Development of cathode materials for intermediate temperature solid oxide fuel cells

Wang, Wei

2006

Wang, W. (2006). Development of cathode materials for intermediate temperature solid oxide fuel cells. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/47165>

<https://doi.org/10.32657/10356/47165>

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DEVELOPMENT OF CATHODE MATERIALS FOR INTERMEDIATE TEMPERATURE SOLID OXIDE FUEL CELLS

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

2006

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ACKNOWLEDGEMENTS

The author would like to express his sincere gratitude to his supervisor, Prof. Jiang San Ping, for his guidance, inspiration and encouragement throughout the period of this work. The author has learnt much from his expertise in the field of solid state electrochemistry and ceramic fuel cells. The author would also like to sincerely thank Prof. Chan Siew Hwa, director of Fuel Cell Laboratory, for his inspiring discussions and generous help on this work.

His sincere thanks also extend to Dr. Chen Xiaojun, Dr. Xia Zetao and Dr. Leng Yongjun, for their valuable discussions and help in carrying out this work. Thanks are also due to his colleagues: Mr. Liu Zengcai, Mr. Zhen Yongda, Mr. Liu Qinglin, Ms. Xu Jianhong, Mr. Ding Ovi Lian, Mr. Tun Win Aung, and other research students and post doctoral fellows, for their supports and unforgettable friendship.

Acknowledgements are also extended to all technicians in Fuel Cell Laboratory, Materials Laboratory and Thermodynamics Laboratory: Ms. Ho Agnes, Mr. Leong Kwok Phui, Ms. Yong Mei Yoke, Mr. Chan Ming Jiu, Mr. Cheong Yuen Kong, for their technical assistance.

Finally, the author would like to express sincere thanks to his beloved wife, Lin Cuiting, for her endless support and encouragement over the past years.

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SUMMARY

Development of high-performance cathode materials is critical to the commercialization of solid oxide fuel cell (SOFC) technology. This raises the urgent need on the better understanding of the fundamental issues of the materials and the electrochemistry that is involved. This work aims to study the effect of polarisation treatments on the electrode behaviour and the microstructure of (La,Sr)MnO₃ (LSM) electrodes, the most commonly used cathode material in SOFC, and to develop high-performance and LSM-based cathodes for intermediate temperature SOFC.

The activation processes of LSM cathodes are systematically investigated under various polarisation conditions. A new mechanism is proposed with the consideration of the surface segregation of Sr species and a modified defect model of LSM. The initially very high electrode polarisation resistance of LSM for the O₂ reduction is most likely related to the surface enriched SrO species, which can be incorporated into the LSM lattice (La/Sr site) under cathodic potential, leading to the significantly enhanced electrochemical activity for the O₂ reduction. Anodic polarisation appears to have opposite effect, i.e., the Sr ions can be pushed out from LSM lattice sites and segregate again onto the LSM surface, leaving cation vacancies on La/Sr sites. Under open circuit condition, segregation of Sr species onto the LSM surface could still occur probably due to the electrical neutrality requirement of oxygen excess in the LSM lattice. This is supported by the very slow relaxation process of the LSM cathodes after the interruption of the cathodic polarisation/current passage. The proposed mechanism of the activation processes has significant implication on the O₂

reduction reaction on LSM cathodes.

The application of cathodic and anodic polarisation can also induce microstructural and morphological changes within LSM bulk phase and at the LSM/YSZ interface region. The original large agglomerates in freshly prepared LSM electrodes are broken down into sphere-shaped grains when exposed to cathodic or anodic current passage. Microstructural changes under cathodic polarisation could be related to the LSM lattice expansion and the pronounced diffusion and migration of oxygen vacancies and Mn ions on the LSM surface, while lattice shrinkage under oxidation conditions most likely contributes to the structural changes under anodic polarisation. Such morphological changes are irreversible and have been found to be beneficial to the performance of LSM electrodes. Cathodic or anodic polarisation treatments can also cause the change of the interface between LSM electrode and YSZ electrolyte. This is indicated by the broadening of the convex rings, which are formed at the O₂/LSM/YSZ three phase interface during the fabrication of LSM cathodes. The similar change in the morphology and topography of the convex ring areas under cathodic and anodic polarisation conditions indicates that the convex rings are most likely the reaction sites for the O₂ incorporation/diffusion between LSM electrode and YSZ electrolyte.

The investigation of the grain growth and sintering behaviour of LSM electrodes under polarisation and open circuit conditions reveals that LSM electrodes with the A-site deficient composition show higher sinterability than that with A-site stoichiometric composition. Under cathodic polarisation condition, the grain growth of LSM electrodes is significantly smaller than that at open circuit under the same

temperature for all the compositions studied. The hindrance of sintering under cathodic polarisation has been attributed to the elimination of the cation vacancies on the A-sites, thus reducing the driving force for the sintering.

Novel structured mixed ionic and electronic conducting cathodes has been developed, based on the LSM electronic conducting structure impregnated with GDC ionic conducting phase. The ion impregnation of oxygen ion conducting GDC phase significantly enhances the electrocatalytic activity of LSM electrodes for the O_2 reduction reaction. With the impregnation of 5.8mgcm^{-2} GDC in the LSM electrode coating, the electrode shows much lower electrode polarisation resistance as compared to those of LSM/YSZ and LSM/GDC composite cathodes and the performance is comparable with those of mixed ionic and electronic conducting oxides such as $(\text{La,Sr})(\text{Co,Fe})\text{O}_3$ and $(\text{Gd,Sr})\text{CoO}_3$. This is most likely due to the unique combination of the high electronic conducting LSM porous structure with high ionic conducting nano-sized GDC phase.

Finally GDC impregnation method is also applied on the Ni anode for the direct utilization of methane in SOFC. GDC-impregnated Ni anode has been found to be very stable when exposed to weakly humidified ($\sim 3\%\text{H}_2\text{O}$) methane under open circuit at 800°C , as compared to Ni and Ni/GDC cermet anodes. The stability of GDC-impregnated Ni in wet methane can be further improved when an anodic current load of 20mAcm^{-2} is applied. The results indicate that through proper composition optimization and materials engineering of the electrode structure, Ni-based anodes can be used for SOFC based on natural gas fuel.

LIST OF ABBREVIATIONS

AFM	Atomic Force Microscopy
CPE	Constant Phase Element
EDS	Energy Dispersive Spectroscopy
EIS	Electrochemical Impedance Spectroscopy
GCI	Galvanostatic Current Interruption
GDC	Gadolinium-doped Ceria
IT-SOFC	Intermediate Temperature Solid Oxide Fuel Cell
LSC	$\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$
LSCF	$\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_3$
LSM	$\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$
MIEC	Mixed Ionic and Electronic Conductor
OCV	Open Circuit Voltage
SDC	Samarium-doped Ceria
SEM	Scanning Electron Microscope
SOFC	Solid Oxide Fuel Cell
TEC	Thermal Expansion Coefficient
TPB	Three-phase Boundary
TPBL	Three-phase Boundary Line
TZ3Y	3mol% Y_2O_3 - ZrO_2
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction
YSZ	Yttria-stabilized Zirconia

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CHAPTER 1.

INTRODUCTION

1.1 Fuel Cell

Recently, with the revelation of serious environmental problems on a global scale caused by the fossil fuel consumption, it has become urgent to develop highly efficient system for fossil fuel energy conversion. Traditional conversion to electrical energy is by gas turbine, steam turbine or reciprocating engine driving a generator, where the Carnot-cycle sets a limit to the efficiency.

A fuel cell is a radically different way of making electrical power from a variety of fuels. A fuel cell is an energy conversion device that produces electricity (and heat) directly from a gaseous fuel by electrochemical combination of the fuel and the oxidant. Such a device bypasses the conversion from chemical energy of the fuel to thermal and mechanical energy, and thus achieves theoretical efficiency significantly higher than that of conventional methods of power generation. In addition to the high conversion efficiency, fuel cells have characteristics of environmental compatibility, modularity, siting flexibility, and multi-fuel capability (*Minh, 1995*).

The discovery of the fuel cell is ascribed to Sir William Grove, who

demonstrated the reversibility of electrolytic water separation in 1839. Originally, fuel cells were considered of little practical use, as the power density was low and other power sources were available. In the middle of twentieth century, the development of fuel cells accelerated. Several types of fuel cell were developed in the global race for the space program. In the nineteen eighties, focus on pollution and demand for higher efficiency in the exploitation of fossil resources initiated a new wave of fuel cell development.

Nowadays, five types of fuel cells, namely, Alkaline Fuel Cell (AFC), Polymer Electrolyte Fuel Cell (PEFC), Phosphoric Acid Fuel Cell (PAFC), Molten Carbonate Fuel Cell (MCFC), and Solid Oxide Fuel Cell (SOFC) have been investigated extensively. Some of the characteristics of each of these fuel cell types are listed in Table 1.1.

Table 1.1 Some characteristics of five common types of fuel cells

	AFC	PEFC	PAFC	MCFC	SOFC
Operation Temperature	<100℃	60-120℃	160-220℃	600-800℃	600-1000℃
Fuel	Highly pure H ₂	Pure H ₂	CO-free H ₂	H ₂ , CH ₄ , CO	H ₂ , CH ₄ , CO
Electrolyte	KOH	Polymer	H ₃ PO ₄	Molten Li ₂ CO ₃ -K ₂ CO ₃	ZrO ₂ +Y ₂ O ₃
Charge carrier	OH ⁻	H ⁺	H ⁺	CO ₃ ²⁻	O ²⁻
Operating pressure	1 to 10atm	1 to 5atm	1 to 8atm	1 to 3atm	1atm
Contaminant tolerance	No CO, CO ₂ No sulfur	<50ppm CO No sulfur	<1 to 2% CO <50ppm sulfur	<ppm sulfur	<10-100ppm sulfur

These fuel cells are characterized by the electrolyte used, which in turn determines the operating temperature. Low temperature fuel cells (AFC, PEFC and

PAFC) have a potential for automobile propulsion, where the time of heat-up must be low and the efficiency has to be compared with about 20-30% for a combustion engine. High temperature fuel cells (MCFC and SOFC) are suited to continuous power production, where the cell temperature can be maintained. In combination with a gas turbine, MCFC and SOFC can reach a total efficiency which is a factor of two higher than a coal-based power plant.

1.2 Solid Oxide Fuel Cell

1.2.1 Operation principles

A solid oxide fuel cell is an all-solid-state energy conversion device that produces electricity by electrochemically combining fuel and oxidant gases across an ionic conducting ceramic. Its operation principle is illustrated in Fig 1.1. An oxide ion conducting ceramic electrolyte membrane is provided with two electrodes, i.e., the

Fig 1.1 Solid Oxide Fuel Cell Operation Principle (*Fuel Cell Handbook, 2000*)

anode and the cathode. Fuel is fed to the anode, undergoes an oxidation reaction, and releases electrons to the external circuit. Oxidant is fed to the cathode, accepts electrons from the external circuit, and undergoes a reduction reaction. The electron flow (from the anode to the cathode) produces direct-current electricity.

