sintered at 1300°C .

To further reduce the electrolyte film thickness, the effect of powder filling techniques on the quality of GDC electrolyte films was studied. A novel spray-copressing process, a combination of wet powder spray filling and dry pressing, has been developed. With this novel process, high quality GDC electrolyte films of $10\text{ }\mu\text{m}$ on porous anode support have been obtained successfully. Compared with the previous dry-pressing process developed by Xia and Liu (2001a), this spray-copressing process is rather flexible. There are no stringent requirements associated with characteristics of raw powders to be met for preparing dense ceramic films using this novel process.

Three single cells with different GDC electrolyte thickness and cathode material were assembled and tested using humidified hydrogen and air. The cell, consisting of a $45\text{-}\mu\text{m}$ -thick GDC electrolyte, a LSCF-GDC composite cathode and a Ni-GDC cermet anode, produced maximum power densities of 581, 377 and 120 mW/cm^2 at 650, 600, and 500°C , respectively. With the GDC electrolyte thickness reduced from $45\text{ }\mu\text{m}$ to $22\text{ }\mu\text{m}$ (the two cells had the same LSCF-GDC cathode and Ni-GDC anode), the power densities were greatly increased to 1004, 595 and 152 mW/cm^2 at 650, 600, and 500°C , respectively. Furthermore, with the incorporation of novel BSCF cathode, the single cell

Chapter 6 Thin Film SOFC with GDC electrolyte

with a 10 μm GDC electrolyte has generated encouraging and impressive power outputs, with peak power densities of 1329 and 454 mW/cm^2 obtained at 600 and 500°C, respectively. In addition, the BSCF cell demonstrates a good performance stability within an initial 33 h period of operation at 500°C. These performance characteristics represent a significant progress in the development of intermediate/low temperature SOFCs.

CHAPTER SEVEN

THIN FILM SOFC WITH YSZ/GDC BILAYER ELECTROLYTE

7.1 Introduction

By reducing the operating temperature of SOFCs from conventional $\sim 1000^{\circ}\text{C}$ to an intermediate temperature range of $500\sim 800^{\circ}\text{C}$, there are many benefits: low material degradation, high system reliability, long stack lifetime, short start-up time and significant reduction of materials and fabrication costs due to the potential utilisation of inexpensive and easily machinable metallic materials for the stack. Over the past few years, considerable efforts have been made to achieve these purposes (Srivastava et al., 1997; Choy et al., 1998; Hibino et al., 2002; Fukui et al., 2002; Chen et al., 2004). In a summary, three approaches have been adopted to lower the operating temperature of SOFCs, i.e., decreasing the electrolyte thickness, utilizing new electrolyte materials with high ionic conductivity at intermediate temperatures and reducing the electrode polarisation resistance. Due to its much higher ionic conductivity at intermediate temperatures compared with the conventional electrolyte material of yttria-stabilized zirconia (YSZ), doped ceria is regarded as one of the most promising electrolyte candidates for intermediate temperature SOFCs (Christie and Berkel, 1996; Steele, 2000; Mogensen et al., 2000; Ralph et al., 2001).

Many research groups have reported the development of intermediate-temperature SOFCs based on the thin film electrolyte of doped ceria, which was fabricated by using various processes such as multi-layer tape casting (Doshi et al., 1999), screen printing (Xia et al., 2001; Peng et al., 2002), dry pressing (Xia and Liu, 2001a), spray coating

Chapter 7 Thin Film SOFC with YSZ/GDC Bilayer Electrolyte

(Zheng et al., 1996; Leng et al., 2004), spin coating (Hibino et al., 2002), etc. Encouraging power densities have been achieved with ceria-based cells at temperatures below 650°C. However, doped ceria is prone to reduction at low oxygen partial pressures. The reduction of ceria from Ce^{4+} to Ce^{3+} will not only give rise to the electronic conduction resulting in a non-negligible loss in the open-circuit voltage (OCV) of the cell (Navarro et al., 1997; Shimonosono et al., 2004), it also brings on lattice expansion of the electrolyte at the fuel side, leading to mechanical stability problems of the cell or stack (Atkinson, 1997; Badwal et al., 1999; Hayashi et al., 2000). To overcome the OCV loss and improve the chemical stability of doped ceria electrolytes in reducing atmosphere, one of the approaches proposed is to coat doped ceria with a very thin YSZ film to form a bilayer electrolyte, where the YSZ film functions as an electronic blocking layer since YSZ is quite stable under reducing atmosphere conditions (Minh and Takahashi, 1995).

Since the ionic conductivity of YSZ is very low at intermediate temperatures, the thickness of YSZ film should be sufficiently small so as to minimise the contribution of the YSZ film to the overall resistance of the bilayer electrolyte. From a thermodynamic viewpoint, when the oxygen partial pressure across the ceria electrolyte is higher than that of the equilibrium of $\text{Ce}_2\text{O}_3/\text{CeO}_2$ redox reaction at a certain temperature, the ceria electrolyte should be chemically stable. Hence, the stability of bilayer electrolytes will be determined by the interfacial oxygen partial pressure between the YSZ film and the ceria substrate. Theoretical investigations have demonstrated that the interfacial oxygen partial pressure is determined by the thickness ratio of the two electrolyte layers and generally a YSZ film of a few μm in thickness should be good enough to prevent the ceria electrolyte from reduction and to avoid the OCV loss as a result of ceria reduction

Chapter 7 Thin Film SOFC with YSZ/GDC Bilayer Electrolyte

(Virkar, 1991; Chan et al., 2003; Marques and Navarro, 1997). Towards this end, many techniques, such as RF sputtering (Yahiro et al., 1988; Mehta et al., 1993), ion plating (Inoue et al., 1989; Eguchi et al., 1992), electrochemical vapor deposition (EVD) (Mehta et al., 1993), metal-organic vapor deposition (MOCVD) (Chour et al., 1997), and sol-gel coating (Mehta et al., 1998; Jang et al., 2002; Kim et al., 2002), have been employed to deposit such a YSZ thin film on the doped-ceria electrolyte.

By reviewing those experimental studies on YSZ/doped ceria bilayer electrolytes reported in the literature, four aspects can be summarized. Firstly, all the studies were associated with YSZ thin film deposited on a relatively thick substrate of doped ceria (0.4-2mm). Secondly, the bilayer electrolytes exhibited an improvement in OCV compared with uncoated doped ceria electrolyte, demonstrating that YSZ deposition is practically effective in suppressing the electronic conduction. However, the improved OCVs seem not to be so fantastic as they still exhibit an obvious deviation from the theoretical electro-motive forces (EMF) except for the bilayer electrolytes with the YSZ film deposited by the ion plating method (Inoue et al., 1989; Eguchi et al., 1992). Thirdly, the fact that the bilayer electrolyte with 1.86 μm YSZ deposited by the ion plating technique on 1.825 mm samaria-doped ceria (SDC) substrate demonstrated an OCV of 1.08 V at 800°C in H_2/O_2 atmospheres, which is quite close to the theoretical EMF, does indicate that the OCV loss for doped ceria electrolyte can be satisfactorily avoided by introducing a YSZ thin film with good quality. Fourthly, all the above methods used for YSZ film deposition involve either costly equipment (such as ion plating and RF sputtering) or complicated processes (such as sol-gel coating).

In view of these aspects, a wet ceramic process combined with co-sintering was selected to fabricate the thin film of YSZ/GDC bilayer electrolyte in this study because

Chapter 7 Thin Film SOFC with YSZ/GDC Bilayer Electrolyte

it is a very simple method and does not require any expensive equipment. With this powder-based wet ceramic process, 10 μm bilayer electrolyte thin films consisting of 3 μm of YSZ and 7 μm of GDC have been successfully obtained after cosintering although Horita et al. (1997) and Nguyen et al. (2004) reported that it was difficult to prepare similar bilayer electrolyte using cosintering process. Based on the high-quality thin film YSZ/GDC bilayer electrolyte supported on Ni-YSZ cermet anode substrate, single cells were assembled with the optimised LSCF-GDC composite as cathode and tested in H_2/air atmospheres. The effect of the use of pore-formers in the anode substrate on the preparation of YSZ film, cell microstructure and cell performance was also investigated.

7.2 YSZ/GDC bilayer electrolyte cell without additional anode porosity created by pore-formers

7.2.1 Microstructure of electrolyte thin films

Single cells were first assembled with electrolyte film supported on the anode substrate in which no pore-formers were used to create additional pores. Figure 7-1a and b show the cross-sectional morphologies of the anode substrate before and after the reduction. After sintering at 1400°C for 2 h, the obtained NiO-YSZ substrate (ca. 18.8 mm diameter, ca. 0.8 mm thick) was fully densified before reduction. After reduction, however, the substrate became porous because of the volume shrinkage of NiO particles by reduction. The porosity of the reduced substrate was measured to be 17.4%.

To well serve as an electronic blocking layer, the YSZ film is required to be dense and crack-free, thus avoiding the exposure of the GDC layer to the fuel. At the same time, the YSZ film should be deposited as thinly as possible to minimise the ohmic resistance. Therefore, before the YSZ/GDC bilayer electrolyte film was prepared,

Chapter 7 Thin Film SOFC with YSZ/GDC Bilayer Electrolyte

attempts were made to deposit a thin monolayer YSZ film onto the anode substrate by colloid coating method. After a number of trials, YSZ films with good quality and ca. 3 μm thick were successfully deposited onto the anode substrate after co-sintering. Figure 7-1c and d shows the surface and cross-sectional SEM images of a YSZ film on a Ni-YSZ cermet substrate (the anode substrate has been reduced). It is clearly seen that the YSZ film is fully dense and there are no cracks or pin-holes in the film. The YSZ film is ca. 3 μm in thickness, and appears to be well bonded to the porous anode substrate. On this basis, the deposition of YSZ/GDC bilayer electrolyte films was tried out using the same wet ceramic process and cosintering parameters. Figure 7-1 e and f show the surface and cross-sectional micrographs of a YSZ/GDC bilayer electrolyte film on the anode substrate. It can be seen that the total thickness of the bilayer electrolyte film is about 10 μm , consisting of a 3 μm YSZ layer and a 7 μm GDC layer. In spite of the presence of GDC layer on the top, the YSZ layer seems to be fully dense and well adhered to the anode substrate after cosintering, as in the case of the monolayer YSZ film. The GDC layer is also highly dense with a porosity of $5.6 \pm 0.8\%$ estimated by quantitative microscopy. Except for some micro-pores at the interface, an excellent bonding has been formed between the two electrolyte layers by the cosintering process. After electrochemical testing in the fuel cell mode, there are no cracks observed on the YSZ/GDC bilayer film, indicating that the thermal expansion coefficients (TEC) of the two electrolyte layers and the anode substrate match well although many references have reported a difference in the TEC between YSZ and doped ceria materials (Inoue et al., 1989; Kharton et al., 2004).

Chapter 7 Thin Film SOFC with YSZ/GDC Bilayer Electrolyte

Figure 7-1 SEM micrographs of the cross-section of a dense NiO-YSZ anode substrate (a) before and (b) after reduction, (c) surface and (d) cross-section of a YSZ film on a reduced anode substrate, and (e) surface and (f) cross-section of a YSZ/GDC bilayer electrolyte film on a reduced anode substrate.

7.2.2 Open circuit voltages of the cell

With quality YSZ/GDC bilayer electrolyte film, single cells were assembled using the optimised LSCF-GDC (50:50 by weight) composite material as the cathode and electrochemically tested in humidified hydrogen (3% H₂O)/air atmospheres. Figure 7-2 shows the open circuit voltages (OCVs) of a YSZ/GDC bilayer electrolyte cell measured in the temperature range of 500-800°C. For the sake of comparison, Figure 7-2 also shows the theoretical OCVs and the measured OCVs for a GDC and a YSZ monolayer electrolyte cell. As can be seen from Figure 7-2, compared with the GDC monolayer electrolyte cell, the YSZ/GDC bilayer electrolyte cell displays greatly increased OCVs, which are almost the same as those for the pure YSZ electrolyte cell. This indicates that the YSZ thin film of 3 μm prepared by the colloid coating and cosintering process has successfully prevented the GDC electrolyte from exposure to the gaseous hydrogen and thus protecting the GDC layer from reduction. Also, the OCV

Figure 7-2 Theoretical OCV and measured OCV vs. temperature for single cells with a 10 μm GDC mono-layer electrolyte, a 10 μm YSZ mono-layer electrolyte and a 3 μm YSZ/7 μm GDC bilayer electrolyte, respectively.

Chapter 7 Thin Film SOFC with YSZ/GDC Bilayer Electrolyte

enhancement becomes larger at higher temperatures. This is due to the increased reducibility or electronic transference number of ceria materials with the increase of temperature under reducing conditions (Kharton et al., 2001; Park and Choi, 2004). The measured OCVs of the YSZ/GDC bilayer electrolyte cell and the pure YSZ electrolyte cell are very close to the corresponding theoretical values. The slight difference observed may be due to instrumental errors such as the inaccuracy of temperature control of the test station furnace or the water bubbler for hydrogen humidification.

Table 7-1 summarises the OCVs for fuel cells based on YSZ/doped-ceria bilayer electrolyte measured in this study and reported in the literature. From Table 7-1, it can be seen that all the bilayer electrolytes reported in the literature had a thick doped-ceria substrate (0.4-3 mm). Also, in terms of the OCV, only the bilayer electrolytes fabricated by RF ion plating method were satisfactory in suppressing the electronic conduction in the doped-ceria electrolyte. It should be highlighted that the anode-supported thin film bilayer electrolytes with YSZ film as an electronic blocking layer were successfully prepared for the first time in this study using a simple and cost-effective wet ceramic co-sintering process.

7.2.3 Cell performance and polarisation analysis

Figure 7-3 shows the current-voltage and current-power density characteristics of the YSZ/GDC bilayer electrolyte cell measured between 700 and 800°C. The obtained maximum power densities are 409, 570 and 678 mW/cm² at 700, 750 and 800°C, respectively. These power outputs are much lower than those for thin film GDC electrolyte cells or thin film YSZ electrolyte cells obtained in this study or reported in the literature (Zha et al., 2004; Kim et al., 1999; Yamahara et al., 2005). It is noticeable

Table 7-1 Comparison of OCVs for SOFCs with YSZ/doped ceria bilayer electrolyte obtained in this study and from references.