The SOFC electrolyte has to be gas impermeable to avoid direct mixing and combustion of the gases. Both the electrolyte and the electrodes are often based on ceramic materials. Table 1.2 summarises the commonly used materials for SOFC construction.

A SOFC single cell can produce current as long as the reactants (fuel and oxidant gases) are provided to the electrodes. However, under typical operating conditions,

Table 1.2 Materials for SOFC components

SOFC component	Material composition	Abbreviation	Main requirements
Electrolyte	$(\text{ZrO}_2)_{1-x}(\text{Y}_2\text{O}_3)_x$	YSZ	1. High ionic conductivity
	$(\text{CeO}_2)_{1-x}(\text{Gd}_2\text{O}_3)_x$	GDC	2. Chemical and dimensional stability in both reducing and oxidizing environments
	$(\text{La,Sr})(\text{Ga,Mg})\text{O}_3$	LSGM	3. Impermeable to reacting gases
Cathode	$(\text{La,Sr})\text{MnO}_3$	LSM	1. High electronic conductivity
	$(\text{La,Sr})(\text{Co,Fe})\text{O}_3$	LSCF	2. Chemical and dimensional stability in oxidizing environment
	$(\text{Sm,Sr})\text{CoO}_3$	SSC	3. Sufficient porosity
Anode	Ni/YSZ cermet	Ni/YSZ	1. High electronic conductivity
	Ni/GDC cermet	Ni/GDC	2. Chemical and dimensional stability in reducing environment
	$(\text{La,Sr})(\text{Cr,Mn})\text{O}_3$	LSCM	3. Sufficient porosity
Interconnect	$(\text{La,Sr})\text{CrO}_3$	LSC	1. High electronic conductivity
	$\text{Fe}_{1-x}\text{Cr}_x$	Cr alloy	2. Chemical and dimensional stability in both reducing and oxidizing environments 3. Impermeable to reacting gases

the voltage output of a single cell is less than 1V. Therefore, practical SOFCs are not operated as single units; rather, they are connected in electrical series in a stack to build up voltage. A stack can in principle comprise any number of cells depending on the desired output, and a fuel cell plant can be designed in modules of stacks connected in series and/or parallel. Fig 1.2 shows two commonly used SOFC designs. One is a tubular design where the electrolyte is supported by a porous tube of the cathode or anode material (Westinghouse seal-less tubular design or

Fig 1.2 Schematic of different SOFC designs (Minh, 1995)

segmented-in-series). The other design is the flat plate design which is more compact, but more problematic in terms of gas manifolding. Other designs also exist, but most of them are derivations of the two main types described above.

1.2.2 Advantages and Challenges

In general high temperature fuel cells (e.g. MCFC and SOFC) exhibit higher efficiency and are less sensitive to fuel purity than low temperature fuel cells. At high temperatures hydrocarbon fuels can be applied directly as a fuel. Comparing the two types of high temperature fuel cells, an unfortunate property of MCFC must be considered. The presence of a molten alkaline salt poses considerable problems with corrosion and creep, and the risk of contaminating an internal reforming catalyst. On the contrast, the key characteristic of the SOFC is its ceramic electrolyte. The use of a solid electrolyte in the SOFC eliminates materials corrosion and electrolyte management problems and permits unique cell designs with performance improvements. Based on the characteristics of various types of fuel cell, Solid Oxide Fuel Cells are chosen for further investigation in this project.

However, the traditionally high operation temperature ($\sim 1000^{\circ}\text{C}$) would cause significant degradation of SOFC components. Therefore, it becomes increasingly important to reduce the operation temperature to $600\text{-}800^{\circ}\text{C}$ in order to enable the use of less expensive materials for SOFC components such as the interconnect and manifolds, and to greatly increase the materials stability and thus to reduce the cost of SOFC. One of the major obstacles in the development of intermediate temperature

SOFC is the high polarisation losses on the electrodes of SOFC. This could be circumvented either by identification of new electrode materials with high electrocatalytic activity, or by continuous modification/improvement of existing materials such as LSM cathodes or Ni anodes. The advantages of existing electrode materials are their proven electrocatalytic activity at high temperatures and good chemical and dimensional stability especially under long term operation conditions.

1.3 Objective

The aim of this project is to develop cathode materials based on conventional LSM perovskite for the application in intermediate temperature SOFC (IT-SOFC). For this purpose, a better understanding on the factors influencing the electrochemical properties of LSM cathodes is essential. Thus, the objectives of this project are to:

- Study the effect of polarisation on the electrode behaviour and microstructure of LSM cathodes;
- Develop high-performance LSM-based cathodes for intermediate temperature SOFC.

1.4 Scopes

The scopes of the research project are outlined as below:

[1]. Investigation on the activation process of LSM cathodes, in particular

- Initial polarisation behaviour of LSM cathodes

- Relaxation behaviour of LSM electrodes
 - Effect of surface status of LSM on the polarisation behaviour
 - Identification of elementary processes for oxygen reduction on LSM cathodes
 - Microstructural characterisation of LSM electrodes under polarisation
 - Topographical examination at LSM/YSZ interface under polarisation
- [2]. Investigation on the sintering behaviour of LSM cathodes, in particular
- Effect of stoichiometry
 - Effect of polarisation conditions
- [3]. Development of LSM-based cathodes for IT-SOFC, in particular
- Fabrication of novel structured LSM-based cathodes by ion impregnation with GDC oxides
 - Microstructural and electrochemical characterisation on GDC-impregnated LSM cathodes
 - Comparative study on the reaction mechanism of oxygen reduction on pure and GDC-impregnated LSM cathodes
- [4]. Development of Ni-based anodes for IT-SOFC, in particular
- Fabrication of novel structured Ni-based anodes by ion impregnation with GDC oxides
 - Evaluation of GDC-impregnated Ni anodes for the direct utilization of methane in SOFC

1.5 Thesis Layout

Chapter 2 is the literature review which comprises the properties of LaMnO_3 -based oxide materials and the recent research activities on LSM-based SOFC cathodes. Chapter 3 contains a general description of the experimental procedures and measurement techniques. From Chapter 4 to Chapter 7, a systematic investigation on the polarisation behaviour of LSM was carried out on various aspects, namely, the origin of activation/deactivation effect of polarisation treatments (Chapter 4), microstructural and morphological changes of LSM cathodes induced by polarisation (Chapter 5), the influence of polarisation on LSM/YSZ interface topography (Chapter 6), and the effect of cathodic polarisation on the sintering behaviour of LSM cathodes (Chapter 7). Chapter 8 presents the development of LSM-based cathode material for intermediate temperature SOFC with ion impregnation method. Chapter 9 shows some preliminary results on the direct utilization of methane with GDC-impregnated Ni anodes. Finally in Chapter 10, the conclusions are summarised together with the major achievements in this work and recommendations for further investigations.

CHAPTER 2.

LITERATURE REVIEW

2.1 LaMnO₃-based Perovskite Oxides

Doped LaMnO₃ has been extensively used as a cathode material in solid oxide fuel cells, owing to its relatively high electrical conductivity in oxidizing atmosphere, high catalytic activity for O₂ reduction and good chemical and thermal compatibility with the commonly used YSZ electrolyte.

2.1.1 Phase Structure and Stability

LaMnO₃ belongs to the class of compounds having a perovskite structure with the general formula ABO₃ (A is a divalent or trivalent cation and B is a tetravalent or trivalent cation). The ideal perovskite structure is cubic, as shown in Fig 2.1, while LaMnO₃-based oxides may undergo atomic distortion leading to orthorhombic, rhombohedral or tetragonal unit cells.

Undoped stoichiometric LaMnO₃ is orthorhombic at room temperature and shows an orthorhombic/rhombohedral crystallographic transformation at about 600°C. This transformation has been attributed to the oxidation of some Mn³⁺ to Mn⁴⁺ ions.

Fig 2.1 Perovskite Structure, ABO_3 (Galasso, 1990)

Doping a lower-valence cation for lanthanum and manganese sites increases the Mn^{4+} concentration in $LaMnO_3$, thus affecting the transformation temperature (Minh, 1995). It is reported that $La_{1-x}Sr_xMnO_{3-\delta}$ displays three lattice types: rhombohedral ($0 \leq x \leq 0.5$), tetragonal ($x=0.5$) and cubic ($x=0.7$) (Li, 1993).

At the SOFC operating temperature, $LaMnO_3$ is stable in oxidizing atmospheres but decomposes under highly reducing conditions. The lowest oxygen partial pressure before $LaMnO_3$ decomposes into multiple phases is termed the critical oxygen partial pressure and is dependent on both dopant level and nonstoichiometry (A/B ratio). Generally, high dopant content results in reduced stability in $LaMnO_3$ (Minh, 1995). Table 2.1 summarised the optimised window for single phase LSM materials. As A/B

Table 2.1 Possible single LSM perovskite phase region in the (La, Sr) MnO_3 system (Zheng, 1999)

A/B	0.900	0.925	0.950	0.980	1.000	1.020	1.050	1.100
Sr	<0.600	<0.500	<0.400	<0.400	<0.400	<0.200	<0.100	No

ratio increases, a smaller Sr content is allowed for single LSM perovskite phase. Possible secondary phases include Mn_3O_4 , $(\text{La}, \text{Sr})\text{Mn}_2\text{O}_4$, La_2O_3 , $\text{La}(\text{OH})_3$, $(\text{La}, \text{Sr})_3\text{Mn}_2\text{O}_7$, $(\text{La}, \text{Sr})_2\text{MnO}_4$.

2.1.2 Electrical Conductivity

LaMnO_3 -based oxides are generally considered as pure electronic conductors with negligible ionic conductivity. For undoped stoichiometric LaMnO_3 , due to the formation of cation vacancies (Kamata, 1995), the material has an intrinsic p -type electronic conductivity of about 10^{-4}Scm^{-1} at room temperature and 0.1Scm^{-1} at 700°C (Minh, 1995).

Substitution of a lower-valence cation such as strontium or calcium, on either the A or B sites, is generally used to enhance the electronic conductivity of LaMnO_3 . The addition of strontium has a two-fold effect on the electrical conductivity. In one aspect, replacement of trivalent lanthanum ions by divalent strontium ions leads to the

Fig 2.2 (a) Temperature dependence with $P_{\text{O}_2} = 1\text{atm}$ and (b) P_{O_2} dependence at 1273K of the electronic conductivity of strontium-doped LaMnO_3 (Mizusaki, 2000a)

formation of acceptors, i.e., electron holes, which, as a consequence, results in a change of the valency of manganese ions from 3+ (base valency of manganese in LaMnO_3) to 4+, as required by the lattice charge neutrality condition:

The oxide has p -type electronic conductivity at higher P_{O_2} . On the other hand, the addition of strontium results in an increase of the concentration of oxygen vacancies, which act as donors. Their effect on conductivity becomes dominant at lower P_{O_2} values. Fig 2.2 shows the effect of Sr substitution on the electronic conductivity of LSM at different temperatures and oxygen partial pressures.

Similar to strontium doping, calcium doping significantly enhances the electronic conductivity of LaMnO_3 , and the conductivity of the calcium-doped compound also occurs via a small polaron hopping mechanism. The substitution of Ca for La sites increases conductivity with the Ca content up to 50mol%. Further substitution decreases the conductivity. The maximum conductivity at 1000°C was found to be 90 S/cm for $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_{3-x}$ (Yamamoto, 1993). Table 2.2 summarises some electronic

Table 2.2 Electronic conductivity data of some doped LaMnO_3

Dopant (MO)	Composition (mol%MO)	Conductivity at 1000°C ($\Omega^{-1}\text{cm}^{-1}$)	Activation energy (kJ/mol)	Ref.
SrO	10	130	15.4	Kua, 1990
SrO	20	175	8.7	Kua, 1990
SrO	50	290	4.5	Mackor, 1991
CaO	25	165	11.6	Mackor, 1991
CaO	45	240	7.9	Mackor, 1991
NiO	20	100	18.6	Lyybkina, 1986
SrO, Cr_2O_3	10, 20	25	13.5	Koc, 1992
SrO, Co_2O_3	20, 20	100	---	Stochniol, 1999

conductivity data of doped LaMnO_3 oxides.

2.1.3 Thermal Expansion

Table 2.3 lists the thermal expansion coefficient (TEC) of doped and undoped LaMnO_3 and TEC varies in the range of $9.5 \times 10^{-6}/\text{K}$ to $14.5 \times 10^{-6}/\text{K}$. The average linear thermal expansion coefficient of the most commonly used YSZ electrolyte is approximately $10.3 \times 10^{-6}/\text{K}$ in the temperature range from 50 to 1000°C in air or in H_2 atmosphere (Mori, 1999). The TEC of Y_2O_3 -stabilised ZrO_2 is nearly unaffected by the oxygen partial pressure and Y_2O_3 composition. Therefore, it is important that the cathode should match TEC of the YSZ electrolyte.

Lanthanum deficiency and oxygen nonstoichiometry appear to lower the thermal expansion of the perovskite oxide (Minh, 1995). Doping LaMnO_3 with strontium increases the material thermal expansion coefficient, and the coefficient increases

Table 2.3 Thermal expansion coefficient of doped- LaMnO_3

Composition	Thermal expansion coefficient ($10^{-6}/\text{K}$)	Ref.
LaMnO_3	11.2	Mori, 1999
CaMnO_3	17.5	Mori, 1999
SrMnO_3	9.8	Mori, 1999
$\text{La}_{0.99}\text{MnO}_3$	11.2	Srilomsak, 1989
$\text{La}_{0.9}\text{Sr}_{0.1}\text{MnO}_3$	12.0	Srilomsak, 1989
$\text{La}_{0.79}\text{Sr}_{0.20}\text{MnO}_3$	12.4	Srilomsak, 1989
$\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$	13.2	Srilomsak, 1989
$\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_{3-z}$	9.92	Yamamoto, 1993
$\text{La}_{0.4}\text{Ca}_{0.6}\text{MnO}_{3-z}$	11.84	Yamamoto, 1993
$\text{La}_{0.65}\text{Sr}_{0.3}\text{MnO}_{3-x}$	12.3	Ullmann, 2000
$\text{La}_{0.75}\text{Sr}_{0.2}\text{Mn}_{0.9}\text{Co}_{0.1}\text{O}_3$	11.5	Stochniol, 1999
$\text{La}_{0.75}\text{Sr}_{0.2}\text{Mn}_{0.8}\text{Co}_{0.2}\text{O}_3$	9.5	Ullmann, 2000
$\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{0.7}\text{Cr}_{0.3}\text{O}_3$	14.5	Palma, 1991

with increasing strontium content.

2.1.4 Defect Chemistry

Lanthanum manganite exhibits a complicated defect structure, which includes oxygen nonstoichiometry and lanthanum nonstoichiometry. The predominant lattice defects and their concentrations strongly depend upon the oxygen partial pressure, P_{O_2} , operating temperature, and even the material processing conditions.

In general, LaMnO_3 -based oxides prepared in air or in an oxygen atmosphere contain excess oxygen and can be denoted by $\text{La}_{1-x}\text{A}_x\text{MnO}_{3+\delta}$ (A: divalent cations, such as Sr^{2+} , Ca^{2+}). The amount of δ is experimentally known to decrease with increasing doping level x at the La site to keep the Mn^{4+} proportion at nearly constant values, i.e., 26-36% (Nakamura, 2002). In reducing atmospheres, the material becomes oxygen deficient. Under highly reducing conditions, LaMnO_3 dissociates into La_2O_3 and MnO , and the dissociation is not reversible (Kuo, 1989).

Sr-doped LaMnO_3 (LSM) is studied in detail with oxygen nonstoichiometry

Fig 2.3 Oxygen nonstoichiometry of (a) $\text{LaMnO}_{3\pm\delta}$ (Mizusaki, 2000b) and (b) $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3\pm\delta}$ at 1273K (Yasumoto, 2001)

(Nowotny, 1998; Mizusaki, 2000b; Yasumoto, 2001). There are three regions in oxygen nonstoichiometry, $\delta > 0$, $\delta = 0$, and $\delta < 0$ against P_{O_2} , as shown in Fig 2.3. At the oxygen excess region, $\delta > 0$, there are metal-like defects, and the oxide ion lattice is filled with oxide ions. At high oxygen partial pressure, in order to compensate for the electrical neutrality raised by Mn oxidation, there can be two possibilities: the interstitial oxide ions or the cation site vacancies. It is noted that the perovskite lattice is a close-packed structure which is difficult to accommodate interstitial oxide ions. Neutron powder diffraction (NPD) results indicate that cation site vacancies, rather than oxygen interstitials, are responsible for the oxygen nonstoichiometry with $\delta > 0$ (Mitchell, 1996). Cation vacancies can form on both the La and Mn sites, though tending towards more La vacancies (de Souza, 1999; Mizusaki, 2000b). The cation movement can bring about the compositional inhomogeneity due to different mobility of the cations. This could affect the long-term stability of the SOFC. Moreover, the cation defect relaxation within cathode materials during long-time operation is accompanied by the lattice creation or annihilation on repeatable sites such as a grain-boundary, and the specimen surface, and thus results in undesirable morphological changes. The study on the creep of $La_{1-x}Sr_xMnO_{3+\delta}$ ceramics revealed that the deformation of the ceramics was most likely controlled by the lattice diffusion of cation defects (Wolfenstine, 1996). In $La_{0.96}MnO_{2.94+\delta}$ oxide, manganese oxide particles were found to precipitate along grain boundaries after long-term heat treatment in oxygen atmosphere at 1273K. This was ascribed to the relaxation of cation vacancy defects (Miyoshi, 2002). To date, the formation and migration of cation defects in $LaMnO_3$

are until not fully understood.

In addition to oxygen nonstoichiometry, LaMnO_3 can also exhibit lanthanum deficiency or excess. LaMnO_3 with lanthanum excess may contain La_2O_3 second phase, which tends to be hydrated to $\text{La}(\text{OH})_3$, or to react with ZrO_2 to form the resistive phase $\text{La}_2\text{Zr}_2\text{O}_7$. Both the hydration and the formation of $\text{La}_2\text{Zr}_2\text{O}_7$ are undesirable for SOFC applications. LaMnO_3 can have up to about 10% lanthanum deficiency without second phase formation. Above this level, Mn_3O_4 is present as the second phase (Nishiyama, 1996). In fact, a surplus of manganese is always used in the fabrication of SOFC electrodes to prevent the reaction between La_2O_3 from the cathode and ZrO_2 from the electrolyte.

2.1.5 Chemical Interaction

The high operation and even higher fabrication temperatures of SOFC raise concerns regarding the chemical compatibility of LaMnO_3 cathode with other cell components, especially the YSZ electrolyte. Such high-temperature heat treatments enable mobile species, e.g. Mn, to react or interdiffuse with adjoining components and thus result in changes on the electrical characteristics or the structure of both the cathode and the electrolyte.

No significant reactions between LaMnO_3 and ZrO_2 have been observed at temperatures below 1200°C . Above 1200°C , the lanthanum manganite reacts with ZrO_2 to produce $\text{La}_2\text{Zr}_2\text{O}_7$. The presence of a dopant in LaMnO_3 suppresses the manganese migration. Thus, substitution of lanthanum in the manganite with a low

dopant concentration reduces the $\text{La}_2\text{Zr}_2\text{O}_7$ formation (Tainatsu, 1992). However, high dopant concentration results in the formation of second phases such as SrZrO_3 , CaZrO_3 . The formation of $\text{La}_2\text{Zr}_2\text{O}_7$ and other second phases at the $\text{LaMnO}_3/\text{YSZ}$ interface is undesirable in SOFCs; these compounds can deleteriously affect the cell performance because they can both act as insulating layers and create thermal stresses at the interface. The electrical conductivity of $\text{La}_2\text{Zr}_2\text{O}_7$ and SrZrO_3 is several orders of magnitude lower than that of LaMnO_3 .

For Sr-doped LaMnO_3 , no significant reactions between LSM and ZrO_2 have been observed at temperatures below 1100°C ; above 1100°C , a reaction occurred at the interface where the major reaction product was $\text{La}_2\text{Zr}_2\text{O}_7$. A small amount of SrZrO_3 was also detected (Chen, 1993a; Kleveland, 1999). Moreover, the products of the inter-reaction between LSM electrodes and the YSZ electrolyte depend strongly on the Sr dopant concentration. For low Sr levels ($<40\text{mol}\%$) the reaction product is the $\text{La}_2\text{Zr}_2\text{O}_7$ phase while at higher Sr levels ($>40\text{mol}\%$) the SrZrO_3 phase exists.

A proposed mechanism for the interaction suggests that manganese could diffuse into the YSZ, resulting in lanthanum excess at the interface, which then reacts with the YSZ to form zirconate (Tainatsu, 1992). Thus, for SOFC application, A-site deficiency in LSM electrodes is preferred to minimize the reaction between LSM and YSZ. The excess Mn allows for Mn diffusion into the YSZ electrolyte without causing lanthanum excess. Nucleation and growth of the lanthanum zirconate could be controlled by controlling the amount of excess manganese (Mitterdorfer, 1998). When the excess manganese is up to 10%, $\text{La}_2\text{Zr}_2\text{O}_7$ formation was not observed,

after sintering at 1373K for 12hr. However, diffusion of Mn into zirconia was observed along YSZ grain boundaries in the early stage of the interface reaction, subsequently enhancing the Sr diffusion also along the YSZ grain boundaries, and resulting in the formation of SrZrO_3 in the case of high Sr dopant level (Kleveland, 1999).