Electrolyte composition	Thickness ratio	OCV (V)			Film deposition method	Cell structure	Reference
		600°C	700°C	800°C			
YSZ/GDC	3 μm /7 μm	1.107	1.081	1.049	Wet ceramic cosintering process	H ₂ , Ni-YSZ YSZ/GDC LSCF-GDC, air	This study
YSZ/YDC	1 μm /1.5mm	0.95	0.89	---	RF sputtering	H ₂ , Pt YSZ/YDC Pt, O ₂	Yahiro et al., 1988
YSZ/SDC	1.86 μm /1.825mm	---	---	1.08	RF ion plating	H ₂ , Pt YSZ/SDC Pt, O ₂	Inoue et al., 1989
YSZ/SDC	2 μm /0.658mm	---	---	1.05	RF ion plating	H ₂ , Ni-YSZ YSZ/SDC LSM, O ₂	Eguchi et al., 1992
YSZ/GDC	2 μm /1 mm	0.88	0.80	0.75	RF sputtering	O ₂ , Pt YSZ/GDC Pt, H ₂	Mehta et al., 1993
YSZ/YDC	3~3.5 μm /1 mm	0.93	0.88	0.84	EVD+RF sputtering	O ₂ , Pt YSZ/YDC Pt, H ₂	Mehta et al., 1993
YSZ/YDC	1.2~2 μm /---	---	0.85	0.79	MOCVD	O ₂ , Pt YSZ/YDC Pt, H ₂	Chour et al., 1997
YSZ/YDC	0.3 μm /---	0.85	0.79	0.73	Sol-gel spin coating	H ₂ , Pt YSZ/YDC Pt, O ₂	Mehta et al., 1998
YSZ/YDC	2 μm /1.6mm	---	0.92	0.85	Sol-gel spin coating	H ₂ , Pt YSZ/YDC Pt, O ₂	Kim et al., 2002
YSZ/GDC	2 μm /0.44mm	0.725 (900°C)			Sol-gel dip coating	H ₂ , Pt YSZ/GDC Pt, O ₂	Jang et al., 2002

Figure 7-3 (a) Cell voltage and (b) power density as a function of current density of a YSZ/GDC bilayer electrolyte cell measured between 700 and 800°C.

Chapter 7 Thin Film SOFC with YSZ/GDC Bilayer Electrolyte

that the current vs. voltage curves exhibit a much steeper drop in the cell voltage at high current densities. This is a typical diffusion polarisation behaviour, suggesting that the cell underwent a severe mass transport limitation at high current densities. Generally, the maximum power density is reached at cell voltage of around 0.45 V. However, the cell voltage starts to drop drastically with increasing current density from about 0.6 V at 800°C and from 0.5 V at 750°C. This implies that the maximum power density at 800°C has been remarkably restricted by the mass transport limitation, whereas it has not been affected so much at lower temperatures.

Mass transport limitations can arise from surface diffusion, gas diffusion, or dissociative adsorption steps (Mizusaki et al., 1987). It should be noted, however, that the limiting current does not seem to increase obviously with increasing temperature, as shown in Figure 7-3a. This suggests that the mass transport limitation is due to the gas diffusion through the electrodes of the cell, since the other two mechanisms are temperature-activated processes which should have strong temperature dependence (Mizusaki et al., 1987). The limiting current incurred by gas diffusion limitations would increase with increasing porosity and pore size in the electrodes.

To get power outputs from a fuel cell, two gaseous reactants are generally supplied. In this study, humidified hydrogen was used as the fuel and air as the oxidant. To verify if the gas diffusion limitation was incurred by hydrogen or air, the effects of air and hydrogen flow rate on the polarisation behavior of the cell were examined at 800°C. The results are shown in Figure 7-4a and b. It can be clearly seen that the limiting current increases with the increase of hydrogen flow rate and does not change with the increase of airflow rate, implying that the observed diffusion polarisation was due to hydrogen transport limitations in the anode. The fact that the limiting current decreases with

Chapter 7 Thin Film SOFC with YSZ/GDC Bilayer Electrolyte

Figure 7-4 Effects of (a) air and (b) hydrogen flow rates and (c) hydrogen concentration on the polarisation behaviour of the YSZ/GDC bilayer electrolyte cell without additional anode porosity created by pore-formers.

Chapter 7 Thin Film SOFC with YSZ/GDC Bilayer Electrolyte

decreasing hydrogen concentration in the fuel gas, as shown in Figure 7-4c, further confirms that hydrogen transport limitations in the anode substrate is the cause of the limiting current behaviour in Figure 7-3a. The anode substrate after reduction (as in Figure 7-1b) had a low porosity of 17.4% and a relatively large thickness of 0.8 mm, which accounts for the hydrogen transport limitation and the resulting diffusion polarisation.

To overcome the diffusion polarisation caused by limited hydrogen supply, a reduction of anode substrate thickness (Visco et al., 1999; Herle et al., 2000) and/or the use of pore-formers to increase the porosity and pore size in the anode substrate (Jiang et al., 2001; Haslam et al., 2005) can be adopted. Considering that the substrate should be strong enough to withstand the weight of the vertical sample holder, polyvinyl butyral (PVB) particles were used as the pore-former in this study to increase the porosity in the anode substrate.

7.3 Bilayer electrolyte cell with additional anode porosity created by pore-formers

7.3.1 Effect of pore-former addition in the anode substrate on the microstructure of the cell

Figure 7-5 a and b show the SEM micrographs of the anode substrate added with pore-formers before and after the reduction in hydrogen atmosphere. After burn-out of the pore-formers added in the anode substrate, the substrate became highly porous with an average pore size of $\sim 12\ \mu\text{m}$. The porosity of the anode substrate was measured to be 30.2% before the reduction. After the reduction, the porosity increased to 43.6%. Under low magnification, the morphology of the anode substrate appears to be similar before

Chapter 7 Thin Film SOFC with YSZ/GDC Bilayer Electrolyte

and after the reduction. Under high magnification (Figure 7-5c), however, two sets of pore size can be observed in the reduced anode substrate. The large pores were formed by the pore-former and the fine pores were created by the reduction of NiO particles. With much increased porosity by use of pore-formers and a reasonable combination of large and fine pores after reduction, the transport of hydrogen in the anode substrate is expected to be enhanced greatly.

Initially, YSZ film was directly deposited onto the anode substrate after the pore-formers added were burned up. However, it was found very difficult to obtain a dense and uniform YSZ thin film on such an anode substrate after sintering. Figure 7-6 shows the defects observed in the YSZ film that was deposited directly onto the anode substrate with the pore-formers burned out. Many pits can be seen on the surface of YSZ film (Figure 7-6 a). Cross-sectional view shows the presence of large pores below the YSZ film (Figure 7-6 b). Part of YSZ film can be seen on the bottom of surface pits (Figure 7-6 c). In the presence of the cathode layer, broken areas of the YSZ film can be clearly seen (Figure 7-6 d and e). Figure 7-6 f shows a large pore under the YSZ film which reduces the contact area between the electrolyte and the electrode and hence increases the resistance for ion conduction through the electrolyte. All these defects on the YSZ film are due to the rough surface of the anode substrate, which was incurred by the pore-formers added. The burn-out of pore-formers leaves many pits on the surface of anode substrate, which influences the uniform spread of YSZ powders on the substrate surface during the deposition process. After sintering, YSZ films with pits and openings are obtained. A single cell based on such a YSZ film produced an OCV of 0.69 V in H₂/air atmospheres at 700°C, indicating that such YSZ films can not be used in YSZ/GDC bilayer electrolyte as an electronic blocking layer.

Chapter 7 Thin Film SOFC with YSZ/GDC Bilayer Electrolyte

Figure 7-5 SEM micrographs of the cross section of the anode substrate with the pore-formers burned out (a) before and (b) after reduction. (c) Local enlargement of (b).

Chapter 7 Thin Film SOFC with YSZ/GDC Bilayer Electrolyte

Figure 7-6 Defects on the YSZ film directly deposited onto the anode substrate with the pore-formers burned out.

Chapter 7 Thin Film SOFC with YSZ/GDC Bilayer Electrolyte

To achieve a uniform spread of YSZ powders on the anode substrate and improve the quality of YSZ film after sintering, the surface of the anode substrate has to be very flat and the large pits caused by the burn-out of pore-formers have to be eliminated. Therefore, an anode interlayer was introduced. In this study, the anode interlayer was prepared by copressing a small amount of anode powders with no addition of pore-formers onto a pre-pressed anode substrate added with pore-formers. Because it contained no pore-formers, the anode interlayer remained very flat even after burn-out of the pore-formers in the substrate. Based on such anode substrates with very flat surface layer, YSZ thin films and YSZ/GDC bilayer electrolyte films were successfully prepared. The morphologies of such YSZ and YSZ/GDC films seemed to be quite similar to those shown in Figure 7-1. Then, single cells were assembled with the optimised LSCF-GDC composite cathode and tested again. Figure 7-7 shows the multi-layer microstructure of such a single cell with YSZ/GDC bilayer electrolyte. It can be seen that under a low magnification (Figure 7-7a), the cell is divided into five distinctive layers: highly porous anode substrate with large pores created by pore-formers, anode interlayer of ca. 50 μm , electrolyte film of ca. 10 μm , cathode layer of ca. 50 μm and Pt current collector of ca. 15 μm . Under a high magnification (Figure 7-7b), it can be further observed that, the electrolyte film consists of two layers: 3 μm YSZ layer and 7 μm GDC layer. The microstructure of the bilayer electrolyte film appears to be the same as that shown in Figure 7-1f. The YSZ layer is fully dense and the GDC layer is highly dense but with some isolated pores. The two electrolyte layers are well bonded to each other after high temperature cosintering except for some pores at the interface between the two electrolyte layers.

Chapter 7 Thin Film SOFC with YSZ/GDC Bilayer Electrolyte

Figure 7-7 Cross-sectional SEM images under (a) low and (b) high magnification of a single cell with YSZ/GDC bilayer electrolyte film deposited onto an anode substrate with an anode interlayer.

7.3.2 Effect of pore-former addition in the anode substrate on the cell performance

The current-voltage and current-power density characteristics of the cell (as in Figure 7-7) are presented in Figure 7-8. In humidified H_2 /air atmospheres, the cell produced OCVs of 1.047, 1.085 and 1.102 V at 800, 700 and 600°C, respectively, which are almost the same as those shown in Figure 7-2 for the cell with an identical YSZ/GDC bilayer electrolyte but without pore-formers added in the anode substrate. This indicates that the bilayer electrolyte film of YSZ/GDC has been successfully fabricated by introducing an anode interlayer on the anode substrate with additional porosity created by the use of pore-formers. The peak power densities of the cell are 1321, 938, 539 and 153 mW/cm^2 at 800, 750, 700 and 600°C, respectively. These power outputs are much higher than those obtained at the same temperatures shown in Figure 7-3b for a similar bilayer electrolyte cell, but with no addition of pore-formers in the

Figure 7-8 Cell voltage (solid symbols) and power density (open symbols) as a function of current density of a YSZ/GDC bilayer electrolyte cell with additional porosity in the anode substrate created by pre-formers, measured between 600 and 800°C.

Chapter 7 Thin Film SOFC with YSZ/GDC Bilayer Electrolyte

anode substrate. Therefore, the addition of pore-formers in the anode substrate has significantly reduced the polarisation in the cell and enhanced the cell performance by increasing the porosity of the anode substrate and hence promoting the hydrogen transport to the reaction sites through the substrate.

It should be noted that the two-layered anode structure, consisting of a thick anode substrate with large pores and a thin anode interlayer with fine pores, is beneficial to minimise both diffusion and activation polarisation. The highly porous anode substrate facilitates rapid transport of fuel gas (e.g., H_2) to and product gas (e.g., H_2O) from the reaction sites so that the diffusion polarisation can be retarded. The anode interlayer with fine pores maximises the Ni/YSZ/gas three-phase boundary area so that the number of electrochemical reaction sites can be multiplied and the activation polarisation can be lowered.

7.3.3 Impedance spectra and polarisation analysis of the cell

From the measured OCVs of the YSZ/GDC bilayer electrolyte cell demonstrated above, it can be deduced that the electronic conduction in the GDC layer was almost completely blocked and the GDC layer exhibited a pure ion-conducting property as in air. Therefore, in terms of electrolyte resistance, the bilayer electrolyte composed of 3 μm YSZ and 7 μm GDC is equivalent to a single YSZ electrolyte of $\sim 6 \mu m$ based on the measured ionic conductivities of the YSZ and GDC using sintered pellets. To examine the influence of the YSZ/GDC interface in the bilayer electrolyte on the electrolyte resistance, impedance spectra of the bilayer electrolyte cell and a 6 μm YSZ electrolyte cell were measured under open-circuit condition. Figure 7-9 shows the measurements between 600 and 800°C. Generally, the high-frequency intercept of the impedance plot with the real axis represents the ohmic resistance of the cell. Considering the significant

Chapter 7 Thin Film SOFC with YSZ/GDC Bilayer Electrolyte

Figure 7-9 Impedance spectra for the YSZ (3 μm)/GDC (7 μm) bilayer electrolyte cell and a 6 μm YSZ electrolyte cell measured under open-circuit condition between 600 and 800°C.

Chapter 7 Thin Film SOFC with YSZ/GDC Bilayer Electrolyte

inductance effect due to the lead wires, the ohmic resistances were determined by fitting the measured impedance spectra to an equivalent circuit of $LR(RQ)(RQ)$ and plotted in Figure 7-10 as a function of temperature. From Figure 7-10, differences can be clearly seen between the ohmic resistances of the two cells within the temperature range under study. As mentioned earlier, the ohmic resistance of a fuel cell includes the electrolyte resistance, electrode ohmic resistance, contact resistance at electrode/electrolyte interfaces and contact resistance between electrodes and current collectors. Since the electrodes (Ni-YSZ cermet anode, LSCF-GDC composite cathode) and current collectors (Pt) in the two cells are the same in material composition and processing parameters, the ohmic resistance difference shown in Figure 7-10 should come from the YSZ/GDC interface in the bilayer electrolyte. Also, it is clear that the difference between the ohmic resistances of the two cells increases with decreasing temperature. This indicates that the ohmic resistance difference is not due to the interfacial contact

Figure 7-10 Ohmic resistances as a function of temperature for the YSZ (3 μ m)/GDC (7 μ m) bilayer electrolyte cell and a 6 μ m YSZ electrolyte cell measured under open-circuit condition between 600 and 800°C.

Chapter 7 Thin Film SOFC with YSZ/GDC Bilayer Electrolyte

between the YSZ and GDC layers since the contact resistance does not change obviously with temperature. Therefore, the higher ohmic resistances for the bilayer electrolyte cell are most likely a result of the formation of reaction products at the YSZ/GDC interface with lower electrical conductivity than both YSZ and GDC during the high temperature cosintering process.

One may argue that the porous GDC layer will affect the performance of the cell in addition to the conductivity of the bilayer electrolyte. The porosity of the GDC layer is estimated at about $5.6 \pm 0.8\%$ by quantitative microscopy. This level of porosity would affect the conductivity of the electrolyte to some extent, but will not obviously affect the ohmic resistance of the thin film electrolyte cell because the electrolyte resistance accounts for a minor portion. For example, the cell with a $6 \mu\text{m}$ YSZ electrolyte exhibits an ohmic resistance of $0.097 \Omega\text{cm}^2$ as shown in Figure 7-10. Based on the ionic conductivity of 0.032 S/cm of YSZ electrolyte at 800°C , the resistance of a $6 \mu\text{m}$ YSZ film is only $0.038 \Omega\text{cm}^2$, about 39% of the overall ohmic resistance of the cell. A major portion (61%) of the ohmic resistance of the cell is due to the contact resistance between the electrodes, electrolyte and current collectors. For the YSZ($3\mu\text{m}$) /GDC($7\mu\text{m}$) bilayer cell, the ohmic resistance is $0.181 \Omega\text{cm}^2$ at 800°C . The pure electrolyte resistance from the bilayer electrolyte film (not counting the interfacial reaction effect) is equivalent to that of $6 \mu\text{m}$ YSZ in terms of their respective ionic conductivities, i.e. $0.038 \Omega\text{cm}^2$ at 800°C . Thus the pure electrolyte resistance only accounts for 21% of the overall ohmic resistance of the bilayer electrolyte cell. Therefore, the conductivity change of the GDC layer due to a porosity of $5.6 \pm 0.8\%$ will have very minor effects on the performance of the bilayer electrolyte cell.