In addition to the reaction with YSZ, doped LaMnO_3 may react with doped LaCrO_3 -based interconnect at high operating temperatures. Strontium and calcium dopants in LaCrO_3 tend to migrate to the interface to form compounds such as $(\text{Sr}, \text{La})_3\text{Mn}_2\text{O}_7$ and $(\text{Ca}, \text{La})_3\text{Mn}_2\text{O}_7$ (Yokokawa, 1991).

2.2 Processing of SOFC cathodes

The fabrication method is important in current SOFC technology. Any SOFC stack design requires appropriate ceramic fabrication and assembly methods to incorporate the cell materials into the stack configuration. Some fabrication processes applied on SOFC cathodes are briefly introduced below.

2.2.1 Thermal spray

Thermal spray is a process of particulate deposition in which particles are heated and propelled by the thermal and kinetic energy of a high energy heat source in a molten, semi-molten or solid state onto a prepared substrate surface. The process can be mainly classified into three major processes, namely, combustion flame spray, wire arc spray and plasma spray. Plasma spray not only extends the temperature range of

Fig 2.4 Schematic of Plasma spray process (Gauckler, 1994)

the heat source to an extremely high temperature (5,000 to 20,000°C), but also allows the spray in the environment of inert plasma gases, which considerably reduced the oxidation of molten particles during their traveling through air and at their incidence on the substrate. Fig 2.4 shows the process of plasma spray. The porosity of SOFC layers can be controlled by the proper selection of the plasma torch nozzle and the plasma parameters. Options to produce porous coatings (cathode and anode) are the reduction of the jet and particle velocity by raising the tank pressure, increasing the spray distance, using coarser spray powders and reducing the torch power.

2.2.2 Tape casting

Tape casting is one of the most common methods that has been used to fabricate the components of SOFC. 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

Fig 2.5 Schematic of tape casting process (Gauckler, 1994)

by passing it under a doctor blade, or onto a fixed casting surface using a traversing casting head. The thin layer of slurry is allowed to dry and a ceramic green tape is formed. Fig 2.5 is a schematic of the tape casting process. Other than the ceramic powder, the most important choice that must be made in the tape casting technique is the selection of a binder/plasticizer/deflocculant system. The commonly used binders include poly-vinyl acetate, poly-vinyl chloride, poly-styrene and poly-vinyl butyral. The key issue in the tape casting process is the optimisation of the slurry formula, which is mainly based on empirical studies and is normally not disclosed in most papers.

2.2.3 Screen printing

Fig 2.6 shows the steps involved in the screen printing process for the preparation of SOFC cathodes. The basic equipment of the screen printing process consists of a stencil screen, which defines the printed pattern, and a squeegee with which the printing medium is forced through the screen onto the surface of the

Fig 2.6 Schematic of screen printing process (Gauckler, 1994)

substrate. The mesh fabric of the screen performs the dual function of holding together the various parts of the screen and also metering the thickness of the ink deposit. Quite a lot of variables may affect the quality of the deposits. These variables may be categorized into the following main groups: (i) ink properties; (ii) screen variables; (iii) machine variables; (iv) drying and firing procedure. Although many parameters may affect the properties of the deposited film, screen-printing technique is an easy way to prepare the electrodes of SOFC.

2.3 Electrochemical Properties of LSM Cathodes

2.3.1 Pure LSM cathodes

Sr-doped lanthanum manganite (LSM) has been a material of choice for the SOFC operating at high temperatures (800-1000°C). Differences in chemical composition, stoichiometry and processing parameters such as starting powder

characteristics, sintering temperature and thickness of cathode coating, will significantly affect the electrochemical properties of LSM cathodes.

Takeda et al. (1987) studied the polarisation behaviour of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ cathodes at 800°C in air. The $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ film was sputtered on the YSZ electrolyte substrate with the thickness around 2µm. It was found that cathodic overpotential decreased with increasing Sr dopant level until $x=0.5$. Further increase in Sr dopant caused the deterioration of polarisation performance. The electrode polarisation on $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ cathodes was suggested to be controlled by the dissociation of adsorbed oxygen molecules to oxygen atoms.

Sasaki et al. (1996) investigated the effects of starting powder characteristics, powder calcination temperature and cathode coating sintering temperature on the final microstructure and electrochemical performance of $\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_3$ cathode on the YSZ electrolyte substrate. With varying synthesis techniques, the mean particle size of $\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_3$ powders ranged in 0.38-3.7µm, and the particle size distribution also differed. It was found that cathodes prepared by powders with narrow particle size distribution or free of agglomeration achieved higher effective electrode area and had much better polarisation performance. Similar observation was also reported by van Berkel et al. (1994) on the study of $\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_3$ cathodes with different powder morphologies. The cathodic polarisation overpotential increased in cases of too high a calcination temperature for the starting powder or too low a sintering temperature for the cathode coating (Sasaki, 1996). The optimal calcination temperature and sintering temperature were found to be 950°C and 1100°C,

respectively. Calcination at temperatures higher than 950°C would reduce the sinterability of LSM powder and thus cause insufficient connection of grains within sintered cathode coating, while sintering at temperatures above 1100°C resulted in significant grain growth and dense cathode structure. In the same study, the effect of cathode coating thickness on the polarisation performance was investigated. A minimum in cathodic polarisation overpotential was found at a thickness of 25µm.

Widmer et al. (1994) reported that LSM cathodes prepared by in-situ sintering might achieve considerably better cell performance as compared to those prepared by conventional sintering at 1150°C. $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ cathode was screen-printed on the YSZ electrolyte substrate, and in-situ sintered at the operating temperature of the fuel cell, usually between 840-900°C. The power output of the cell with in-situ fired LSM is 324mW/cm² at 840°C, much higher than 189mW/cm² of the cell with conventionally sintered LSM. However, the in-situ fired LSM usually tends to be mechanically friable and should be overcome by employing fluxes and sintering aids.

Øsergård et al. (1995) compared the electrochemical performance of $\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_3$ electrodes prepared by fine and coarse powders by electrochemical impedance spectroscopy technique. It was found that the polarisation resistance was noticeably higher in the samples prepared with coarse grained LSM than in those prepared with a mixture of fine and coarse LSM powders. It was believed that mixtures of fine and coarse grained powders resulted in samples with better adhesion because the gaps between the larger particles could be connected with the smaller ones, and the three phase boundary was therefore longer for these samples than for the

ones prepared only with fine or coarse grained LSM powders.

In practical SOFC application, A-site deficient LSM cathodes are generally used to avoid the formation of resistive $\text{La}_2\text{Zr}_2\text{O}_7$ at the LSM/YSZ interface. The stoichiometry of LSM electrodes has significant effect on the electrochemical performance. As reported by Jiang et al. (1999a), the overpotential loss of a stoichiometric $(\text{La}_{0.8}\text{Sr}_{0.2})_{1.0}\text{MnO}_3$ electrode was $279 \pm 104 \text{ mV}$ at 250 mA cm^{-2} and 900°C in air, and significantly decreased to $130 \pm 18 \text{ mV}$ after cathodic current treatment at 250 mA cm^{-2} for 3hr. In comparison, the overpotential loss of an A-site deficient $(\text{La}_{0.8}\text{Sr}_{0.2})_{0.9}\text{MnO}_3$ electrode was much lower under the same testing condition, i.e., $134 \pm 40 \text{ mV}$ and $52 \pm 7 \text{ mV}$ before and after cathodic current treatment, respectively. The considerably higher overpotential loss on stoichiometric LSM electrode was attributed to the presence of a deleterious resistive $\text{La}_2\text{Zr}_2\text{O}_7$ layer, which could be permanently removed by cathodic current treatment. At the same time, detailed investigation of the shelf-life and performance of LSM cathodes as a function of A-site stoichiometry revealed that LSM electrodes with A-site stoichiometric (i.e., $(\text{La}+\text{Sr})/\text{Mn}=1$) and sub-stoichiometric (i.e., $(\text{La}+\text{Sr})/\text{Mn}<1$) compositions were stable under the humidity range of 20 to 84% at ambient temperatures for ~ 350 days. No essential change was observed in the adhesion, chemical and electrochemical properties of LSM electrodes after long term storage (Jiang, 2000c).

The cell performance of SOFCs based on LSM cathodes and YSZ electrolyte varies in the literature, probably due to different processing techniques and testing conditions used. An electrolyte supported cell was fabricated by slip casting process

with a $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ cathode and a NiO/10wt%YSZ cermet anode (Setoguchi, 1990). The thickness of the YSZ electrolyte substrate was 150 μm . The maximum power density of 695mW/cm² at 1000°C was achieved with humidified H₂ as fuel. Srivastava et al. (1997), using a DC magnetron sputtering technique, deposited highly dense and impervious films of YSZ electrolyte (5-16 μm) on the porous NiO/YSZ anode substrate. $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ was screen-printed on the electrolyte film as a cathode. The maximum power density of the button cell with H₂/H₂O steam fuel was 600mW/cm² at 800°C, 440mW/cm² at 750°C and 210mW/cm² at 700°C. Larger area cells (50mm×50mm) produced a maximum power density of 300mW/cm² at 800°C. Extremely high cell performance was demonstrated by de Souza et al. (1997) on a planar SOFC with $\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_3$ cathode, YSZ thin-film electrolyte and NiO/YSZ cermet anode. The maximum power density was 1935mW/cm² at a current density of 4.5A/cm² at 800°C with air as oxidant and H₂/H₂O steam as fuel. The cell was operated at a power density of 800mW/cm² for more than 700hr with no detectable loss in performance.

2.3.2 LSM-based composite cathodes

Although LSM cathode has been extensively used in high temperature SOFC, its application in intermediate temperature (600-800°C) SOFC is strongly limited by the extremely low ionic conductivity, which in turn restricts the electrode reactions at the three-phase boundary area and results in high cathodic potential loss. One commonly used strategy is to replace pure LSM cathode with the composite of LSM and

electrolyte materials such as YSZ, GDC or (La,Sr)(Ga,Mg)O₃ (LSGM).

The composite LSM/YSZ cathode was first demonstrated by Kenjo et al. (1992). It was shown that by adding 50wt% YSZ to the LaMnO₃ cathode, the polarisation resistance could be reduced to ~25% of its original value. Even lower polarisation resistance has been obtained when replacing stoichiometric LaMnO₃ with A-site deficient La_{0.85}MnO₃ cathodes. The electrode polarisation resistance was 0.77Ωcm² for pure La_{0.85}MnO₃ electrode at 900°C in air, and significantly reduced to 0.16Ωcm² when 50wt% YSZ was added to La_{0.85}MnO₃ electrode. Subsequent studies showed further improvements using a variety of cathode arrangements and fabrication methods. Øsergård et al. (1995) reported that the addition of up to 40wt% YSZ to the (La_{0.85}Sr_{0.15})_{0.9}MnO₃ cathode greatly improves its performance as a result of better adhesion to the YSZ electrolyte substrate and the increased area of the three-phase boundary. Composite electrodes made with a mixture of fine and coarse LSM powders had lower resistance than electrodes comprising only fine or coarse LSM powders. Kim et al. (2001) also found that the minimum polarisation resistance of LSM/YSZ composite cathodes occurred at a composition of 40wt% YSZ and a sintering temperature of 1200°C.

Jørgensen et al. (2001b) studied the correlation between sintering temperature, microstructure and performance of composite electrodes comprising 50wt% (La_{0.75}Sr_{0.25})_{0.95}MnO₃ and 50wt% YSZ with a current collector of LSM. The microstructure of the composite LSM/YSZ cathode was found to be less dense and to contain smaller grains as the sintering temperature was decreased in the range of

1300-1150°C. This in turn increased the active three phase boundary line between electrode, electrolyte and gas phase, leading to a decrease in the polarisation resistance with decreasing temperature. Decreasing the sintering temperature of the LSM current collecting layer also improved the performance. The results on the in-situ sintering of composite LSM-YSZ electrodes showed that the optimum sintering temperature was around 950-1000°C.

Durability testing on a 60wt% $(\text{La}_{0.85}\text{Sr}_{0.15})_{0.9}\text{MnO}_3$ /40wt% YSZ composite cathode was performed with and without a current load of 300mA cm^{-2} at 1000°C for up to 2000hr (Jørgensen, 2000). It was found that composite LSM/YSZ electrodes tested without a current load showed little or no degradation after 2000hr at 1000°C in air. For electrodes tested galvanostatically at 300mA cm^{-2} and 1000°C in air, the increase in electrode overvoltage exceeded 100% of the initial value. It was thus argued by Jørgensen et al. that, the current load, rather than the operation temperature, was responsible for the degradation. Structural analysis showed an increase in the porosity at the electrode/electrolyte interface when the electrode had been polarized, whereas no such structural changes were found for electrodes tested without current load. The degradation was thus ascribed to pore formation in the electrode material induced by an electric field.

In addition to sintering temperature, the thickness of the cathode coating and the contact between cathode and electrolyte substrate can also influence the performance of LSM/YSZ composite cathodes. It was shown that at the intermediate temperature range (700-850°C), increasing the composite cathode layer thickness had a positive

effect on the electrode performance in the thickness range below 12 μm (Juhl, 1996). This implies that the bulk of the LSM/YSZ composite cathode is active for the oxygen reduction reaction. At high temperatures ($\sim 1000^\circ\text{C}$), the polarisation resistance is less sensitive to thickness variations than that at intermediate temperatures. Moreover, application of a porous layer of YSZ particles between the electrolyte and the composite cathode decreased the polarisation resistance at 700°C and 850°C , whereas no significant effect was observed at 1000°C . Such YSZ particle layer was believed to extend the active three phase boundary length.

Leng et al. (2004) used a spray-coating technique to deposit a 45 μm -thick YSZ electrolyte film on a porous NiO/YSZ anode substrate, followed by co-firing at 1400°C . The composite cathode was prepared from the mixture of $\text{La}_{0.72}\text{Sr}_{0.18}\text{MnO}_3$ and YSZ powders at a ratio of 50wt%:50wt%. Hydrogen saturated with water at room temperature was used as fuel at a flow rate of 250ml/min, and air as the oxidant gas at a flow rate of 500ml/min. The maximum power density achieved was 900, 520, 260 and 140 mW/cm^2 at 800°C , 750°C , 700°C and 650°C , respectively.

Other than YSZ, oxide materials with higher oxygen ion conductivity at reduced temperatures are also employed in LSM-based composite cathodes. Murray et al. (2001) studied the electrochemical performance of $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3/\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_2$ composite cathodes with GDC content varying in the range of 30-60wt%. It was found that the polarisation resistance of LSM/GDC composite cathodes decreased as the GDC content increased to 50wt%, whereas further increase in GDC content above 50wt% caused rapid increase in the polarisation resistance. This was attributed to the

decrease in the continuity of the LSM phase in the composite, and hence the decrease in the electrode performance. In comparison, the polarisation resistance of LSM/50wt%GDC composite cathode was 2-3 times lower than that of LSM/50wt%YSZ composite cathode and ~7times lower than that of pure LSM at the testing temperature range of 600-750°C. The high ionic conductivity and high oxygen surface exchange coefficient of GDC were suggested as the two main factors aiding electrode processes on LSM/GDC composite cathodes. Armstrong et al. (2002) demonstrated an anode-supported SOFC with a $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3/\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_3$ (LSM/LSGM) composite cathode, a thin (~10µm) YSZ electrolyte and a Ni/YSZ cermet anode. The LSGM content ranged from 30wt% to 70wt%, and the effect of the sintering temperature on the cell performance was studied at the temperature range of 1000-1200°C. The best cell performance was achieved on the cell with 50wt%LSM/50wt%LSGM composite cathode fired at 1150°C. The area specific cell resistance was $0.18\Omega\text{cm}^2$ and the maximum power density was $1.4\text{W}/\text{cm}^2$ at 800°C with air as the oxidant and $\text{H}_2/\text{H}_2\text{O}$ steam as the fuel. However, in spite of the high performance achieved by LSM/GDC and/or LSM/LSGM composite cathodes, the mismatch on thermal expansion coefficients of GDC and/or LSGM with YSZ substrate should be taken into account in the SOFC design.

2.3.3 Ion impregnation method

Ion impregnation has been shown to be an effective method of introducing nanosized oxides or precious metal particles into a porous electrode structure. Gorte et

al. (2000; Cracium, 1999; Wang, 2001; Kim, 2002; Park, 2000) has developed Cu/YSZ cermet anodes for direct oxidation of hydrocarbon fuels by impregnation method. In their work, porous YSZ structure was impregnated with a concentrated $\text{Cu}(\text{NO}_3)_2$ solution, followed by calcination to decompose the nitrate and form the oxide. Other components, including CeO_2 , can also be added into the anode structure using the same impregnation method.

Jiang et al. (2002b) showed that ion impregnation of $\text{Zr}_{0.97}\text{Y}_{0.03}(\text{NO}_3)_x$ and $\text{Ce}_{0.8}\text{Sm}_{0.2}(\text{NO}_3)_x$ solutions is effective in enhancing the microstructure and performance of Ni/TZ3Y and Ni/TZ8Y electrodes. By impregnation of very fine oxide particles in the Ni/YSZ cermet, the sintering, grain growth and agglomeration of Ni grains during the high-temperature sintering and reducing stages were significantly inhibited, leading to the enhancement of the Ni and YSZ phase distribution and thus significant improvement in the electrochemical activity and stability of the Ni/YSZ cermet anodes for the H_2 oxidation reaction. In the case of Ni/TZ3Y anodes, the overpotential was 237mV at 250mAcm^{-2} for the H_2 oxidation reaction on the anode without impregnation treatment at 800°C . After impregnation treatment with 3M $\text{Zr}_{0.97}\text{Y}_{0.03}(\text{NO}_3)_x$ and $\text{Ce}_{0.8}\text{Sm}_{0.2}(\text{NO}_3)_x$ solutions, the overpotential was reduced to 111 and 72mV, respectively, under the same testing conditions. This was attributed to the enlargement of three phase boundary in the Ni/YSZ cermet for the H_2 oxidation by the deposition of fine ionic conducting $(\text{Zr,Y})\text{O}_2$ and $(\text{Ce,Sm})\text{O}_2$ oxide particles around Ni grains. For the pure Ni anodes impregnated with $\text{Ce}_{0.8}\text{Gd}_{0.2}(\text{NO}_3)_x$ solution, a unique microstructure was obtained, in which nanosized

GDC particles were deposited on the surface of Ni grains, forming a thin and uniform GDC layer (Jiang, 2004). With the impregnation of 8.5vol% GDC in Ni anodes, the electrode resistance was $0.71\Omega\text{cm}^2$ at 800°C , close to the good performance value of $0.24\Omega\text{cm}^2$ reported on a 50vol%Ni/50vol%YSZ cermet anode at the same temperature. Impregnation of GDC phase also substantially decreased the polarisation overpotential for the H_2 oxidation on Ni anodes. η was reduced from 195mV at 200mAcm^{-2} and 900°C on pure Ni to 136mV and 53mV on impregnated Ni anodes with 3.5vol% and 8.5vol% GDC, respectively, under the same conditions.

Watanabe et al. (1994) impregnated $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_2$ (SDC) anodes with precious metal ions such as Pt, Ru and Pd etc. The precious metal ion content is 0.1mg/cm^2 ($\sim 0.25\text{wt}\%$) and the firing temperature ranged from 400°C to 800°C in H_2 atmosphere, resulting in the formation of microcrystalline metals with average particle size of 14-28nm. It was found that the anodic polarisation resistance and the activation energy of the SDC electrode for the H_2 oxidation were greatly decreased by loading only a small amount of catalysts (i.e. Pt, Ru and Rh). The polarisation loss at the anode showed a minimum value by using the SDC particles with a mean diameter of 1.5 to $2\mu\text{m}$.

Ion impregnation is equally effective on the improvement of the electrode performance of SOFC cathodes. Uchida et al. (1999b) reported that the dispersion of nano-sized Pt catalysts on LSM cathodes by ion impregnation method greatly enhanced the electrode performance, the magnitude of which depended on the temperature ($800\text{-}1000^\circ\text{C}$) and the microstructure of LSM. It was found that the

improvement of the electrode performance by ion impregnation of Pt catalyst was much higher at intermediate temperature (800°C) than that at high temperature (1000°C). The particle size of the LSM was 3.8µm and the size of the impregnated Pt catalyst was much smaller (19-40nm). By decreasing the particle size of the Pt catalyst, the Pt loading in the LSM electrode can be reduced significantly. The enhanced electrode performance of the Pt-impregnated LSM was ascribed to the high electrocatalytic activity of the nano-sized Pt particles, which promote the dissociation of oxygen molecules to O_{ad} and/or the sequential exchange reaction between oxygen atoms and oxygen vacancies in the LSM. Similar enhancing effect of the Pt impregnation was also reported on (La,Sr)CoO₃ (LSC) cathodes, in which the current density at an overpotential of -50mV and 800°C was increased from 360mAcm⁻² on pure LSC cathode to 600mAcm⁻² on a Pt-impregnated LSC cathode with Pt loading of 0.1mg/cm² (~3.3wt%) (Uchida, 1999a).