Chapter 7 Thin Film SOFC with YSZ/GDC Bilayer Electrolyte

Figure 7-11 shows the voltage vs. current density curves for the YSZ/GDC bilayer electrolyte cell measured at 800 and 700°C, where the total voltage drop is separated into ohmic (iR_{Ω}) and electrode ($\eta_a + \eta_c$) components. The ohmic drop due to the interface in the YSZ/GDC bilayer electrolyte is also indicated in Figure 7-11. It can be seen that at both 800 and 700°C, the ohmic drop dominates the total voltage drop of the cell. The portion of the ohmic drop due to the YSZ/GDC interface accounts for a relatively marked percentage. For example, at 800°C, the ohmic drop accounts for about 84% of the total voltage drop at cell voltage of 0.45 V, of which 36% comes from the YSZ/GDC interface, whereas the electrode polarisation only accounts for 16% of the total voltage drop. When the temperature is decreased to 700°C, at cell voltage of 0.45 V, the electrode polarisation contribution substantially increases to 34%, but still the ohmic drop plays a major role in the total voltage drop. The ohmic drop contribution due to the YSZ/GDC interface decreases from 36% at 800°C to 27% at 700°C due to increased electrode polarisation percentage in the total voltage drop. Therefore, to further enhance the cell performance, the ohmic resistance of the bilayer electrolyte cell has to be reduced. Since the present electrolyte film (10 μm) is already very thin, further reduction in the bilayer electrolyte thickness would not help a lot. Instead, cell performance would be further improved by reducing the ohmic resistance arisen from the interfacial reaction between YSZ and GDC layers during the co-sintering process.

7.3.4 Reaction or inter-diffusion between YSZ and GDC

To detect the compositional changes at the YSZ/GDC interface due to inter-diffusion, the bilayer electrolyte cell was embedded in an epoxy resin and polished very carefully to get a smooth cross section. Then, electron dispersive X-ray spectroscopy (EDX) line scan analysis was carried out across the cross section of the bilayer

Chapter 7 Thin Film SOFC with YSZ/GDC Bilayer Electrolyte

Figure 7-11 Voltage vs. current density curves for the YSZ/GDC bilayer electrolyte cell measured at 800 and 700°C, showing the separation of the voltage drop into ohmic (iR_{Ω}) and electrode ($\eta_a + \eta_c$) components. R_{Ω} values for iR_{Ω} calculation are given in Figure 7-10.

Figure 7-12 EDX line composition analysis of Zr and Ce across the YSZ/GDC bilayer electrolyte film. The arrow line and the vertical line indicate the analysis location and the YSZ/GDC interface, respectively.

electrolyte film. Figure 7-12 shows the compositional distributions of Ce and Zr across the YSZ/GDC electrolyte film. It can be seen that a diffusion region of ca. 4 μm in thickness was formed in the vicinity of the YSZ/GDC interface. And also, it is obvious that compositional curves for Zr and Ce are asymmetric with reference to the YSZ/GDC interface. A larger amount of the Ce component was detected in the YSZ side than the amount of the Zr component detected in the GDC side, indicating that the interfacial reaction between the YSZ and GDC layers was primarily caused by diffusion of the Ce

Chapter 7 Thin Film SOFC with YSZ/GDC Bilayer Electrolyte

component into the YSZ. This is in agreement with the findings reported by Eguchi et al. (2000). Horita et al. (1997) observed arrays of pores in the ceria side close to the interface in the tape-cast GDC/YSZ/GDC multilayer structures that were co-fired at 1550°C. They ascribed this phenomenon to Kirkendall effect, which is related to the difference of the diffusivity of Ce in YSZ and Zr in GDC. The compositional curves of Ce and Zr obtained in this study seem to well explain the above phenomenon. The present bilayer electrolyte cell also exhibits an array of pores at the GDC/YSZ interface (see Figure 7-7), but it cannot be confirmed that they were caused due to Kirkendall effect because the GDC layer also shows similar pores. Additionally, it is to be validated whether Kirkendall effect is strong enough to produce pores at the interface of GDC and YSZ layers after sintering at 1400°C for 2 h, which is significantly lower than 1550°C used by Horita et al. (1997).

In conclusion, some new phases, which are different from the YSZ and GDC, may have been formed due to inter-diffusion between the YSZ and GDC layers.

To further verify the interfacial reaction between the YSZ and GDC layers during high temperature co-sintering, X-ray diffraction (XRD) analysis was conducted on compacts of YSZ-GDC (1:1 by weight) mixture after heat treatment at 1400°C for 2 h, the same processing parameters as those for bilayer electrolyte co-sintering. The acquired XRD pattern is shown in Figure 7-13. The diffraction pattern for a green pellet, which is also included in Figure 7-13, is attributed to a mixture of two fluorite phases from YSZ and GDC with different lattice constants. After firing at 1400°C for 2 h, all the peaks from both YSZ and GDC phases disappear. Instead, the observed peaks represent a different single fluorite phase which has been formed due to the inter-diffusion between YSZ and GDC particles. This means that $\text{ZrO}_2\text{-YO}_{1.5}\text{-CeO}_2\text{-GdO}_{1.5}$ solid solutions can also be

Figure 7-13 XRD patterns for YSZ-GDC (1:1 by weight) mixture samples before and after heating at 1400°C for 2 h.

formed at the YSZ/GDC interface in the bilayer electrolyte during the co-sintering process.

As a result of interfacial diffusion, a series of GDC-YSZ solid solutions with different compositions may be formed near the interface in the bilayer electrolyte. To examine the ionic conductivity of these solid solutions, a series of GDC-YSZ powder mixture samples were sintered at 1400°C to form solid solutions with different compositions of GDC and YSZ. Figure 7-14 shows the ionic conductivity of $(\text{GDC})_x(\text{YSZ})_{1-x}$ system as a function of GDC fraction measured at 800°C in air. It is clear that the GDC-YSZ solid solutions have lower ionic conductivities than pure GDC or YSZ samples under ambient oxygen partial pressure, in good agreement with the observations reported by other researchers (Sammes and Cai, 1997; Huang et al., 2000;

Chapter 7 Thin Film SOFC with YSZ/GDC Bilayer Electrolyte

Eguchi et al., 2000). In particular, a minimum conductivity, i.e. 0.0024 S/cm, is reached for the solid solution with a GDC molar fraction of 0.6. Eguchi et al. observed a minimum conductivity of 0.0051 S/cm at 800°C in air for $\text{Y}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ - $\text{Y}_{0.15}\text{Zr}_{0.85}\text{O}_{1.925}$ (50:50 in mol.%) solid solution, whereas Zhou et al. (2004) measured a lower ionic conductivity of 0.0022 S/cm at 800°C in air for the solid solution of $(\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95})_x$ - $(\text{Y}_{0.16}\text{Zr}_{0.84}\text{O}_{1.92})_{1-x}$ with $x=0.75$ than that with $x=0.5$. Anyway, the present conductivity is one order of magnitude lower than that of YSZ (0.032 S/cm) and GDC (0.068 S/cm) at the same temperature. This result confirms that the solid-state reaction or inter-diffusion between YSZ and GDC phases significantly lower the electrical conductivity. This also well explains the greatly increased ohmic resistances for the bilayer electrolyte cell as presented in Figure 7-10.

As has been revealed above, the formation of solid solutions at the YSZ/GDC interface is not desirable because such solid solutions exhibit much lower ionic conductivities and will deteriorate the performance of SOFCs with YSZ/GDC bilayer

Figure 7-14 Ionic conductivity of $(\text{GDC})_x(\text{YSZ})_{1-x}$ system as a function of GDC fraction measured at 800°C in air.

Chapter 7 Thin Film SOFC with YSZ/GDC Bilayer Electrolyte

electrolyte. However, the formation of such solid solutions at the YSZ/GDC interface may be helpful in improving the mechanical stability of bilayer electrolyte cells which would otherwise be a serious problem due to the difference in the thermal expansion coefficient (TEC) between pure YSZ and GDC. It was reported that the TEC of $(\text{GDC})_x(\text{YSZ})_{1-x}$ system increases with increasing GDC fraction from that of pure YSZ ($\sim 10.7 \times 10^{-6} \text{ K}^{-1}$) to that of pure GDC ($\sim 13.2 \times 10^{-6} \text{ K}^{-1}$) (Zhou et al., 2004). This implies that the formation of solid solutions at the YSZ/GDC interface would create a functionally-graded layer between YSZ and GDC layers in terms of thermal expansion behavior, which helps to reduce the mechanical breakdown of YSZ/GDC bilayer electrolyte cells.

7.4 Summary

Thin films of YSZ(3 μm)/GDC(7 μm) bilayer electrolyte were fabricated on the anode substrate using a wet ceramic co-sintering process for the first time. Single cells based on the bilayer electrolyte film demonstrated the OCVs close to the theoretical ones, implying that the electronic conduction in the GDC electrolyte was successfully blocked by the YSZ film.

The bilayer electrolyte cell with the anode substrate free of pore-former-induced porosity exhibited severe diffusion polarisation due to limited mass transport in the thick and low-porosity anode substrate, which accounts for the measured relatively low peak power density, i.e., 409, 570 and 678 mW/cm^2 at 700, 750 and 800°C, respectively. To reduce the diffusion polarisation in the anode, pore-formers were used to increase the porosity. However, the large surface pits on the anode substrate caused by the burn-up of pore-formers made it difficult to achieve good quality YSZ films. By introducing an anode interlayer to the porous anode substrate, YSZ/GDC bilayer electrolyte films

Chapter 7 Thin Film SOFC with YSZ/GDC Bilayer Electrolyte

with good quality were successfully prepared. With enhanced porosity created by pore-formers, the diffusion polarisation in the thick anode substrate was greatly decreased and the bilayer electrolyte cell achieved significantly enhanced performance. Maximum power densities of 153, 539, 938 and 1321 mW/cm² were obtained at 600, 700, 750 and 800°C, respectively.

The polarisation analysis for the bilayer electrolyte cell with enhanced porosity in the substrate clearly reveals that the ohmic drop absolutely dominates the overall cell voltage loss. A substantial contribution to the ohmic drop has been attributed to the interfacial reaction between the YSZ and GDC layers during the co-sintering process. The conductivity measurements of YSZ-GDC mixtures show that the solid solutions formed between YSZ and GDC possess much lower ionic conductivities than either YSZ or GDC, which well explains the large ohmic resistances of the bilayer electrolyte cell. To further improve the power densities of the bilayer electrolyte cell, it is necessary to decrease the sintering temperature to minimize the YSZ/GDC interfacial reaction.

CHAPTER EIGHT

GENERAL DISCUSSION

The rate of the chemical reaction of the fuel and oxygen in a SOFC cell can be limited by many effects that show up as polarisation of the cell. Polarisation causes voltage drops within the cell that limit the output voltage of the fuel cell and consequently reduce the area-specific output power at a given current density. Three types of polarisation can be present in the fuel cell, i.e. charge transfer or activation polarisation, resistance or ohmic polarisation, and concentration or diffusion polarisation. Polarisation reduces the performance of the fuel cell. Moreover, polarisation increases with decrease of temperature. Therefore, to achieve high performance SOFCs operating at intermediate temperatures, all these types of polarisation have to be minimised.

8.1 Minimisation of ohmic polarisation

Ohmic polarisation occurs because of the ohmic resistance of the cell, which includes resistance to the ionic transport through the electrolyte, resistance to the flow of electrons through the electrodes (both cathode and anode) and contact resistance between the electrolyte and the electrodes. Ohmic polarisation is proportional to the ohmic resistance and expressed as a product of current and ohmic resistance. Thus, minimising ohmic polarisation means minimising ohmic resistance. In electrolyte-supported SOFCs, the electrolyte resistance, i.e. the resistance to the ionic transport through the electrolyte, dominates the ohmic resistance of the cell. Therefore, to reduce the ohmic resistance of the cell, reduction of the electrolyte resistance should be

considered in the first place. In this study, electrolyte resistance was minimised by choosing superior electrolyte material, controlling electrolyte processing parameters and preparing anode-supported thin film electrolyte.

Gadolinia-doped ceria (GDC) was used as the raw material for the electrolyte since it has much better ionic conductivity than the conventional yttria-stabilised zirconia (YSZ) at intermediate temperatures. To achieve a high-conductivity GDC electrolyte, the effects of starting powder characteristics and processing conditions (including compaction pressure and sintering temperature) on the densification behaviour and the electrical property of GDC electrolytes were investigated, which are presented in Chapter 4. It was found that high density and small grain size are of great importance for a high-conductivity GDC electrolyte. For GDC electrolytes densely sintered at temperatures below 1400°C, the grains are small with an average grain size of <1µm and the ionic conductivity shows no obvious difference. When the sintering temperature increases to 1500°C, the ionic conductivity of the electrolyte is deteriorated significantly due to decreased grain boundary conductivity. Therefore, the sintering temperature of the electrolyte must be controlled below 1400°C with the present GDC powder to ensure a high-conductivity electrolyte.

Another effective approach to the reduction of electrolyte resistance is to prepare supported thin film electrolyte. GDC electrolyte films were successfully fabricated on the anode substrate after cosintering at 1300°C. The cell consisting of a 45 µm GDC electrolyte, LSCF-GDC composite cathode and Ni-GDC cermet anode produced maximum power densities of 581, 377, 227 and 120 mW/cm² at 650, 600, 550 and 500°C, respectively. The polarisation analysis illustrated in Figure 6-10 clearly indicates that the cell performance at temperatures above 550°C is dominated by the ohmic

polarisation (iR_{Ω}), whereas at temperatures below 550°C the electrode polarisation (including cathode polarisation and anode polarisation) ($\eta_c + \eta_a$) dominates the total cell polarisation. This means that further improvement of the cell performance should be based mainly on the reduction of the ohmic polarisation and of the electrode polarisation for temperatures above and below 550°C, respectively. This has been confirmed by the performance measurements of the cell with a 22 μm GDC electrolyte. With the electrolyte film reduced from 45 μm to 22 μm , the maximum power densities were greatly increased to 1004, 595, 316, 152 mW/cm^2 at 650, 600, 550 and 500°C, respectively. Accordingly, the corresponding increase in maximum power density is estimated to be 72.8% (650°C), 57.8% (600°C), 39.2% (550°C) and 26.7% (500°C). Obviously, the increase in maximum power density drops rapidly with decreasing operating temperature. The increase in maximum power density achieved at temperatures above 550°C is much larger than that below 550°C.