Yoon et al. (2002) demonstrated improved performance of LSM-based cathodes by coating thin films of YSZ or SDC within the pores of the La_{0.85}Sr_{0.15}MnO₃ cathodes by a sol-gel technique, followed by calcinations at 600°C for 2hr. It was reported that the electrode polarisation resistance of the conventional LSM/YSZ composite cathode was ~10Ωcm² at 700°C in air, whilst coating of YSZ or SDC thin films on pure LSM cathodes dramatically reduced the electrode polarisation resistance to 2.5Ωcm² and 0.19Ωcm² respectively, under the same testing conditions. The enhancement of cathode performance was attributed to no formation of resistive compounds at the electrode/electrolyte interface due to the low processing

temperature of the sol-gel coating and also resulted from an increase of the three phase boundary due to the formation of YSZ or GDC coating films. The maximum power densities of the cell made with Ni-YSZ cermet anode, YSZ thin film electrolyte and SDC-coated LSM cathode were 530mW/cm^2 at 750°C and 190mW/cm^2 at 650°C with humidified H_2 as the fuel and air as the oxidant.

By impregnation of the GDC phase into the LSM structure, Jiang et al. (2003b) reported that the electrode polarisation resistance of the impregnated LSM decreased to $0.72\Omega\text{cm}^2$ at 700°C as compared to $26.4\Omega\text{cm}^2$ for pure LSM electrode, a reduction in electrode polarisation resistance by 36times. Moreover, at 300mAcm^{-2} and 700°C , the overpotential for the O_2 reduction was reduced from 0.79V on pure LSM to 0.19V on impregnated LSM electrodes, a reduction in overpotential by four times. This indicates that the performance of ion-impregnated LSM electrodes is better than that of conventional LSM/YSZ and LSM/GDC composite electrodes, and is also compatible with those of mixed ionic and electronic conducting electrodes, as reported in the literature. Nevertheless, the long-term stability of such impregnated cathodes has not yet been fully demonstrated. Another important issue that has not been clearly addressed so far concerns the changes on the reaction mechanism and kinetics for the O_2 reduction on impregnated LSM cathodes.

2.3.4 Polarisation behaviour of LSM cathodes

Among the cathode materials reported, LSM-based perovskite oxides are the most extensively studied and investigated materials for the application on SOFC.

Despite the significant effort, however, fundamental questions on the mechanism and kinetics of the O_2 reduction reaction and on the electrode behaviour of LSM materials under fuel cell operation conditions until remain. The rate-determining step has been attributed to oxygen dissociative adsorption process (Gharbage, 1994; Siebert, 1995), gas-phase O_2 diffusion (Tsuneyoshi, 1989; van Herle, 1996), oxygen diffusion on the LSM surface (Matsuzaki, 1999; Mizusaki, 1991; Jiang, 1999a), and oxygen diffusion through the LSM bulk (Brichzin, 2000; Kuznecov, 2003). Also, as pointed out by Jørgensen and Mogensen (2001a), it is until difficult to get a consistent set of values of cathodic polarisation resistance for LSM cathodes from the literature. For example, the polarisation resistance of LSM/YSZ composite cathodes at 700°C reported in the literature ranged from $2.49\Omega\text{cm}^2$ (Murray, 2001) to $27\Omega\text{cm}^2$ (Juhl, 1996). Although the discrepancy, either on the reaction mechanism or on the electrochemical performance, may be partly due to the differences in materials and various processing techniques used, it could be intrinsically linked to the variability in LSM/YSZ interfacial contact, and to the significant polarisation effect on the microstructure and electrochemical properties of LSM materials.

The performance of LSM electrodes is substantially improved by cathodic current passage/polarisation treatment. It was shown that the electrode polarisation resistance of $\text{La}_{0.72}\text{Sr}_{0.18}\text{MnO}_3$ cathode at 900°C was reduced from $6.2\Omega\text{cm}^2$ initially to $0.7\Omega\text{cm}^2$ after cathodic current passage at 200mAcm^{-2} for 15mins (Jiang, 2002a). Chen et al. (2004a) reported that the initial cathodic overpotential of the newly prepared $\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_3$ cathode was 576mV at 850°C and 300mAcm^{-2} , which

dropped significantly and tended to stabilise after 30mins of cathodic current treatment. The cathodic overpotential finally reached 69mV at 300mAcm^{-2} after 60mins of cathodic current treatment. The interpretation pertaining to the activation behaviour of LSM electrodes under cathodic polarisation varies from partial reduction of the LSM electrode (Lee, 1995), microstructure changes under polarisation (Tsukuda, 1994), to removal of the passivation species such as SrO and/or MnO_x at activation sites on the LSM surface (Jiang, 2001b). On the contrary, anodic polarisation was found to have deactivation effect on the electrode performance of LSM. With application of anodic current at 150mAcm^{-2} and 850°C in air, the overpotential of the LSM cathode sharply increased from 60mV for the electrode just after 60mins cathodic current treatment to 210mV for the electrode after 30mins of anodic treatment, and finally to 250mV after 60mins anodic current treatment (Chen, 2004a).

The impedance behaviour for the O_2 reduction on LSM electrodes is also strongly affected by cathodic current treatment. van Heuveln et al. (1997b) reported that cathodic polarisation with a constant current of 100mAcm^{-2} significantly altered the impedance response of LSM cathodes, which can be separated into two electrode processes at high and low frequencies, respectively. The effect of cathodic polarisation was found to be much more pronounced at the low frequency process, and was attributed to the enhanced diffusion of intermediate oxygen species. Depending on the conditions of the cathodic current treatment such as current density, temperature and polarisation period, Jiang et al. (1999a) found that the impedance behaviour of $\text{La}_{0.72}\text{Sr}_{0.18}\text{MnO}_3$ cathode can be characterized with between one and

three arcs. The initial impedance of the O_2 reduction on the LSM cathode at $800^\circ C$ in air was consisted of three arcs. With cathodic current passage at $250 mA cm^{-2}$, the low frequency arc was greatly affected and reduced in size. After cathodic current passage at $250 mA cm^{-2}$ for 4hr, the low frequency arc almost disappeared and the impedance response could be characterized by two distributed arcs. On increasing the current density to $350 mA cm^{-2}$ and a current flow for 6hr, the electrode process could almost be described by a single depressed arc. The effect of cathodic current passage was related to disappearance of a passive layer which inhibited the oxygen adsorption and dissociation reaction and some Mn diffusion into the YSZ electrolyte surface layer. Thus, the cathodic current treatment on LSM electrodes not only enhances the rate of oxygen reduction reaction but also affects the reaction mechanism.

Primarily due to the rather small ionic conductivity of LSM, surface diffusion path via three phase boundary areas rather than bulk path through LSM materials is generally preferred for oxygen reduction reactions. However, in thin electrodes and/or under strong cathodic bias, the bulk path has been discussed to play an important role (Siebert, 1995; Kuznecov, 2003; Brichzin, 2000). Brichzin et al. (2000) studied the impedance spectra and dc polarisation behaviour of geometrically defined, thin and circular $(La_{0.8}Sr_{0.2})_{0.92}MnO_3$ microelectrodes deposited on the YSZ substrate. Based on the observation that the polarisation resistance and the electrode capacitance showed d^{-2} and d^2 dependencies, respectively, where d represented the microelectrode diameter, the authors concluded that the rate-determining processes directly involved the electrode area rather than depending on the length of TPB. Horita et al. (1998)

investigated the active sites for the oxygen reduction at the LSM/YSZ interface by secondary-ion mass spectrometry (SIMS) and found that, under cathodic polarisation, oxygen can diffuse through the dense LSM electrode to the interface of LSM/YSZ interface. This was ascribed to the formation of oxygen vacancies in the LSM electrode under cathodic potential, and was believed to contribute the electrode reaction. Siebert et al. (1995) reported that a sharp current increase was observed under high cathodic polarisation at the i-V curves of LSM cathodes. The authors proposed that at high overpotential, the LSM electrode becomes substantially reduced, creating a large concentration of oxygen vacancies near the interface. This non-equilibrium population of oxygen vacancies thereby creates a facile transport path through the bulk of the material. At low overpotential, LSM is until an electronic conductor and thus the bulk path is closed off.

In addition to the changes in electrochemical properties of LSM, the cathodic polarisation treatment can also cause microstructural and morphological changes in LSM electrodes. Tsukuda et al. (1994) reported that microstructure changes occurred at the LSM/YSZ interface after cathodic polarisation. Formation of voids was observed which were attributed to the flux of oxygen vacancies from the YSZ electrolyte to LSM cathode under cathodic potential. Mizusaki et al. (1996), on the study of oxygen reduction on dense LSM films, observed the formation of grains of submicrometer size with clear and deep grain boundaries on originally dense and smooth LSM films after cathodic polarisation, an indication of structural change induced by the cathodic polarisation. Jiang et al. (2003a) also reported a

microstructural improvement at the $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3/\text{YSZ}$ interface after cathodic current passage at 500mAcm^{-2} for 3hr, in which microcracks at the LSM/YSZ interface region initiated by the formation of thin $\text{La}_2\text{Zr}_2\text{O}_7$ layer disappeared after cathodic polarisation, leading to good contact between LSM cathode and YSZ electrolyte.

2.4 Summary

With the rapid progress in the thin-film technology, as well as the identification of alternative electrolyte materials with higher ionic conductivity, the overall performance of an SOFC system is increasingly dominated by the polarisation loss of the electrodes, especially for the O_2 reduction on the cathode side. This raises the urgent need in the understanding of the factors influencing the reaction mechanism and kinetics of oxygen reduction on commonly used electrodes such as LSM cathodes. Polarisation treatment has been found to have significant impact on the electrode behaviour and microstructure of LSM cathodes, which might be responsible for the large discrepancies on the electrochemical performance of LSM and on the reaction mechanism and kinetics for the oxygen reduction on LSM cathodes. Thus, it is critical to systematically investigate the electrode behaviour of LSM cathodes under various polarisation conditions.

By adding electrolyte materials into the LSM structure, composite LSM cathodes demonstrate high electrocatalytic activity even at reduced temperatures. In comparison, ion impregnation of oxygen ion conducting phases into the LSM

structure could bypass the mechanical mixing of ceramic powders and thereafter high-temperature heat treatment on composite cathodes, resulting in the uniform distribution of nano-sized and oxygen ion conducting particles in the LSM structure. The performance of GDC-impregnated LSM is found to be better than that of composite LSM cathodes, and even compatible with that of mixed ionic and electronic conducting cathodes, indicating that ion impregnation method is promising on the development of LSM-based cathode materials for intermediate temperature SOFC.

CHAPTER 3.

EXPERIMENTAL PROCEDURES

In this chapter, general descriptions of the sample preparation, the electrochemical set-ups, the electrochemical measurement techniques and the materials characterisation techniques are given. Details about various sample treatments and test parameters will be described in relevant chapters. The experimental issues on the anode material will be presented separately in Chapter 9.

3.1 Sample preparation

3.1.1 Raw materials

The cathode material under study is $(\text{La}_{0.8}\text{Sr}_{0.2})_{0.9}\text{MnO}_3$ (LSM) powders with A-site nonstoichiometry. Without specifications, the LSM powder used was obtained from Ceramic Fuel Cells Ltd., Australia, which was prepared by co-precipitation and calcined at 900°C in air.

In this project, a solid-state reaction method was also used to synthesise A-site nonstoichiometric LSM powders. Starting materials used were La_2O_3 (MERCK, 99% purity), SrCO_3 (MERCK, 99% purity) and MnCO_3 (MERCK, 99% purity). The La_2O_3 was precalcined at 1000°C for 10hr. The required amounts of La_2O_3 , SrCO_3 and MnCO_3 were mixed for 24hr using a plastic rolling bottle. Thereafter, the powders

Fig 3.1 XRD patterns of LSM powders prepared at 1000°C, 1050°C and 1100°C, respectively.

were calcined for 30hr at different temperatures of 1000°C, 1050°C and 1100°C. After calcination, the powders were ground in a mortar with a pestle, then wet milled in a zirconia jar with ethanol for 10hr. X-ray diffraction (XRD) measurement confirmed single phase structure of perovskite in all the final products, as shown in Fig 3.1.

The electrolyte material was 8mol% Y_2O_3 -stabilised ZrO_2 (YSZ) or 3mol% Y_2O_3 stabilised ZrO_2 (TZ3Y) powders which were commercial products supplied by Tosoh Corporation, Japan.

3.1.2 Single cell preparation

A standard single cell preparation procedure was adopted in this work, as shown in Fig 3.2(a). The YSZ (or TZ3Y) powders were mixed with ~1.25wt% PVB binder

Fig 3.2 (a) Flowchart of the single cell fabrication procedure and (b) example of a testing cell

and cold-pressed into discs at a pressure of 50MPa. The green-state YSZ discs were then sintered at 1550°C in air for 4hr. The thickness and diameter of sintered YSZ electrolyte discs were ~1 mm and 18 mm, respectively. The relative density of YSZ discs after sintering was $97.4 \pm 1.1\%$. Pt paste (Ferro Corporation, USA) was painted onto the YSZ electrolyte substrate as the counter electrode and reference electrode. The counter electrode was symmetrically positioned at the center, opposite to the LSM working electrode. The reference electrode was painted as a ring around the counter electrode. The counter and reference electrodes were fired at 1100°C for 1hr. The gap between counter and reference electrodes was ~4mm (see Fig 3.2b).

LSM electrode ink was prepared by thoroughly mixing LSM powder (Ceramic

Fuel Cells Ltd, Australia) with polyethylene glycol (MERCK, 99% purity) in a agate mortar in a ratio of 70wt% LSM and 30wt% polyethylene glycol, and then applied to the other side of electrolyte substrate by slurry coating, followed by sintering at 1150°C in air for 2hr. Electrode coating thickness was $\sim 15\mu\text{m}$ and electrode coating area was 0.5cm^2 . Fig 3.2(b) shows an example of the single cell.

3.2 Electrochemical Characterisation

3.2.1 SOFC test station

A SOFC test station was built in this project. Since the SOFC is generally operated at high temperatures ($>600^\circ\text{C}$), a vertical tube furnace was included in this test station, as shown in Fig 3.3(a). A setpoint programming temperature controller (Eurotherm 2416, Carbolite, UK) was used to provide precise temperature control, as shown in Fig 3.3(b). Oxygen (SOXAL, 99.9% purity) balanced by nitrogen (SOXAL,

Fig 3.3 SOFC test station

99.9%) was used to achieve desired oxygen partial pressures. Two Mass Flow Meters (Model 5850E, Brooks Instrument, US) in combination with one Control & Read Out Unit (Model 0154, Brook Instrument, US) were used to adjust the flow rates of O_2 and N_2 respectively, as shown in Fig 3.3(c). A humidifier for H_2 was also included in the test station.

3.2.2 Testing cell arrangement

A three-electrode cell arrangement was used in the electrochemical test, as shown in Fig 3.4. Three electrodes are working electrode (WE), which is the electrode under investigation, counter electrode (CE) and reference electrode (RE). The counter

Fig 3.4 Schematic of a four-probe cell measurement (left) and three electrode arrangement (right).

electrode is on the opposite side of the working electrode, and the area of CE is just the same with that of WE, a so-called symmetrical arrangement.

It has been known that the cell configuration affects the measurement accuracy (*Chan, 2001; Kato, 2000; Winkler, 1998; Hashibon, 2002*). It is considered that to minimize the experimental error, the reference electrode should be far from both the working and the counter electrodes (*Winkler, 1998*). In this context, two types of symmetrical cell configuration are generally adopted, i.e. (i) a pellet-type cell with large electrolyte thickness (*Winkler, 1998*); (ii) a disk-shaped cell with the reference electrode locating adjacent to WE or CE, as shown in Fig 3.4. The first design is mainly used at Risø National Laboratory, Denmark. However, the complexity of the electrolyte geometry requires machining, and the large ohmic drop of the electrolyte might affect the accuracy of the determination of the electrode polarization resistance (*Jørgensen, 2001*). On the other hand, the second design is simple and easy to fabricate, and shows reliability and reproducibility in cases where thick electrolyte is used (*Jiang, 2004b*). The reliability and accuracy of such design have been discussed by Chan et al. (2001) and Kato et al. (2000), respectively.

The cell was mounted inside the furnace with WE exposed in constant flow of air and CE and RE exposed in static air. In some cases, the cell was sealed with ceramic paste and balanced O_2/N_2 was introduced to WE, to achieve desired oxygen partial pressures. Four-probe cell measurement was used in which two Pt leads are voltage probes and the other two Pt leads are current probes. This set-up has advantages over the two-probe measurement in that the cell can be tested both at open-circuit voltage

(OCV) or under polarised conditions. Current was passed through the working electrode and the counter electrode, and the potential of the electrode was measured against RE using a separate Pt wire as voltage probe. Thereby, the overvoltage at the working electrode can be determined if the iR drop between the working electrode and reference electrode is known.

3.2.3 Electrochemical Impedance Spectroscopy

(1) Principle

Electrochemical impedance spectroscopy (EIS) is a powerful technique for the electrochemical characterisation of a wide range of electrochemical systems and the investigation on the kinetics of electrochemical reactions. The EIS technique in general involves the measurement of current through a solid electrolyte cell when a sinusoidal voltage of low amplitude is applied. The sine wave is used in impedance measurements because for a sinusoidal signal, the inputs and outputs have the same form and the angular frequency.

In a linear system, the applied potential is given by:

$$E(t) = \Delta E \exp(j\omega t) \quad (3.1)$$

The current output of the system is also sinusoidal and has the same angular frequency ω . Differences in amplitude and phase from the voltage signal may occur depending on the elements in the circuit and can be represented by:

$$I(t) = \Delta I \exp(j\omega t + \phi) \quad (3.2)$$

where Φ is the phase angle, ΔE is the amplitude of the voltage and ΔI the amplitude

of the current signal. For a pure resistor, the phase shift is zero.

Since Ohm's law holds true in the time or the frequency domain, the impedance of a circuit consisting of resistors, capacitors and/or inductors is the ratio of the voltage signal divided by the current flowing through the circuit. The impedance of the circuit ($Z(\omega)$) at any frequency ω , can be represented in both polar and Cartesian form and has both the magnitude Z and the phase angle Φ .

$$Z(\omega) = E(t) / I(t) = Z \exp(-j\phi) = Z \cos \phi - jZ \sin \phi = Z_R - jZ_I \quad (3.3)$$

where j is a complex number with value of $\sqrt{-1}$, Z_R and Z_I are real and imaginary parts of the impedance.

For the simple impedance circuit such as a capacitor in parallel to a resistor, the geometric response of the circuit as a function of frequency in the complex impedance plane is a semicircle with its center on the real or x-axis. The difference of low (right) and high (left) frequency intercepts of the semicircle on the real axis gives the value of the resistance. The value of the capacitance and the time constant of the circuit can be calculated from the frequency (f_0) at the top of the semicircle ($\omega_0 = 2\pi f_0 = 1/\tau = 1/RC$). If a resistor, R_1 is added in series with this circuit, the response in the impedance plane will shift to the right for the value of this resistor whereas in the admittance plane, the response will be that of semicircle with its intercepts on the real axis at $1/(R_1+R)$ (low frequency) and $1/R_1$ (high frequency).

(2) Data analysis

The equivalent circuit approach, in which the circuit model is constructed based on the prior understanding of electrochemical processes in a solid electrolyte system, is commonly adopted for most applications. Alternatives to this approach generally involve deriving mathematical expressions from microscopic analysis of all possible electrochemical processes in the system and require kinetic parameters which are usually unknown (*Armstrong, 1979*). Thus the equivalent circuit approach is a widely accepted method of interpreting impedance data for systems based on solid state ionic conductors. Fig 3.5 shows an example of the fitting of the impedance response from a LSM electrode/ YSZ electrolyte system with the aid of equivalent circuit.

In the simplest representation, a solid electrolyte cell can be considered to consist

Fig 3.5 Fitting of the impedance spectra of LSM electrode at 850°C and $P_{O_2}=0.1\text{atm}$.

Symbol represents the experimental data. Line (solid and dot) is the fitting curve determined from the equivalent circuit shown in (b).

of a series network of several resistors and capacitors in parallel with each sub-circuit representing a different electrode or electrolyte process. If each sub-circuit (or an electrochemical process represented by it) has a different time constant associated with it, the response of the equivalent circuit in the complex impedance plane will consist of several semicircles each corresponding to a sub-circuit. In electrochemical cells, if the time constants of various processes are less than two orders of magnitude apart, the arcs are not well separated and a significant overlap of individual semicircles will occur.

The impedance of solid electrolyte systems, in reality cannot be well approximated by the impedance of an equivalent circuit involving a limited or finite number of ideal resistors and capacitors which give rise to perfect semicircular arcs with discrete time constants for each electrochemical process. The commonly observed behaviour of a solid electrolyte system in the impedance plane is rarely in the form of semicircular arcs with their origin on the real impedance axis, but instead consists of depressed arcs. Such impedance response can be approximated by the inclusion of a constant phase element (CPE) in the equivalent circuit. The expression of CPE is:

$$Z_{CPE} = A(j\omega)^{-n} \quad (3.4)$$

where ω is the angular frequency and $j = \sqrt{-1}$. For $n=0.5$, the CPE is a Warburg-type diffusion impedance and for $n=1$, the CPE is a pure capacitance with $C=A^{-1}$ (Jiang, 1997). The physical origin of CPE has not been fully established. However, it has been shown that the surface roughness is an important contributing

factor to the observed frequency dispersion (Scheider, 1975).