8.2 Minimisation of activation polarisation

Activation polarisation is generally due to one or more slow rate-determining steps in the electrode reaction. The slow step could be related to adsorption of reactant onto the surface of the electrode, electron transfer, desorption of product, or any other step in the reaction. When a fuel cell is in operation, two types of electrode reactions are involved, i.e., oxygen reduction reaction on the cathode and hydrogen oxidation reaction on the anode. To minimise the activation polarisation of the fuel cell, both cathode polarisation and anode polarisation should be reduced. Nickel was used as the anode material in this study because of its high catalytic activity for hydrogen oxidation reaction (Jiang et al., 2000a). To further promote the hydrogen oxidation reaction and

Chapter 8 General Discussion

reduce the anode polarisation, certain amount of GDC or YSZ was added to nickel to form a cermet anode in which the reaction region is extended from the interface of the electrolyte and the electrode. Considering that ohmic polarisation and cathode polarisation are often the main factors that limit the cell performance, the electrochemical performance of the Ni-based cermet anode was not investigated and optimised specially in this study. Therefore, the minimisation of activation polarisation of the cells in this study was based mainly on the enhancement of cathode performance.

(La,Sr)(Co,Fe)O₃ (LSCF) was chosen as the cathode material for the intermediate temperature SOFCs developed in this study. As a mixed ionic-electronic conducting material, LSCF shows much lower polarisation resistance for oxygen reduction reaction than the conventional (La,Sr)MnO₃ (LSM) material (Adler et al., 1996). To optimise the cathode performance, the effects of sintering temperature and GDC addition on the electrochemical properties of LSCF cathodes on GDC electrolytes were investigated, which are presented in Chapter 5. After sintering at 900°C for 2 h, the LSCF cathode produced an optimal polarisation resistance of 2.54 Ωcm² at 600°C. Although LSCF is a mixed ionic-electronic conductor with high electronic and appreciable ionic conductivity, its ionic conductivity is much lower compared with GDC material. Consequently, the electrochemical performance of LSCF cathode has been greatly enhanced by addition of GDC. The LSCF cathode added with 50 wt.% GDC generated the lowest polarisation resistance, e.g., 0.26 Ωcm² at 600°C, a reduction by a factor of 9 compared with the pure LSCF cathode. With this optimum LSCF-GDC composite as the cathode, the cell based on a 22 μm GDC electrolyte demonstrated encouraging power outputs in the temperature range of 500-650°C. As mentioned earlier, compared with the cell based on a 45 μm GDC electrolyte, the increase in maximum power

density is estimated to be 72.8% at 650°C and 26.7% at 500°C. Obviously, the increase in maximum power density achieved at 650°C is much higher than that at 500°C. This is because the cathode polarisation makes more and more contributions to the total cell polarisation as the temperature decreases. When the temperature decreases to below 550°C, the cathode polarisation dominates the cell performance (see Figure 6-10). Therefore, to further improve the cell performance at around 500°C, although a reduced electrolyte film thickness is still useful, it is more important to improve the cathode performance or develop alternative cathode materials with lower polarisation resistance.

With the incorporation of novel (Ba,Sr)(Co,Fe)O₃ (BSCF) cathode, the single cell with a 10 µm GDC electrolyte has generated impressive power outputs. The measured maximum power densities were 1329, 863 and 454 mW/cm² at 600, 550 and 500°C, respectively. Compared with the 22 µm GDC electrolyte cell with LSCF-GDC cathode, the increase in maximum power density is estimated to be 123.4% (600°C), 173.1% (550°C) and 198.7% (500°C). It is clear that the increase in maximum power density achieved with the BSCF cell at 600°C is much lower than that at 500°C. This reflects the relative importance of cathode performance enhancement in improving the cell performance at lower temperatures.

8.3 Minimisation of diffusion polarisation

Diffusion polarisation appears when the electrode reaction is hindered by mass transport limitations, i.e., when the feeding velocity of the reactant and/or the removing velocity of the reaction product from the electrode is slower than that corresponding to the discharge current. In SOFCs, the reactants must diffuse through the porous anode and cathode, so the electrode structure (including porosity and pore size) is important.

Compared with electrolyte-supported SOFCs, electrode-supported SOFCs are more likely to suffer diffusion polarisation because hydrogen must transport through a thick anode substrate, or oxygen must transport through a thick cathode substrate. Therefore, the structure of the electrode substrate is very crucial in an electrode-supported SOFC. In this study, organic pore-formers were added to the anode substrate to increase the porosity and enhance the diffusion of hydrogen, thus reducing the diffusion polarisation.

As shown in Figure 7-3a, the i -V curves of the cell demonstrate a typical diffusion polarisation behaviour, characterized by a much steeper voltage drop at high current densities than at low to medium ones. Due to the severe diffusion polarisation which remarkably restricted the cell performance, the cell produced low and relatively close power outputs at different temperatures. The maximum power densities of the cell are 409, 570 and 678 mW/cm² at 700, 750 and 800°C, respectively. The tests on the effects of air and hydrogen flow rates and hydrogen concentration in the fuel gas diluted with nitrogen on the polarisation behaviour of the cell confirmed that the observed diffusion polarisation was due to the hydrogen transport limitation in the anode substrate. To overcome the diffusion polarisation caused by limited hydrogen supply, pore-formers were added to the anode substrate to increase the porosity and promote the hydrogen diffusion through the anode substrate. As a result, the diffusion polarisation in the anode substrate was greatly decreased and the bilayer electrolyte cell achieved significantly enhanced performance, with maximum power densities of 539, 938 and 1321 mW/cm² obtained at 700, 750 and 800°C, respectively.

CHAPTER NINE

CONCLUSIONS AND RECOMMENDATIONS

9.1 Conclusions

The objective of this research is to investigate and develop high performance intermediate temperature SOFCs based on GDC electrolyte material. To this end, the sintering behaviour and the ionic conductivity of GDC electrolytes were first studied. Then the electrochemical properties of LSCF and LSCF-GDC cathodes on dense GDC electrolytes were investigated. Finally, considerable efforts were made to fabricate and characterise GDC-based thin film SOFCs (including GDC electrolyte SOFCs and YSZ/GDC bilayer electrolyte SOFCs). In this work, the following concluding remarks are made:

1. The calcination of the as-received nanosized GDC powder at 750°C for 2 h significantly changed the powder characteristics by reducing the specific surface area from 157.8 m²/g to 23.4 m²/g and diminishing the particle agglomeration. Sintering investigations revealed that the sinterability of raw powders was improved by the calcination. Sintering temperature and the compaction pressure for green pellet preparation have a great effect on the relative density of sintered electrolytes. With a high compaction pressure, dense GDC electrolytes can be obtained at a relatively low sintering temperature.
2. The ionic conductivity measurements were correlated with the microstructural characteristics (such as porosity and grain size) of the GDC electrolytes. It was found that the grain interior conductivity is predominantly related to the relative

Chapter 9 Conclusions and Recommendations

density and insensitive to the grain size of the electrolyte, whereas the grain boundary conductivity is strongly related to both the relative density and the grain size of the electrolyte. Microstructures with high density and small grain size are of great significance for a high-conductivity GDC electrolyte.

3. The electrochemical impedance spectroscopy revealed that sintering conditions have a significant influence on the electrochemical properties of LSCF cathodes. SEM observations showed that the microstructure adequately explains the difference in the cathode performance due to different sintering temperature. Appropriate sintering temperature can provide fine grain size, large surface area, proper porosity, good connections between cathode particles and good adhesion between cathode and electrolyte, thus leading to an optimal electrochemical reaction activity. After sintering at 900°C for 2 h, pure LSCF cathode produced the lowest polarisation resistance of 2.54 Ωcm^2 at 600°C.
4. The addition of GDC phase to LSCF cathode on GDC electrolyte substantially improved the electrochemical properties. A reduction by a factor of 9 in the polarisation resistance was achieved as a result of adding 50 wt.% GDC to LSCF. The significant enhancement in the electrochemical properties of LSCF-GDC composite cathodes indicates that the triple phase boundary (TPB) has a great contribution to the electrochemical performance of LSCF-GDC composite cathodes.
5. GDC electrolyte films of 45 μm in thickness were successfully fabricated from non-porous raw powders on porous anode substrates by a simple, cost-effective dry-pressing process. A proper match between the sintering behaviors of GDC films and NiO-GDC anode substrates is important to obtain high quality electrolyte/anode bilayers after co-sintering.

Chapter 9 Conclusions and Recommendations

6. Powder filling techniques have great effects on the quality of GDC electrolyte films.

A novel spray-copressing process, a combination of wet-powder spray filling and dry pressing, has been developed. With this process, dense and crack-free GDC films of 10 μm have been successfully obtained. This spray-copressing process is rather flexible. No stringent requirements associated with raw powder characteristics should be met for preparing dense ceramic films using this novel process.

7. With humidified hydrogen as the fuel and air as the oxidant, high performance was demonstrated by thin film GDC electrolyte SOFCs in the temperature range of 500-650°C. A single cell, consisting of 45- μm -thick GDC electrolyte, LSCF-GDC composite cathode and Ni-GDC cermet anode, produced maximum power densities of 581, 377, 227 and 120 mW/cm^2 at 650, 600, 550 and 500°C, respectively. With the GDC electrolyte thickness reduced from 45 μm to 22 μm , the maximum power densities were greatly increased to 1004, 595, 316 and 152 mW/cm^2 at 650, 600, 550 and 500°C, respectively. Furthermore, with the incorporation of novel BSCF cathode, the single cell with a 10 μm GDC electrolyte has generated encouraging and impressive power outputs, with peak power densities of 1329, 863 and 454 mW/cm^2 obtained at 600, 550 and 500°C, respectively. These performance characteristics represent a quantum leap in the development of intermediate temperature SOFCs.
8. Thin films of YSZ(3 μm)/GDC(7 μm) bilayer electrolyte were fabricated on the anode substrate using a wet ceramic co-sintering process for the first time. Single cells based on the bilayer electrolyte film demonstrated the OCVs close to the theoretical ones, implying that the electronic conduction in the GDC electrolyte was successfully blocked by the YSZ film.

Chapter 9 Conclusions and Recommendations

9. The YSZ/GDC bilayer electrolyte cell with the anode substrate free of pore-former-induced porosity exhibited severe diffusion polarisation due to limited mass transport in the thick and low-porosity anode substrate, which accounts for the relatively low peak power density, i.e. 409, 570 and 678 mW/cm² at 700, 750 and 800°C, respectively. To reduce the diffusion polarisation in the anode, pore-formers were used to increase the porosity. However, the large surface pits on the anode substrate caused by the burn-up of pore-formers made it difficult to achieve good quality YSZ films. By introducing an anode interlayer to the porous anode substrate, YSZ/GDC bilayer electrolyte films were successfully prepared. With increased porosity created by pore-formers, the diffusion polarisation in the thick anode substrate was greatly decreased and the bilayer electrolyte cell achieved significantly enhanced performance. Maximum power densities of 153, 539, 938 and 1321 mW/cm² were obtained at 600, 700, 750 and 800°C, respectively.
10. The polarisation analysis on the YSZ/GDC bilayer electrolyte cell with enhanced porosity in the anode substrate clearly reveals that the ohmic drop absolutely dominates the overall cell voltage loss. A substantial contribution to the ohmic drop has been attributed to the interfacial reaction between the YSZ and GDC layers. The conductivity measurements of YSZ-GDC mixtures show that the solid solutions formed between YSZ and GDC possess much lower ionic conductivities than either YSZ or GDC, which well explains the large ohmic resistances of the bilayer electrolyte cell. To reduce the ohmic resistance, the co-sintering temperature should be decreased to lessen the interfacial reaction between the YSZ and GDC layers.

9.2 Contributions and achievements

Major contributions and achievements made in the project are summarized below:

1. A novel spray-copressing process has been developed. With this process, dense and crack-free GDC films of 10 μm have been successfully obtained. This spray-copressing process is rather flexible. No stringent requirements associated with raw powder characteristics should be met for preparing dense ceramic films using this novel process.
2. The incorporation of novel BSCF cathode into GDC-based thin film SOFCs has generated encouraging and impressive power outputs at reduced temperatures. Peak power densities of 1329, 863 and 454 mW/cm^2 are obtained at 600, 550 and 500°C, respectively. These performance characteristics represent a quantum leap in the development of intermediate temperature SOFCs.
3. Thin films of YSZ(3 μm)/GDC(7 μm) bilayer electrolyte have been fabricated on the anode substrate using a wet ceramic co-sintering process for the first time. The OCVs observed for the bilayer electrolyte cell are very close to the theoretical ones, implying that the electronic conduction in the GDC electrolyte is successfully blocked by the YSZ film.
4. The interfacial reaction between YSZ and GDC as well as its effect on the cell performance has been studied in detail based on polarization analysis, conductivity measurement, phase structure identification and elemental distribution examination. These analyses indicate that a substantial contribution to the ohmic drop of the bilayer electrolyte cell is attributed to the interfacial reaction between the YSZ and GDC layers.

9.3 Recommendations for future work

1. It was reported that $\text{Gd}_{0.1}\text{Ce}_{0.9}\text{O}_{1.95}$ electrolytes can reach an ionic conductivity of 0.0095 S/cm at 500°C (Steele, 2000). However, much lower ionic conductivity was obtained for the GDC electrolyte prepared in this research, e.g. 0.0053 S/cm at 500°C. The great difference may be due to the silica impurity present in the raw powder. To analyse the silicon level in the raw powder, inductively coupled plasma (ICP) technique can be used.
2. The BSCF cathode showed much larger grains than the Ni-GDC anode although the former was sintered at 950°C while the latter at 1300°C. To improve the cathode performance, it is necessary to optimise the processing conditions and microstructure of the BSCF cathode. In addition, it is of significance to investigate the electrochemical properties of BSCF-GDC composite cathode.
3. Due to the excellent performance of BSCF cathode at low temperatures, the fuel cell with BSCF cathode has demonstrated impressive and encouraging power outputs. Therefore, it is important to understand the mechanisms of oxygen reduction reaction occurring on the BSCF electrode. Moreover, more examinations are necessary on the long-term stability of the BSCF cathode for potential industrial applications.
4. The cell with YSZ/GDC bilayer electrolyte showed much increased ohmic resistance due to the interaction between the YSZ and GDC layers during the high temperature co-sintering process. The solid solutions formed at the interface of YSZ and GDC exhibit much lower ionic conductivity than YSZ or GDC, thus significantly deteriorating the cell performance. On the other hand, these solid solutions may be helpful in improving the mechanical stability of the bilayer

Chapter 9 Conclusions and Recommendations

electrolyte cell in terms of thermal expansion. Therefore, co-sintering parameters should be optimised to achieve bilayer electrolyte SOFCs with high performance and good mechanical stability.

5. Ceria is liable to reduction in reducing atmospheres. The reduction of Ce^{4+} to Ce^{3+} has substantial effects on the cell performance. It produces electronic conductivity, decreases the OCV, and brings risks of mechanical breakdown of the cell. So, it is important to make more detailed investigations on the ceria reduction, such as quantitative evaluation of the extent of this reduction and the effect of $\text{Ce}^{4+}/\text{Ce}^{3+}$ concentration on the cell performance.

LIST OF PUBLICATIONS

Q.L. Liu, K.A. Khor and S.H. Chan, High performance low temperature SOFCs with novel BSCF cathode, *Journal of Power Sources*, 161 (2006) 123–128

Q.L. Liu, K.A. Khor, S.H. Chan, X.J. Chen, Anode-supported SOFC with YSZ/GDC bilayer electrolyte prepared by wet ceramic cosintering process, *Journal of Power Sources*, 162 (2006) 1036–1042

Q.L. Liu, K.A. Khor and S.H. Chan, Optimization of LSCF-GDC composite cathodes for thin film GDC electrolyte solid oxide fuel cells, *Proceedings of the 3rd International Conference of Materials Processing for Properties and Performance*, Singapore, 24-26 November 2004.

Q.L. Liu, K.A. Khor and S.H. Chan, Intermediate-temperature SOFC with GDC electrolyte films prepared by dry-pressing process, *Proceedings of International Ceramic Conference and Exhibition Austceram 2004*, Melbourne, Australia, 29 November-1 December 2004.

Q.L. Liu, K.A. Khor and S.H. Chan, Intermediate-temperature SOFC with anode-supported LSGM electrolyte, Ni-GDC cermet anode and LSCF-GDC composite cathode, *Proceedings of World Hydrogen Technologies Convention 2005*, Singapore, 3-5 October 2005.

Q.L. Liu, K.A. Khor and S.H. Chan, Preparation and characterization of anode-supported solid oxide fuel cell with YSZ/GDC bilayer electrolyte, *Proceedings of the 5th International Conference of Materials Processing for Properties and Performance*, Singapore, 11-15 December 2006.

Q.L. Liu, K.A. Khor and S.H. Chan, Sintering of gadolinium-doped ceria electrolytes with nanosized raw powders, *International conference of development in Materials, Processes and Applications of Nanotechnology (MPA-2007)*, Belfast, UK, 15 January, 2007.

REFERENCES

- Abellan, J.P., Shemet, V., Tietz, F., Singheiser, L., et al. (2001), Ferritic steel interconnect for reduced temperature SOFC, in: Proceedings of 7th International Symposium on Solid Oxide Fuel Cell, edited by H. Yokokawa and S.C. Singhal, The Electrochemical Society, Pennington, NJ, 2001, pp. 811-819
- Abraham, F., Boivin, J.C., Mairesse, G., Nowogrocki, G. (1990), The BIMEVOX series: a new family of high-performance oxide ion conductors, *Solid State Ionics*, 40-41, pp. 934-937
- Adler, S.B., Lane, J.A., Steele, B.C.H. (1996), Electrode kinetics of porous mixed-conducting oxygen electrodes, *Journal of the Electrochemical Society*, 143(11), pp.3554-3564
- Aizawa, M., Nishiyama, H., Ueno, A., Kuroishi, M., et al. (1993), in: Proceedings of Third International Symposium on Solid Oxide Fuel Cells, edited by S.C. Singhal and H. Iwahara, Electrochemical Society, Pennington, NJ, 1993, pp.38-43
- Appel, C.C., Bonanos, N. (1999), Structural and electrical characterization of silica-containing yttria-stabilized zirconia, *Journal of the European Ceramic Society*, 19, pp. 847-851
- Arachi, Y., Sakai, H., Yamamoto, O., Takeda, Y., et al. (1999), Electrical conductivity of the $\text{ZrO}_2\text{-Ln}_2\text{O}_3$ (Ln=lanthanides) system, *Solid State Ionics*, 121, pp. 133-139
- Arai, H. (1989), in: Proceedings of First International Symposium on Solid Oxide Fuel Cells, edited by S.C. Singhal, Electrochemical Society, Pennington, NJ, 1989, pp.10-16
- Atkinson, A. (1997), Chemically-induced stresses in gadolinium-doped ceria solid oxide fuel cell electrolytes, *Solid State Ionics*, 95, pp. 249-258
- Atkinson, A., Barnett, S., Gorte, R.J., Irvine, J.T.S., et al. (2004), Advanced anodes for high-temperature fuel cells, *Nature Materials*, 3, pp. 17-27
- Azad, A. M., Larose, S., Akbar, S. A. (1994), Bismuth oxide-based solid electrolytes for fuel cells: a review, *Journal of Materials Science*, 29, pp. 4135-4151
- Badwal, S.P.S., Ciacchi, F.T., Hannink, R.H.J. (1990), Relationship between phase stability and conductivity of yttria tetragonal zirconia, *Solid State Ionics*, 40-41, pp. 882-885
- Badwal, S.P.S. (1992), Zirconia-based solid electrolytes: microstructure, stability and ionic conductivity, *Solid State Ionics*, 52, pp. 23-32

References

- Badwal, S.P.S., Deller, R., Foger, K., Ramprakash, Y., et al. (1997), Interaction between chromia forming alloy interconnects and air electrode of solid oxide fuel cells, *Solid State Ionics*, 99, pp. 297-310
- Badwal, S.P.S., Ciacchi, F.T., Drennan, J. (1999), Investigation of the stability of ceria-gadolinia electrolytes in solid oxide fuel cell environments, *Solid State Ionics*, 121, pp. 253-262
- Bi, Z., Yi, B. Wang, Z., Dong, Y., et al. (2004), A high performance anode-supported SOFC with LDC/LSGM bilayer electrolytes, *Electrochemical and Solid-State Letters*, 7, A105-A107
- Brunauer, S., Emmet, H.P., Teller, E. (1938), Adsorption of gasses in Multimolecular Layers, *Journal of the American Chemical Society*, 60, pp. 309-313.
- Brylewski, T., Nanko, M., Maruyama, T., Przybylski, K. (2001), Application of Fe-16Cr ferritic alloy to interconnector for a solid oxide fuel cell, *Solid State Ionics*, 143, pp. 131-150
- Cai, Z., Lan, T.N., Wang, S., Dokiya, M. (2002), Supported Zr(Sc)O_2 SOFCs for reduced temperature prepared by slurry coating and co-firing, 152-153, pp. 583-590
- Cassidy, M., Kendall, K., Lindsay, C. (1996), in: *Proceedings of 2nd European Solid Oxide Fuel Cell Forum*, edited by B. Thorstensen, European SOFC Forum, Oberrohrdorf, Switzerland, 1996, pp. 667-672
- Chan, S.H., Chen, X.J., Khor, K.A. (2003), A simple bilayer electrolyte model for solid oxide fuel cells, *Solid State Ionics*, 158, pp. 29-43
- Chan, S.H., Ding, O.L. (2004), Simulation of a solid oxide fuel cell power system fed by methane, *International Journal of Hydrogen Energy*, 30, pp.167-179
- Charpentier, P., Fragnaud, P., Schleich, D.M., Gehain, E. (2000), Preparation of thin film SOFCs working at reduced temperature, *Solid State Ionics*, 135, pp. 373-380
- Chen, C.C., Nasrallah, M.M., Anderson, H.U. (1994), Synthesis and characterization of YSZ thin film electrolytes, *Solid State Ionics*, 71-72, pp. 101-108
- Chen, X.J., Khor, K.A., Chan, S.H., Yu, L.G. (2002), Preparation yttria-stabilized zirconia electrolyte by spark-plasma sintering, *Materials Science and Engineering A*, 341, pp.43-48
- Chen, X.J., Khor, K.A., Chan, S.H. (2003), Identification of O_2 reduction processed at yttria stabilized zirconia/doped lanthanum manganite interface, *Journal of Power Sources*, 123, pp. 17-25
- Chen, X., Wu, N.J., Smith, L., Ignatiev, A. (2004), Thin-film heterostructure solid oxide fuel cells, *Applied Physics Letters*, 84(14), pp. 2700-2702

References

- Chiba, T., Ishii, T., Yoshimura, F. (1996), Temperature dependence of ionic conductivity in $(1-x)\text{ZrO}_2-(x-y)\text{Sc}_2\text{O}_3-y\text{Yb}_2\text{O}_3$ electrolyte material, *Solid State Ionics*, 91, pp. 249-256
- Chick, L.A., Pederson, L.R., Maupin, G.D., Bates, J.L., et al. (1990), Glycine-nitrate combustion synthesis of oxide ceramic powders, *Materials Letters*, 10 (1), pp.6-12
- Chour, K., Chen, J., Xu, R. (1997), Metal-organic vapor deposition of YSZ electrolyte layers for solid oxide fuel cell applications, *Thin Solid Films*, 304, pp. 106-112
- Choy, K., Charojrochkul, B.S., Steele, B.C.H. (1998), The development of intermediate temperature solid oxide fuel cells for the next millennium, *Journal of Power Sources*, 71, pp. 361-369
- Christie, G.M., Berkel, F.P.F. (1996), Microstructure-ionic conductivity relationships in ceria-gadolinia electrolytes, *Solid State Ionics*, 83, pp. 17-27
- Cifrain, M., Kordesch, K.V. (2004), Advances, aging mechanism and lifetime in AFCs with circulating electrolytes, *Journal of Power Sources*, 127, pp. 234-242
- Craciun, R., Park, S., Gorte, R.J., Rohs, J.M., et al. (1999), A novel method for preparing anode cermets for solid oxide fuel cells, *Journal of the Electrochemical Society*, 146(11), pp. 4019-4022
- Daza, L., Rangel, C.M., Baranda, J., Cassais, M.T., et al. (2000), Modified nickel oxides as cathode materials for MCFC, *Journal of Power Sources*, 86, pp. 329-333
- Diethelm, R., Schmidt, M., Honegger, K., Batawi, E. (1999), in: *Proceedings of 6th International Symposium on Solid Oxide Fuel Cell*, edited by S.C. Singhal and M. Dokiya, The Electrochemical Society, Pennington, NJ, 1999, pp. 60
- Doshi, R., Richards, V.L., Carter, J.D., Wang, X., et al. (1999), Development of solid oxide fuel cells that operate at 500°C, *Journal of the Electrochemical Society*, 146(4), pp. 1273-1278
- Dubois, B., Ruffier, D., Odier, P. (1989), Preparation of fine, spherical yttria-stabilized zirconia by the spray pyrolysis method, *Journal of the American Ceramic Society*, 72, pp. 713-715
- Dusastre, V., Kilner, J.A. (1999), Optimisation of composite cathodes for intermediate temperature SOFC applications, *Solid State Ionics*, 126, pp. 163-174
- Eguchi, K., Akasaka, N., Mitsuyasu H., Nonaka, Y. (2000), Process of solid state reaction between doped ceria and zirconia, *Solid State Ionics*, 135, pp. 589-594
- Eguchi, K., Setoguchi, T., Inoue, T., Arai, H. (1992), Electrical properties of ceria-based oxides and their application to solid oxide fuel cells, *Solid State Ionics*, 52, pp.165-172

References

- Elangovan, S., Hartvigsen, J.J., Kung, S.C., Goettler, R.W., et al. (2001), Planar solid oxide fuel cell development at SOFCs., in: Proceedings of 7th International Symposium on Solid Oxide Fuel Cell, edited by H. Yokokawa and S.C. Singhal, The Electrochemical Society, Pennington, NJ, 2001, pp. 94-99
- Endo, A. Fukunaga, H., Wen, C., Yamada, K. (2000), Cathodic reaction mechanism of dense $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$ and $\text{La}_{0.81}\text{Sr}_{0.09}\text{MnO}_3$ electrodes for solid oxide fuel cells, *Solid State Ionics*, 135, pp. 353-358
- Endo, A., Ihara, M., Komiyama, H., Yamada, K. (1996), Cathodic reaction mechanism for dense Sr-doped lanthanum manganite electrodes, *Solid State Ionics*, 86-88, pp. 1191-1195
- Feret, J.M. (1990), Westing house air-cooled PAFC technology, *Journal of Power Sources*, 29, pp. 59-69
- Fergus, J.W. (2004), Lanthanum chromite-based materials for solid oxide fuel cell interconnects, *Solid State Ionics*, 171, pp. 1-15
- Figueiredo, F.M., Marques, F.M.B., Frade, J. R. (1999), Electron hole conductivity of gadolinia-doped ceria, *Journal of the European Ceramic Society*, 19, pp. 807-810
- Fukui, T., Ohara, S., Murata, K., Yoshida, H., et al. (2002), Performance of intermediate temperature solid oxide fuel cells with LSGM electrolyte film, *Journal of Power Sources*, 106, pp. 142-145
- Ganesan, P., Colon, H., Haran, B., Popov, B.N. (2003), Performance of $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ coated NiO as cathodes for molten carbonate fuel cells, *Journal of Power Sources*, 115, pp. 12-18
- Gardner, F.J., Day, M.J., Brandon, N.P., Pashley, M.N., et al. (2000), SOFC technology development at Rolls-Royce, *Journal of Power Sources*, 86, pp. 122-129
- Gerhardt, R., Nowick, A.S., Mochel, M.E., Dumler, I. (1986), Grain boundary effect in ceria doped with trivalent cations: I, electrical measurements, *Journal of the American Ceramic Society*, 69, pp. 641-646
- Gerhardt R., Nowick, A.S., Mochel, M.E., Dumler, I. (1986), Grain-boundary effect in ceria doped with trivalent cations: II. Microstructure and microanalysis, *Journal of the American Ceramic Society*, 69, pp. 647-651
- Gibson, I.R., Dransfield, G.P., Irvine, J.T.S. (1998), Sinterability of commercial 8 mol% yttria-stabilized zirconia powders and the effect of sintered density on the ionic conductivity, *Journal of Materials Science*, 33, pp. 4297-4305
- Godfrey, B., Gillespie, R., Foger K. (1999), Competitive positioning of planar SOFC technology, in: Proceedings of 6th International Symposium on Solid Oxide Fuel Cell,

References

edited by S.C. Singhal and M. Dokiya, The Electrochemical Society, Pennington, NJ, 1999, pp. 75-79

Godickemeier, M., Gauckler, L. J. (1998), Engineering of solid oxide fuel cells with ceria-based electrolytes, *Journal of the Electrochemical Society*, 145(2), pp. 414-421

Gödickemeier, M., Sasaki, K., Gauckler, L. J., Riess, I. (1996), Perovskite cathodes for solid oxide fuel cells based on ceria electrolytes, *Solid State Ionics*, 86-88, pp. 691-701

Gorte, R.J., Park, S., Rohs, J.M., Wang, C. (2000), Anodes for direct oxidation of dry hydrocarbons in a solid oxide fuel cell, *Advanced Materials*, 12(19), pp. 1465-1469

Gremillard, L., Epicier, T., Chevalier, J., Fantozzi, G (2000), Microstructural study of silica-doped zirconia ceramics, *Acta Materialia*, 48, pp. 4647-4652

Gulzow, E. (1996), Alkaline fuel cells: a critical view, *Journal of Power Sources*, 61, pp. 99-104

Hall, D.J. (1997), Transient modelling and simulation of a solid oxide fuel cell, Ph.D. thesis, University of Pittsburgh

Haslam, J.J., Pham, A.Q., Chung, B.W., Dicarlo, J.F., et al. (2005), Effects of the use of pore formers on performance of an anode-supported solid oxide fuel cell, *Journal of the American Ceramic Society*, 88(3), pp. 513-518

Hatchwell, C., Sammes, N.M., Brown, I.W.M. (1999), Fabrication and properties of CGO electrolyte-based tubular solid oxide fuel cells, *Solid State Ionics*, 126, pp. 201-208

Hayashi, H., Manoh, M., Quan C.J., Inaba, H., et al. (2000), Thermal expansion of Gd-doped ceria and reduced ceria, *Solid State Ionics*, 132, pp. 227-233

Hayashi, K., Yamamoto, O., Nishigaki, Y., Minoura, H. (1997), Sputtered LaSrMnO₃-YSZ composite film electrodes for SOFC, *Solid State Ionics*, 98, pp. 49-55

Henne, R., Muller, M., Prob, E., Schiller, G., et al. (1999), Near-net shape forming of metallic bipolar plates for planar solid oxide fuel cells by induction plasma spraying, *Journal of Thermal Spray Technology*, 8, pp. 110-116

Herle, J.V., Ihringer, R., Sammes, N.M., Tompsett, G., et al. (2000), Concept and technology of SOFC for electroc vehicles, *Solid State Ionics*, 132, pp. 333-432

Hibino, T., Hashimoto, A., Asano, K., Yano, M., et al. (2002), An intermediate temperature solid oxide fuel cell providing higher performance with hydrocarbons than with hydrogen, *Electrochemical and Solid-State Letters*, 5(11), A242-A244

Horita, T., Sakai, N., Yokokawa, H., Kokiya, M. et al (1997), Ceria-zirconia composite electrolyte for solid oxide fuel cells, *Journal of Electroceramics*, 1 (2), pp. 155-164

References

- Horita, T., Yamaji, K., Ishikawa, M., Sakai, N., et al. (2001), Electrode reaction of $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ cathodes on $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$ electrolyte in solid oxide fuel cells, *Journal of the Electrochemical Society*, 148(5), A456-A462
- Hu, H., Liu, M.L. (1998), Interfacial studies of solid-state cells based on electrolytes of mixed ionic-electronic conductors, *Solid State Ionics*, 109, pp. 259-272
- Huang, K., Lee, H. Y., Goodenough, J.B. (1998a), Sr- and Ni-doped LaCoO_3 and LaFeO_3 perovskites new cathode materials for solid-oxide fuel cells, *Journal of the Electrochemical Society*, 145(9), pp. 3220-3227
- Huang, K., Wan, J.H., Goodenough, J.B. (2001), Increasing power density of LSGM-based solid oxide fuel cells using new anode materials, *Journal of the Electrochemical Society*, 148(7), A788-A794
- Huang, K, Tichy, R. S., Goodenough, J.B. (1998b), Superior perovskite oxide-ion conductor: Strontium- and magnesium-doped LaGaO_3 : I phase relationships and electrical properties, *Journal of the American Ceramic Society*, 81 (10), pp.2565-2575
- Huang, K, Tichy, R.S., Goodenough, J.B. (1998c), Superior perovskite oxide-ion conductor: Strontium- and magnesium-doped LaGaO_3 : III performance tests of single ceramic fuel cells, *Journal of the American Ceramic Society*, 81(10), pp. 2581-2585
- Huang, P., Horky, A., Petric, A. (1999), Interfacial reaction between nickel oxide and lanthanum gallate during sintering and its effect on conductivity, *Journal of the American Ceramic Society*, 82 (9), pp. 2402-2410
- Huang W., Shuk, P., Greenblatt M., Croft M., et al. (2000), Structural and electrical characterization of a novel mixed conductor: $\text{CeO}_2\text{-Sm}_2\text{O}_3\text{-ZrO}_2$ solid solution, *Journal of the Electrochemical Society*, 147 (11), pp. 4196-4202
- Huijsmans, J.P.P., Berkel, F.P.F.V., Christie, G.M. (1998), Intermediate temperature SOFC—a promise for the 21st century, *Journal of Power Sources*, 71, pp. 107-110
- Ihringer, R., Van-Herle, J., McEvoy, A. J. (1997), in: *Proceeding of 5th International Conference of Solid Oxide Fuel Cells*, edited by Singhal S.C., Tagawa H. and Lehnert W., *Electrochemical Society*, Pennington, NJ, 1997, pp. 340
- Inaba, H., Tagawa, H. (1996), Ceria-based solid electrolytes, *Solid State Ionics*, 83, pp.1-16
- Inoue, T., Setoguchi, T., Eguchi, K., Arai, H. (1989), Study of a solid oxide fuel cell with a ceria-based solid electrolyte, *Solid State Ionics*, 35, pp. 285-291
- Ishihara, T., Matsuda, H., Takita, Y. (1994), Doped LaGaO_3 perovskite type oxide as a new oxide ionic conductor, *Journal of the American Chemistry Society*, 116, pp. 3801-3803

References

- Ishii, T., Tajima, Y. (1994), Low temperature operation of solid oxide fuel cell with a $\text{ZrO}_2\text{-Sc}_2\text{O}_3\text{-Al}_2\text{O}_3$ system electrolyte, *Journal of the Electrochemical Society*, 141 (2), pp. 641-646
- Itoh, H., Yamamoto, T., Mori, M. (1997), Configurational and electrical behavior of Ni-YSZ cermet with novel microstructure for solid oxide fuel cell anodes, *Journal of the Electrochemical Society*, 144(2), pp. 641-646
- Iwahara, H., Mori, T., Hibino, T. (1995), Electrochemical studies on ionic conduction in Ca-doped BaCeO_3 , *Solid State Ionics*, 79, 177-182
- Jang, W.S., Hyun, S.H., Kim, S.G. (2002), Preparation of YSZ/YDC and YSZ/GDC composite electrolytes by the tape casting and sol-gel dip-drawing coating method for low temperature SOFC, *Journal of Materials Science*, 37, pp. 2535-2541
- Jiang, S. P. (2002), A comparison of O_2 reduction reactions on porous LSM and LSCF electrodes, *Solid State Ionics*, 146, pp.1-22
- Jiang, S.P., Callus, P.J., Badwal, S.P.S. (2000a), Fabrication and performance of Ni/3 mol% YSZ cermet anodes for solid oxide fuel cells, *Solid State Ionics*, 132, pp1-14
- Jiang, S.P., Chan, S.H. (2004), A review of anode materials development in solid oxide fuel cells, *Journal of Materials Science*, 39, pp. 4405-4439
- Jiang, S.P., Leng, Y.J., Chan, S.H., Khor, K.A. (2003), Development of $(\text{La,Sr})\text{MnO}_3$ -based cathodes for intermediate temperature solid oxide fuel cells, *Electrochemical and Solid-State Letters*, 6(4), A67-A70
- Jiang, S.P., Love, J.G. (2003), Observation of structural change induced by cathodic polarization on $(\text{La,Sr})\text{MnO}_3$ electrodes of solid oxide fuel cells, *Solid State Ionics*, 158, pp. 45-53
- Jiang, S.P., Zhang, J.P., Foger, K. (2000b), Deposition of chromium species at Sr-doped LaMnO_3 electrodes in solid oxide fuel cells II. Effect on O_2 reduction reaction, *Journal of the Electrochemical Society*, 147, pp. 3195-3250
- Jiang, S.P., Zhang, J.P., Zheng, X.G. (2002), A comparative investigation of chromium deposition at air electrodes of solid oxide fuel cells, *Journal of the European Ceramic Society*, 22, pp.361-373
- Jiang, S.P., Zhang, S., Zhen, Y.D., Koh, A.P. (2004), Performance of GDC-impregnated Ni anodes of SOFCs, *Electrochemical and Solid-State Letters*, 7(9), A282-A285
- Jiang, Y., Virkar, A.V., Zhao, F. (2001), The effect of testing geometry on the measurement of cell performance in anode-supported solid oxide fuel cells, *Journal of the Electrochemical Society*, 148 (2001), A1091-1099

References

- Jin, H.C., Jong, H.J., Ji, H. R., Seung, M. O. (2000), Microstructure and cathodic performance of LaSrMnO_3 electrodes according to particle size of starting powder, *Journal of Power Sources*, 87, pp. 92–100
- Joerger, M.B., Gauckler, L.J. (2001), Catalytically active anodes for SOFC, in: *Proceedings of 7th International Symposium on Solid Oxide Fuel Cell*, edited by H. Yokokawa and S.C. Singhal, The Electrochemical Society, Pennington, NJ, 2001, pp. 662-670
- Jorgensen, M. J., Mogensen, M. (2001), Impedance of solid oxide fuel cell LSM/YSZ composite cathodes, *Journal of the Electrochemical Society*, 148(5), A433-A442
- Jørgensen, M. J., Primdahl, S., Bagger, C., Mogensen, M., (2001), Effect of sintering temperature on microstructure and performance of LSM–YSZ composite cathodes, 139, pp. 1-11
- Joseph, M., Manoravi, P. (2002), Preparation of LSGM thin films by pulsed laser deposition and conductivity studies, *Journal of Applied Physics*, 92, pp. 997-1001
- Kawada, T., Sakai, N., Yokokawa, H., Dokiya, M. (1990), Characteristics of slurry coated nickel zirconia cermet anodes for solid oxide fuel cells, *Journal of the Electrochemical Society*, 137(10), pp. 3042-3047
- Kharton, V.V., Figueiredo, F.M., Navarro, L., Naumovich, E.N., et al. (2001), Ceria-based materials for solid oxide fuel cells, *Journal of Materials Science*, 36, pp. 1105-1117
- Kharton, V.V., Kovalevsky, A.V., Viskup, A.P., Shaula, A.L., et al. (2003), Oxygen transport in $\text{Gd}_{0.2}\text{Ce}_{0.8}\text{O}_{2-\delta}$ -based composite membranes, *Solid State Ionics*, 160, pp. 247-258
- Kharton, V.V., Marques, F.M.B., Atkinson, A. (2004), Transport properties of solid oxide electrolyte ceramics: a brief review, *Solid State Ionics*, 174, pp.135-149
- Kim, J.H., Yoo, H.I. (2001), Partial electronic conductivity and electrolytic domain of $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_3$, *Solid State Ionics*, 140, pp. 105-113
- Kim, K.W., Virkar, A.V., Fung, K Z., Mehta, K., et al. (1999), Polarisation effects in intermediate temperature anode-supported solid oxide fuel cells, *Journal of the Electrochemical Society*, 146, pp. 69-78
- Kim, S.J., Virkar, A.V., Fung, K.Z., Karun, M., et al. (1997), Characteristics of ultrafine powders prepared by the glycine-nitrate process, *Proceedings of the 5th International Conference on Properties and Application of Dielectric Materials*, May 25-30, 1997, Korea, pp. 886-891

References

- Kim, S.G., Yoon, S.P., Nam, S.W., Hyun, S.H., et al. (2002), Fabrication and characterization of a YSZ/YDC composite electrolyte by a sol-gel coating method, *Journal of Power Sources*, 110, pp. 222-228
- Knauth, P., Tuller, H. L. (2002), Solid state ionics: roots, status and future prospects, *Journal of the American Ceramic Society*, 85(7), pp. 1654-1680
- Kobayashi, K., Takahashi, I., Shiono, M., Dokiya, M. (2000), Supported Zr(Sc)O₂ SOFCs for reduced temperature prepared by electrophoretic deposition, *Solid State Ionics*, 152-153, pp. 591-596
- Kokai, F., Amano, K., Ota, H., Ochiai, Y., et al. (1992), XeCl laser ablative deposition and characterization of yttria-stabilized zirconia thin films on glass and CeO₂-Sm₂O₃, *Journal of Applied Physics*, 72, pp. 699-704
- Kostogloudis, G.C., Ftiko, C. (1999), Properties of A-site-deficient La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O₃-based perovskite oxides, *Solid State Ionics*, 126, pp.143-151
- Kuroda, K., Hashimoto, I., Adachi, K., Akikusa, J., et al. (2000), Characterization of solid oxide fuel cell using doped lanthanum gallate, *Solid State Ionics*, 132, pp.199-208
- Kurokawa, H., Kawamura, K., Maruyama, T. (2004), Oxidation behavior of Fe-16Cr alloy interconnect for SOFC under hydrogen potential gradient, *Solid State Ionics*, 168, pp. 13-21
- Lang, M., Hene, R., Schaper, S., Schiller, G. (2001), Development and characterization of vacuum plasma sprayed thin film solid oxide fuel cells, *Journal of Thermal Spray Technology*, 10, pp. 618-625
- Larring, Y., Haugsrud, R., Norby, T. (2003), HT corrosion of a Cr-5 wt % Fe-1 wt % Y₂O₃ alloy and conductivity of the oxide scale, *Journal of the Electrochemical Society*, 150(8), B374-379
- Leng, Y. J., Chan, S. H., Khor, K. A., Jiang, S. P., et al. (2003), Effect of characteristics of Y₂O₃-ZrO₂ powders on fabrication of anode-supported solid oxide fuel cells, *Journal of Power Sources*, 5458, pp. 1-9
- Leng, Y.J., Chan, S.H., Jiang, S.P., Khor, K.A. (2004), Low temperature SOFC with thin film GDC electrolyte prepared in situ by solid-state reaction, *Solid State Ionics*, 170, pp. 9-15
- Linderroth, S., Hendriksen, P.V., Mogensen, M. (1996), Investigations of metallic alloys for use as interconnects in solid oxide fuel cell stacks, *Journal of Materials Science*, 31, pp. 5077-5082
- Litster, S., McLean, G. (2004), PEM fuel cell electrodes, *Journal of Power Sources*, 130, pp. 61-76

References

Liu, M.L., Hu, H. (1996), Effect of interfacial resistance on determination of transport properties of mixed-conducting electrolytes, *Journal of the Electrochemical Society*, 143, L109-L112

Liu, M.L., Wu, Z.L. (1998), Significance of interfaces in solid-state cells with porous electrodes of mixed ionic-electronic conductors, *Solid State Ionics*, 107, pp. 3105-110

Liu, Y., Zha, S., Liu, M. (2004), Novel nanostructured electrodes for solid oxide fuel cells fabricated by combustion chemical vapor deposition (CCVD), *Advanced Materials*, 16(3), pp. 256-260

Livermore, S.J.A., Cotton, J.W., Ormerod, R.M. (1999), in: *Proceedings of 6th International Symposium on Solid Oxide Fuel Cell*, edited by S.C. Singhal and M. Dokiya, The Electrochemical Society, Pennington, NJ, 2001, pp. 593-599

Lubke, S., Wiemhofer, H. D. (1999), Electronic conductivity of Gd-doped ceria with additional Pr-doping, *Solid State Ionics*, 117, pp. 229-243

Lundberg, W. L., Stephen, E. V. (2001), Conceptual design and performance analysis of a 300 MW LNG-fueled pressurized SOFC/gas turbine power plant, in: *Proceedings of 7th International Symposium on Solid Oxide Fuel Cell*, edited by H. Yokokawa and S. C. Singhal, Electrochemical Society, Pennington, NJ, 2001, pp. 78-87

Macdonald, J.R. (1987), *Impedance spectroscopy-emphasizing solid materials and systems*, A Wiley Interscience Publication, John, Wiley & Sons

Maguire, E., Gharbage, B., Marques, F. M. B., Labrincha, J. A. (2000), Cathode materials for intermediate temperature SOFCs, *Solid State Ionics*, 127, pp. 329-335

Maric, R., Ohara, S., Fukui, T., Yoshida, H., et al. (1999), Solid oxide fuel cells with doped lanthanum gallate electrolyte and LaSrCoO₃ cathode and Ni-samarium-doped ceria cermet anode, *Journal of the Electrochemical Society* 146 (6), pp. 2006-2010

Maricle, D.L., Swarr, T.E., Karavolis, S. (1992), Enhanced ceria—a low temperature SOFC electrolyte, *Solid State Ionics*, 52, pp. 173-182

Marina, O.A., Bagger, C., Primdahl, S., Mogensen, M. (1999), A solid oxide fuel cell with a gadolinia-doped ceria anode: preparation and performance, *Solid State Ionics*, 123, pp. 199-208

Marques, F. M. B., Navarro, L. M. (1996), Performance of double layer electrolyte cells Part I: Model behavior, *Solid State Ionics*, 90, pp. 183-192

Marques, F. M. B., Navarro, L. M. (1997), Performance of double layer electrolyte cells Part II: GCO/YSZ, a case study, *Solid State Ionics*, 100, pp. 29-38

References

- Martin, S.W. (1992), An evaluation of the ionic conductivity in AgI-doped glasses: the graded-percolation model, *Solid State Ionics*, 51, pp19-26
- Mathews, T., Rabu, N., Sellar, J. R., Muddle, B. C. (2000), Fabrication of $\text{La}_{1-x}\text{Sr}_x\text{Ga}_{1-y}\text{Mg}_y\text{O}_{3-(x+y)/2}$ thin films by electrophoretic deposition and its conductivity measurement, *Solid State Ionics*, 128, pp. 111-115
- Matsui, T., Kosaka, T., Inaba, M., Mineshige, A., et al. (2005a), Effects of mixed conduction on the open-circuit voltage of intermediate-temperature SOFCs based on Sm-doped ceria electrolytes, *Solid State Ionics*, 176, pp. 663-668
- Matsui, T., Inaba, M., Mineshige, A., Ogumi, Z. (2005b), Electrochemical properties of ceria-based oxides for use in intermediate-temperature SOFCs, *Solid State Ionics*, 176, pp. 647-654
- Mehta, K., Hong, S.J., Jue, J.F., Virkar, A.V. (1993), Fabrication and characterization of YSZ-coated ceria electrolytes, in: *Proceedings of 3rd International Symposium on Solid Oxide Fuel Cell*, edited by S.C. Singhal and M. Dokiya, The Electrochemical Society, Pennington, NJ, 1993, pp. 92-103
- Mehta, K., Xu, T., Virkar, A.V. (1998), Two-layer fuel cell electrolyte structure by sol-gel processing, *Journal of Sol-Gel Science and Technology*, 11, pp. 203-207
- Mendelson, M.I. (1969), Average grain size in polycrystalline ceramics, *Journal of the American Ceramic Society*, 52, pp. 443-446.
- Milliken, C., Guruswamy, S., Khandkar, A. (1999), Evaluation of ceria electrolytes in solid oxide fuel cells electric power generation, *Journal of the Electrochemical Society*, 146(3), pp. 873-882
- Minh, N.Q., Gibson, R.A. (1994), Production of reduced temperature solid oxide fuel cells by tape calendering, *Proceeding of the First European Solid Oxide Fuel Cell Forum*, edited by Bossel U. and Kinzel J., 1994, pp.587-596
- Minh, N.Q., Takahashi, T. (1995), *Science and Technology of Ceramic Fuel Cells*, Elsevier, Amsterdam, The Netherlands
- Minh, N.Q. (1993), Ceram fuel cells, *Journal of the American Ceramic Society*, 76(3), pp. 563-588
- Minh, N.Q. (2004), Solid oxide fuel cell technology: futures and applications, *Solid State Ionics*, 174, pp. 271-274
- Mishima, Y., Mitsuyasu, H., Ohtaki, M., Eguchi, K. (1998), Solid oxide fuel cell with composite electrolyte consisting of samaria-doped ceria and yttria-stabilized zirconia, *Journal of the Electrochemical Society*, 145(3), pp. 1004-1007

References

- Mizusaki, J., Amano, K., Yamauchi, S., Feki, K. (1987), Electrode reaction at Pt, O₂(g)/stabilised zirconia interfaces. Part I: Theoretical consideration of reaction model, *Solid State Ionics*, 22, pp. 313-322
- Mogensen, M., Skaarup, S. (1996), Kinetic and geometric aspects of solid oxide fuel cell electrodes, *Solid State Ionics*, 86-88, pp. 1151-1160
- Mogensen, M., Sammes, N.M., Tompsett, G.A. (2000), Physical, chemical and electrochemical properties of pure and doped ceria, *Solid State Ionics*, 129, pp. 63-94.
- Mori, M. (2002), Enhancing effect on densification and thermal expansion compatibility for La_{0.8}Sr_{0.2}Cr_{0.9}Ti_{0.1}O₃-based SOFC interconnect with B-Site doping, *Journal of the Electrochemical Society*, 149(7), A797-A803
- Murray, E. P., Sever, M. J., Barnett, S. A. (2002), Electrochemical performance of (La,Sr)(Co,Fe)O₃-(Ce,Gd)O₂ composite cathodes, *Solid State Ionics*, 148, pp. 27-34
- Murray, E. P., Tsai, T., Barnett, S. A. (1999), A direct-methane fuel cell with a ceria-based anode, *Nature*, 400, pp. 649-651
- Murray, E.P., Barnett, S.A. (2001), (La,Sr)MnO₃-(Ce,Gd)O_{2-x} composite cathodes for solid oxide fuel cells, *Solid State Ionics*, 143, pp 265-273
- Murray, E.P., Tsai, T., Barnett, S.A. (1998), Oxygen transfer processes in (La,Sr)MnO₃/YSZ cathodes: an impedance spectroscopy study, *Solid State Ionics*, 110, pp. 235-2453
- Nakagawa, N., Yoshioka, H., Kuroda, C., Ishida, M. (1989), Electrode performance of a thin-film YSZ cell set on a porous ceramic substrate by rf sputtering technique, *Solid State Ionics*, 35, pp. 249-255
- Navarro, L., Marques, F., Frade, J. (1997), n-type conductivity in gadolinia-doped ceria, *Journal of the Electrochemical Society*, 144, pp. 267-273
- Nguyen, T.L., Kobayashi, K., Honda, T., Iimura, Y., et al. (2004), Preparation and evaluation of doped ceria interlayer on supported stabilized zirconia electrolyte SOFCs by wet ceramic processes, *Solid State Ionics*, 174, pp. 163-174
- Nuridin, M. (2001), *The fuel cell home*, Lucerne, Switzerland
- Ohri, H., Matsushima, T., Hirai, T. (1998), Performance of a solid oxide fuel cell fabricated by co-firing, *Journal of Power Sources*, 71, pp. 185-189
- Pal, U.B., Singal, S.C. (1990), Electrochemical vapor deposition of yttria-stabilised zirconia films, *Journal of the Electrochemical Society*, 137(9), pp.2937-2941
- Park, H.J., Choi, G.M. (2004), Oxygen permeability of gadolinium-doped ceria at high temperature, *Journal of the European Ceramic Society*, 24, pp. 1313-1317

References

- Park, S., Vohs, J.M., Gorte, R. (2000), Direct oxidation of hydrocarbons in a solid oxide fuel cell, *Nature*, 404, pp. 265-277
- Peng, R.R., Xia, C.R., Liu, X.Q., Peng, D.K., et al. (2002), Intermediate-temperature SOFCs with thin $\text{Ce}_{0.8}\text{Y}_{0.2}\text{O}_{1.9}$ films prepared by screen-printing, *Solid State Ionics*, 152-153, pp. 561-565
- Perry, M.L., Fuller, T.F. (2002), A historical perspective of fuel cell technology in the 20th century, *Journal of the Electrochemical Society*, 149 (7), S59-S67
- Pham, A.Q., Chung, B.W., Haslam, J.J., Lenz, D.J., et al. (2001), Demonstration of high power density planar solid oxide fuel cell stacks, in: *Proceedings of 7th International Symposium on Solid Oxide Fuel Cell*, edited by H. Yokokawa and S.C. Singhal, The Electrochemical Society, Pennington, NJ, 2001, pp. 148-154
- Qiu, L., Ichikawa, T., Hirano, A., Imanishi, N., et al. (2002), $\text{Ln}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ ($\text{Ln}=\text{Pr, Nd, Gd}$; $x=0.2, 0.3$) for the electrodes of solid oxide fuel cells, *Solid State Ionics*, 158, pp. 55-65
- Ralph, J.M., Schoeler, A.C., Krumpelt, M. (2001), Materials for lower temperature solid oxide fuel cells, *Journal of Materials Science*, 36, pp. 1161-1172
- Rambabu, B., Ghosh, S., Zhao, W. (2005), Innovative processing of dense LSGM based electrolytes/LSCM electrodes for all perovskite based IT-SOFCs, *International Conference on Materials and Advanced Technology*, July 2005, Singapore
- Riess, I., Braunshtein, D., Tannhauser, D.S. (1981), Density and ionic conductivity of sintered $(\text{CeO}_2)_{0.82}(\text{GdO}_{1.5})_{0.18}$, *Journal of the American Ceramic Society*, 64, pp. 479-485
- Riess, I., Godickemeier, M., Gauckler, L.J. (1996), Characterization of solid oxide fuel cells based on solid electrolytes or mixed ionic electronic conductors, *Solid State Ionics*, 90, pp. 91-104
- Ruckdaschel, R., Henne, R., Schiller, G., Greiner, H. (1997), Functional layers for the bipolar plates of planar solid oxide fuel cells produced by vacuum plasma spraying, in: *Proceedings of 5th International Symposium on Solid Oxide Fuel Cell*, edited by U. Stimming, S.C. Singhal, H. Tagawa and W. Lehnert, The Electrochemical Society, Pennington, NJ, 1997, pp. 1273-1282
- Sammes, N.M., Cai, Z. (1997), Ionic conductivity of ceria/yttria stabilized zirconia electrolyte materials, *Solid State Ionics*, 100, pp. 39-44
- Sasaki, K., Wurth, J. P., Godickemeier, M., Mitterdorfer, A., et al. (1994), Processing –microstructure-property relation of solid oxide fuel cell cathode, *Proceedings of the First European Solid Oxide Fuel Cell Forum*, edited by Bossel U., and Kruckerei J., 1994, pp. 475-491

References

- Sato, T., Nauer, M., Carry, C. (1991), Influence of residual impurities on phase partitioning and grain growth processes of Y-TZP materials, *Journal of the American Ceramic Society*, 74, pp. 2615-2621
- Scott, S.P., Mantzavinos, D., Hartley, A., Sahibzada, M., et al. (2002), Reactivity of LSCF perovskites, *Solid State Ionics*, 152-153, pp.777-781
- Shao, Z., Dong, H., Xiong, G., Cong, Y., et al. (2001), Performance of a mixed-conducting ceramic membrane reactor with high oxygen permeability for methane conversion, *Journal of Membrane Science*, 183, pp. 181-192
- Shao, Z.P., Haile, S.M. (2004), A high performance cathode for the next generation of solid oxide fuel cells, *Nature (London)* 431, pp.170-173
- Shao, Z.P., Yang, W.S., Cong, Y., Dong, H., et al. (2000), Investigation of the permeation behavior and stability of a BSCF oxygen membrane, *Journal of Membrane Science*, 172, pp. 177-188
- Shemilt, J.E., Stanway, C.L., Williams, H.M. (2000), Effect of plastic forming on the conductivity of a samaria-doped ceria electrolyte, *Solid State Ionics*, 134, pp. 111-117
- Shimonosono, T., Hirata, Y., Ehira, Y., Sameshima, S., et al. (2004), Electronic conductivity measurement of Sm- and La-doped ceria ceramics by Hebb-Wagner method, *Solid State Ionics*, 174, pp. 27-33
- Simner, S.P., Bonnett, J.F., Canfield, N.L., Meinhardt, K.D., et al. (2002), Optimized lanthanum ferrite-based cathodes for anode-supported SOFCs, *Electrochemical and Solid-State Letters*, 5(7), A173-A175
- Singhal, S.C. (2000), Advances in solid oxide fuel cell technology, *Solid State Ionics*, 135, pp. 305-313
- Singhal, S.C. (1999), Progress in tubular solid oxide fuel cell technology, in: *Proceedings of 6th International Symposium on Solid Oxide Fuel Cell*, edited by S.C. Singhal and M. Dokiya, The Electrochemical Society, Pennington, NJ, 1999, pp. 39-51
- Singhal, S.C., Kendall, K. (Eds.) (2003), *High temperature solid oxide fuel cells: fundamentals, design and applications*, Elsevier, Oxford, UK
- Sishtla, C., Koncar, G., Platon, R., Gamburzev, S., et al. (1998), Performance and endurance of a PEMFC operated with synthetic reformat fuel feed, *Journal of Power Sources*, 71, pp. 249-255
- Skinner, S.J. (2001), Recent advances in perovskite-type materials for solid oxide fuel cell cathodes, *International Journal of Inorganic Materials*, 3, pp. 113-121

References

- Slater, P. R., Irvine, J. T. S., Ishihara, T., Takita, Y. (1998), The structure of the oxide ion conductor LSGM by powder neutron diffraction, *Solid State Ionics*, 107, pp. 319-323
- Souza, S.D., Visco, S.J., Jonghe, L.C.D. (1997), Thin film solid oxide fuel cell with high performance at low temperature, *Solid State Ionics*, 98, pp.57-61
- Srivastava, P.K., Quach, T., Duan, Y.Y., Donelson, R., et al. (1997), Electrode supported solid oxide fuel cells: electrolyte films prepared by DC magnetron sputtering, *Solid State Ionics*, 99, pp. 311-319
- Steele, B. C. H. (2000), Appraisal of $\text{Ce}_{1-y}\text{Gd}_y\text{O}_{2-2/y}$ electrolytes for IT-SOFC operation at 500°C, *Solid State Ionics*, 129, pp.95-110
- Steele, B.C.H. (1996), Survey of materials selection for ceramic fuel cells II. Cathode and anode, *Solid State Ionics*, 86-88, pp. 1223-1234
- Tai, L.W., Nasrallah, M.M., Anderson, H.U., Sparlin, D.M., et al. (1995a), Structure and electrical properties of $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_3$ Part 1. The system $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{1-y}\text{Fe}_y\text{O}_3$, *Solid State Ionics*, 76, pp. 259-272
- Tai, L.W., Nasrallah, M.M., Anderson, H.U., Sparlin, D.M., et al. (1995b), Structure and electrical properties of $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_3$ Part 2. The system $\text{La}_{1-x}\text{Sr}_x\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$, *Solid State Ionics*, 76, pp. 273-283
- Takeda, Y., Kanno, R., Noda, M., Tomida, Y., Yamamoto, O. (1987), Cathodic polarisation phenomena of pervoskite oxide electrodes with stabilized zirconia, *Journal of the Electrochemical Society*, 134, pp. 2656-2660
- Tao, S., Irvine, J.T.S. (2002), Optimization of mixed conducting properties of $\text{Y}_2\text{O}_3\text{--ZrO}_2\text{--TiO}_2$ and $\text{Sc}_2\text{O}_3\text{--Y}_2\text{O}_3\text{--ZrO}_2\text{--TiO}_2$ solid solutions as potential SOFC anode materials, *Journal of Solid State Chemistry*, 165, pp. 12-18
- Tao, S., Irvine, J.T.S. (2003), A redox-stable efficient anode for solid oxide fuel cells, *Nature materials*, 2, pp. 320-323
- Tietz, F., Buchkremer, H.P., Stover, D. (2002), Components manufacturing for solid oxide fuel cells, *Solid State Ionics*, 152-153, pp. 373-381
- Torrens, R.S., Sammes, N.M., Tompsett, G.A. (1998), Characterisation of $(\text{CeO}_2)_{0.8}\text{--}(\text{GdO}_{1.5})_{0.2}$ synthesised using various techniques, *Solid State Ionics*, 111, pp. 9-15.
- Tsai, T., Barnett, S.A. (1997), Increased solid oxide fuel cell power density using interfacial ceria layers, *Solid State Ionics*, 98, pp.191-196
- Tsai, T., Barnett, S.A. (1998), Effect of mixed conducting layers on solid oxide fuel cell anode performance, *Journal of the Electrochemical Society*, 145(5), pp. 1696-1701

References

- Tsai, T., Perry, E., Barnett, S.A. (1997), Low-temperature solid oxide fuel cells utilizing thin bilayer electrolytes, *Journal of the Electrochemical Society*, 144(5), L130-L132.
- Uchida, H., Suzuki, S., Watanabe, M. (2003), in: *Proceedings of 8th International Symposium on Solid Oxide Fuel Cell*, edited by S.C. Singhal and M. Dokiya, The Electrochemical Society, Pennington, NJ, 2003, pp. 728-736
- van Doorn, R.H.E., Burggraaf, A.J. (2000), Structural aspects of the ionic conductivity of $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$, *Solid State Ionics*, 128, pp. 65-78
- Vazquez, J.C., Tao, S.W., Irvine, J.T.S. (2003), Electrical properties in $\text{La}_2\text{Sr}_4\text{Ti}_6\text{O}_{19-\delta}$: a potential anode for high temperature fuel cells, *Solid State Ionics*, 159, pp. 159-165
- Veen, A.C. Rebeilleau, M., Farrusseng, D., Mirodatos, C. (2003), Studies on the performance stability of mixed conducting BSCFO membranes in medium temperature oxygen permeation, *Chemical Communication*, pp. 32-33
- Virkar, A.V. (1991), Theoretical analysis of solid oxide fuel cells with two layer, composite electrolytes: electrolyte stability, *Journal of the Electrochemical Society*, 138(5), pp. 1481-1488
- Visco, S.J., Jacobson, C.P., Jonghe, L.C.D. (1999), Thin film fuel cells, in: *Proceedings of 6th International Symposium on Solid Oxide Fuel Cell*, edited by S.C. Singhal and M. Dokiya, The Electrochemical Society, Pennington, NJ, 1999, pp. 861-868
- Wachsman, E.D., Jayawera, P., Jiang, N., Lowe, D.M., et al. (1997), Stable high conductivity ceria/bismuth oxide bilayered electrolytes, *Journal of the Electrochemical Society*, 144(1), 233-236
- Waller, D., Lane, J.A., Kilner, J.A., Steele, B.C.H. (1996), The effect of thermal treatment on the resistance of LSCF electrodes on gadolinia doped ceria electrolytes, *Solid State Ionics*, 86-88, pp. 767-772
- Wang, H.B., Song, H.Z., Xia, C.R., Peng, D.K., et al. (2000), Aerosol-assisted MOCVD deposition of YDC thin films on (NiO+YDC) substrates, *Materials Research Bulletin*, 35, pp. 2363-2370
- Wang, L.S., Barnett, S.A. (1993), Sputter-deposited medium temperature SOFCs with multi-layer electrolytes, *Solid State Ionics*, 61, pp. 273-281
- Wang, S., Katsuki, M., Dokiya, M., Hashimoto, T. (2003), High temperature properties of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$ - phase structure and electrical conductivity, *Solid State Ionics*, 159, pp. 71-78
- Watanabe, M., Uchida, H., Shibata, M., Mochiauki, N., et al. (1994), High performance catalyzed-reaction layer for medium temperature operating solid oxide fuel cells, *Journal of the Electrochemical Society*, 141(2), pp. 342-346

References

- Weber, A., Tiffée, E.I. (2004), Materials and concepts for solid oxide fuel cells in stationary and mobile applications, *Journal of Power Sources*, 127, pp. 273-283
- Will, J., Mitterdorfer, A., Kleinlogel, C., Perednis, D., et al. (2000), Fabrication of thin electrolytes for second-generation SOFCs, *Solid State Ionics*, 131, pp. 79-96
- Wu, Z., Liu, M.L. (1998), Ag-Bi_{1.5}Y_{0.5}O₃ composite cathode materials for BaCe_{0.8}Gd_{0.2}O₃-based solid oxide fuel cells, *Journal of the American Ceramic Society*, 81(5), pp. 1215-1220
- Wu, Z.L., Liu, M.L. (1997), Modelling of ambipolar transport properties of composite mixed ionic-electronic conductors, *Solid State Ionics*, 93, pp. 65-84
- Xia, C.R., Liu, M.L. (2001a), A simple and cost-effective approach to fabrication of dense ceramic membranes on porous substrates, *Journal of the American Society*, 84(8), pp. 1903-1905
- Xia, C.R., Liu, M.L. (2001b), Low temperature SOFCs based on Gd_{0.1}Ce_{0.9}O_{1.95} fabricated by dry pressing, *Solid State Ionics*, 144, pp. 249-255
- Xia, C.R., Liu, M. L. (2002a), Microstructures, conductivities, and electrochemical properties of Ce_{0.9}Gd_{0.1}O₂ and GDC–Ni anodes for low-temperature SOFCs, *Solid State Ionics*, 152-153, pp. 423-430
- Xia, C.R., Liu, M.L. (2002b), Novel cathodes for low temperature solid oxide fuel cells, *Advanced Materials*, 14, pp. 521-523
- Xia, C.R., Chen, F.L., Liu, M.L. (2001) Reduced temperature solid oxide fuel cells fabricated by screen printing, *Electrochemical and Solid-State Letters*, 4, A52-A54
- Xia, C.R., Rauch, W., Chen, F.L., Liu, M.L. (2002), Sm_{0.5}Sr_{0.5}CoO₃ cathodes for low temperature SOFCs, *Solid State Ionics*, 149, pp. 11-19
- Xia, C.R., Zhang, Y.L., Liu, M.L. (2003), LSM-GDC composite cathodes derived from a sol-gel process: effect of microstructure on interfacial polarization resistance, *Electrochemical and Solid-State Letters*, 6(12), pp. 1-3
- Yahiro, H., Baba, Y., Eguchi, K., Arai, H. (1988), High temperature fuel cell with ceria-yttria solid electrolyte, *Journal of the Electrochemical Society*, 135(8), pp. 2077-2080
- Yamahara, K., Jacobson, C.P., Visco, S.J., Zhang, X.F., et al. (2005), Thin film SOFCs with cobalt-infiltrated cathodes, *Solid State Ionics*, 176, pp. 275-279
- Yamaji, K., Horita, T., Ishikawa, M., Sakai, N., et al. (1998), Compatibility of LSGM as the electrolyte for SOFCs, *Solid State Ionics*, 108, pp. 415-421
- Yamaji, K., Horita, T., Ishikawa, M., Sakai, N., et al. (1999), The chemical stability of LSGM at reducing atmosphere, *Solid State Ionics*, 121, pp. 217-223

References

- Yamamoto, O. (2000), Solid oxide fuel cells: fundamental aspects and prospects, *Electrochimica Acta*, 45, pp. 2423-2435
- Yamamoto, O., Arati, Y., Takeda, Y., Imanishi, N., et al. (1995), Electrical conductivity of stabilized zirconia with yttria and scandia, *Solid State Ionics*, 79, pp. 137-142
- Yan, J., Matsumoto, H., Enoli, M., Ishihara, T. (2005), High power SOFC using LSGM/SDC composite film, *Electrochemical and Solid State Letters*, 8(8), A389-A391
- Yang, J.C., Park, Y.S., Weo, S.H., Lee, H.J., et al. (2002), Development of a 50 kW PAFC power generation system, *Journal of Power Sources*, 106, pp. 68-75
- Yasuda, I., Ogasawara, K., Hishinuma, M., Kawada, T., et al. (1996), Oxygen tracer diffusion coefficient of (La, Sr)MnO₃, *Solid State Ionics*, 86-88, pp. 197-2001
- Yi, Y., Tao, A.D., Brouwer, J., Samuelsen, G.S. (2005), Fuel flexibility study of an integrated 25 kW SOFC reformer system, *Journal of Power Sources*, 144, pp. 67-76
- Yoshioka, T., Dosaka, K., Sato, T., Okuwaki, A., et al. (1992), Preparation of spherical ceria-doped tetragonal zirconia by the spray pyrolysis method, *Journal of Materials Science Letters*, 11, pp. 51-55
- Young, J. L., Etsell, T. H. (2000), Polarized electrochemical vapor deposition for cermet anodes in solid oxide fuel cells, *Solid State Ionics*, 135, pp. 457-462
- Zha, S.W., Moore, A., Abernathy, H., Liu, M.L. (2004), GDC-based low temperature SOFCs powered by hydrogen fuels, *Journal of the Electrochemical Society*, 151, A1128-A1133
- Zha, S.W., Xia, C.R., Meng, G.Y. (2003), Effect of Gd (Sm) doping on properties of ceria electrolyte for solid oxide fuel cells, *Journal of Power Sources*, 115, pp. 44-48
- Zha, S.W., Xia, C.R., Meng, G.Y. (2001), Calculation of the emf of solid oxide fuel cells, *Journal of Applied Electrochemistry*, 31, pp. 93-98
- Zha, S.W., Cheng, J.G., Fu, Q.X., Meng, G.Y. (2002), Ceramic fuel cells based on ceria-carbonate salt composite electrolyte, *Materials Chemistry and Physics*, 77, pp. 594-597
- Zhang, T. (2002), Development, characterization of ceramics for solid oxide fuel cell, Ph. D. thesis, Nanyang Technological University, Singapore
- Zhang, T., Hing, P., Huang, H., Kilner, J. (2002), Ionic conductivity in the CeO₂-Gd₂O₃ system prepared by oxalate co-precipitation, *Solid State Ionics*, 148, pp. 567-573
- Zhang, T., Ma, J., Kong L.B., Chan S.H. (2004), Effect of SiO₂ on the ionic conductivity of CGO ceramics, *Journal of Materials Science*, 39, pp. 6371-6373

References

- Zheng, K., Steele, B.C.H., Sahibzada, M., Metcalfe, I.S. (1996), Solid oxide fuel cells based on CGO electrolytes, *Solid State Ionics*, 86-88, pp. 1241-1244
- Zhitomirsky, I., Petric, A. (2000), Electrophoretic deposition of ceramic materials for fuel cell applications, *Journal of the Electrochemical Society*, 20, pp. 2055-2061
- Zhou, X.D., Huebner, W., Kosacki, I., Anderson, H.U. (2002), Microstructure and grain boundary effect on electrical properties of gadolinium-doped ceria, *Journal of the American Ceramic Society*, 85(7), pp.1757-1762
- Zhou, X.D., Scarfino, B., Anderson, H.U. (2004), Electrical conductivity and stability of Gd-doped ceria/Y-doped zirconia ceramics and thin films, *Solid State Ionics*, 175, pp.19-22
- Zhu, B. (1999), Fast ionic conducting film ceramic membranes with advanced applications, *Solid State Ionics*, 119, pp. 305-310
- Zhu, B., Yang, X.T., Xu, J., Zhu, Z.G., et al. (2003), Innovative low temperature SOFCs and advanced materials, *Journal of Power Sources*, 118, pp. 47-53
- Zhu, W.Z., Deevi, S.C. (2003), A review on the status of anode materials for solid oxide fuel cells, *Materials Science and Engineering*, A362, pp. 228-239

APPENDIX A

Reliability analysis of impedance measurements for cathode optimisation

A technical measurement involves measuring equipment, sample and measuring conditions. Fluctuations in any of them will result in errors of the measurement results. Generally, differences observed in the measurement results are regarded due to significant change of sample and/or measuring conditions only if they are well outside the range of measurement errors.

To get information about errors in the cathode optimization study, the electrochemical system (Autolab PG30/FRA, Eco Chimie, Netherlands) was first examined using a dummy cell by impedance spectroscopy measurement. The dummy cell has a configuration of $R(RC)$. The measurement was carried out continuously for three times at room temperature in a frequency window of 100 kHz to 0.1 Hz. Figure 1 shows the impedance spectra. The three impedance spectra are totally overlaid, indicating that the error of the electrochemical system in impedance measurement is negligible. Then, the error due to sample and measuring conditions fluctuations was checked. Three half-cell samples with porous LSCF cathodes on GDC electrolytes were prepared using identical processing procedures as presented in Chapter 3 (Experimental Procedure) of the thesis. All the three LSCF cathodes were sintered at 900°C for 2 h. Figure 2 shows the impedance spectra of the three cathodes measured at 600°C in air under identical conditions. The high frequency intercept represents the electrolyte resistance, while the high and low frequency intercept difference represents the interfacial polarization resistance. The difference of the high frequency intercept may be

due to the electrolyte thickness variation. The polarization resistances of the three samples are determined as 2.78, 2.38 and 3.05 Ωcm^2 , respectively. The average value is 2.74 Ωcm^2 and the relative error is about 13%. This indicates that the impedance change caused by sample fluctuation is much smaller than the observed impedance change due to variations of sintering temperature and cathode composition (up to 9 times). Therefore, the previous optimization results are reliable, which reflect significant changes of the electrochemical activity of the LSCF cathodes due to variations of sintering temperature and GDC addition.

Figure 1 Impedance spectra of a R(RC) dummy cell measured for three times.

Figure 2 Impedance spectra of three similar LSCF cathodes measured at 600°C in air under identical conditions.