(3) Instrumentation

Impedance spectroscopy measurements in this project were performed using a Solartron 1260 frequency response analyser in combination with a Solartron 1287 electrochemical interface. Generally, a frequency range of 0.1Hz to 100KHz and a signal amplitude of 10mV were used in this study.

3.2.4 Galvanostatic Current Interruption Technique

The study of electrode kinetic and transport properties in solid state electrochemical systems by the impedance technique can be complimented by the use of a galvanostatic current interruption technique (GCI). The GCI technique involves analyzing potential decay over a short time scale (of the order of milliseconds or less) after interruption of a steady current flowing through the electrochemical system. The time dependent (or transient) behaviour consists of ohmic losses due to finite resistance of the electrolyte and other overpotential losses due to various superimposed electrochemical processes at the electrode/electrolyte interface. In a solid electrolyte system, the current is passed between the working electrode and the counter electrode and the voltage is measured across working and reference electrode. The use of a third (reference) electrode through which no current passes allows the cathodic and anodic processes to be studied separately. On applying of a constant current to an electrochemical device, the potential rises to a steady state value corresponding to the potential drop across all resistors in the measured circuit

(working and reference electrodes).

In general, capacitances associated with solid electrolyte processes are several orders of magnitude smaller than the interfacial capacitance and the behaviour is almost as same as that of a pure resistor. On interruption of a constant current with a fast switch, the ohmic potential drops disappear almost instantaneously because of the very small time constant associated with these processes (unless an associated capacitance exists as in oxide and passive layers). The electrode processes are much slower, which have much larger time constants and the slow part of the potential-time transients usually corresponds to overpotential losses across the electrode/electrolyte interface. Appropriate data acquisition equipment with resolution on a micro-second

Fig 3.6 Galvanostatic current interrupt transient for a LSM/YSZ system. Data points were collected at 50 μ s intervals. R_{el} represents the ohmic resistance of the electrolyte; R_p represents the electrode polarisation (interface) resistance

scale allows the ohmic contribution to be separated with no data recorded in the first few microseconds. Fig 3.6 shows an example of a GCI measurement on an LSM electrode/YSZ electrolyte system at 800°C in air with a Solartron 1287 electrochemical interface. A constant current of 200mAcm⁻² was applied to LSM/YSZ system until the potential reached a steady state. The potential decay curve following current interruption was recorded with a sampling rate of 50μs. It can be found that in the time domain of the GCI, both the ohmic potential drops and the interfacial losses can be easily separated.

3.3 Materials Characterisation

3.3.1 X-ray diffraction (XRD)

A Philips MPD 1880 Diffractometer System (XRD) was used to study phase composition of raw materials and the sintered SOFC components, and to check the phase change of the SOFC components before and after the operation. X-ray scans were run over a 2θ spectrum of 10°-90° at a scan rate of 0.5°/min, and Cu K_α radiation was employed. An example of XRD patterns of LSM powders is given in Fig 3.1.

3.3.2 Scanning Electron Microscope (SEM)

A Leica S360 scanning electron microscope (SEM) equipped with an energy-dispersive X-ray spectroscopy (EDS, Oxford) was employed to study the microstructural characteristics of the sintered SOFC components. The specimen was coated with Pt or Au before SEM examination. With EDS attachments, microscopic

qualitative and quantitative element analysis can be conducted by the characteristic X-rays emitted from the elements present in the sample.

3.3.3 Atomic Force Microscopy (AFM)

A Nanoscope IIIA atomic force microscopy (Digital Instruments, US) was used to carry out topographical observation on the specimen surface. The AFM is a three-dimensional imaging tool that measures surface structure from the atomic level to mm scale. In order to examine the LSM/YSZ interface, the LSM electrode coatings were removed by hydrochloric acid treatment in an ultrasonic bath at room temperature. Thereafter, the specimen was cleaned with ethanol and distilled water and dried before AFM examination. No coating is required for the measurement. The combination with the Tapping Mode imaging technique allows high resolution topographic imaging of sample surfaces.

CHAPTER 4.

ACTIVATION PROCESS OF LSM UNDER POLARISATION

4.1 Introduction

O₂ reduction reaction at the (La,Sr)MnO₃ (LSM) cathode is one of the most important and also complex reactions in solid oxide fuel cells (SOFC). Despite significant progress in the development of SOFC technologies, there are still considerable discrepancies in the mechanism and kinetics for O₂ reduction reactions on LSM electrodes in the literature. Various reaction mechanisms have been proposed and the O₂ reduction process has been considered to be limited by the surface exchange reaction (*Steele, 1995 and 1996*), surface diffusion (*Mizusaki, 1991*), dissociation and adsorption of oxygen on the LSM surface (*Kamata, 1998; Jiang, 1998*), surface diffusion of oxygen (*Jiang, 2002a; van Heuveln, 1997a*), and charge transfer (*Göddickemeier, 1997*). A close correlation between the oxygen diffusion coefficient and electrode polarisation resistance of the O₂ reduction reaction has also been quantitatively demonstrated by using gaseous Cr species as the diagnostic agent (*Jiang, 2001a*). Reaction sites have been considered to be associated with the three-phase boundary area where LSM, YSZ and O₂ gas are met (*Mizusaki, 1991*;

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Fukunaga, 1996). On the other hand, *Odgaard et al. (1996)* found that the polarisation resistance of $\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_3$ electrode decreases with increasing the LSM/YSZ intimate contact area. *Brichizin et al. (2000)* studied the geometric dependence of cathode potential on a well-defined thin LSM microelectrode and found that the polarisation resistance varies inversely with the area of the electrodes. This suggests that the rate-determining step of the reaction would be related to the surface area of LSM or the LSM/electrolyte interface area. The limiting step associated with bulk diffusion of oxygen was suggested for the reaction on porous $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ electrode at 950°C (*Kuznecov, 2003*).

The information regarding the electrochemical behaviour for the O_2 reduction reaction on the LSM electrode is also not consistent. On pin-shaped LSM in contact with YSZ electrolyte, *Siebert et al. (1995)* observed only one impedance arc at temperature range of $800\text{-}1000^\circ\text{C}$. On porous $\text{La}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$, a depressed arc was observed (*Mizusaki, 1991*). *Jiang et al. (2002c)* showed two clearly separated impedance arcs for O_2 reduction on porous $\text{La}_{0.74}\text{Sr}_{0.16}\text{MnO}_3$ in the temperature range of $850\text{-}1000^\circ\text{C}$. *Østergard and Mogensen (1993)* found three limiting reaction steps for the O_2 reduction on porous $\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_3$ electrode sintered at 1300°C . Three impedance arcs were also observed for the O_2 reduction reactions on porous $\text{La}_{0.72}\text{Sr}_{0.18}\text{MnO}_3$ electrodes (*Jiang, 2000a*). Additional impedance arc was observed to appear at low frequencies under low oxygen partial pressure probably due to gas phase diffusion (*Chen, 2003*).

The discrepancies with respect to the mechanism and reaction limiting steps for

O₂ reduction on the LSM electrode may be related to the variability of LSM/YSZ interfacial contact and the remarkable effect of polarisation on the microstructure and morphology of LSM materials. Cathodic polarisation has significant effect not only on the microstructure and morphology of LSM electrodes (*Jiang, 2003a; Chapter 5*), but also on the morphology of the three-phase boundary at the LSM/YSZ interface (*Chapter 6*). Moreover, the significant dependence of the electrochemical behaviour on the polarisation for the O₂ reduction on LSM electrodes also complicates the issues of reaction mechanism and kinetics. Depending on the cathodic current/polarisation treatment, impedance behaviour of the LSM electrode can be characterized with between one and three impedance arcs (*Jiang, 1999a*).

In this chapter, the mechanism and kinetics of O₂ reduction reaction were studied in detail by examining the electrochemical behaviour of LSM electrodes as a function of cathodic and anodic current passage/polarisation conditions. Three reaction steps were identified and showed very different sensitivities to the polarisation treatments, producing fresh evidence for the reaction mechanism of O₂ reduction on LSM electrodes. Moreover, to elucidate the origin of the activation and degradation effect of LSM cathodes under cathodic and anodic polarisation conditions, a comparative study was done on the LSM electrode with dilute acid etching in HCl solution. The results indicate that surface enriched species and probably the dominant cation defects would have a profound effect on the kinetics of O₂ reduction on LSM electrodes.

4.2 Experimental details

A-site deficient ($\text{La}_{0.8}\text{Sr}_{0.2}$) $_{0.9}\text{MnO}_3$ (LSM) cathode and YSZ electrolyte substrate were used in this chapter. Details on the sample preparation and testing cell arrangement can be found in Chapter 3. Dilute acid etching was carried out by immersing freshly-prepared LSM electrode into 1M HCl solution for ~15min at room temperature, followed by thoroughly washing with distilled water and dried in air. Both LSM electrodes, freshly-prepared or after acid etching, were subjected to the same electrochemical testing.

The electrode behaviour of LSM was investigated under cathodic and anodic polarisation conditions with a constant current density of 200mAcm^{-2} at 800°C in air. Sequential cathodic, anodic and cathodic polarisation treatment for 9hr was conducted in this study. Duration for each individual polarisation section was kept at 3hr. The polarisation was interrupted from time to time for the electrochemical impedance spectroscopy (EIS) measurement using a Solartron 1260 FRA in combination with a Solartron 1287 electrochemical interface. EIS measurements were performed in a three-electrode arrangement at open-circuit. The impedance spectra were analysed by the equivalent circuit, using a non-linear least-square (NLLS) fitting program.

The relaxation experiment was carried out on freshly-prepared LSM electrodes which were prior polarised with a constant cathodic current of 200mAcm^{-2} for 3hr at 700, 800 and 900°C . The impedance responses of LSM electrodes were monitored under open-circuit condition after the cathodic current was terminated. The electrode polarisation resistance (R_E) in the relaxation experiment was obtained directly from

the difference between the high-frequency and low-frequency intercepts on impedance curves.

4.3 Results

4.3.1 Electrode behaviour of freshly-prepared LSM

Fig 4.1 shows the Nyquist and Bode plots of impedance responses for the reaction on a freshly-prepared LSM electrode as a function of cathodic current passage time at 200mAcm^{-2} and 800°C in air. In the Nyquist plot, symbols represent the experimental data and solid lines are fitted results. The equivalent circuit for the fitting is shown in the inset in Fig4.1a, where L is inductance, R_0 the ohmic resistance between cathode and reference electrode, R_{H^+} , R_H , R_L and Q_{H^+} , Q_H , Q_L are the resistances and constant phase elements (or CPE) for the extra-high (above 10kHz), high and low frequency arcs, respectively. The electrode ohmic resistance (R_Ω) was measured from the high frequency intercept and the electrode polarisation resistance (R_E) was the sum of R_{H^+} , R_H and R_L . The time behaviour of R_Ω and R_E under cathodic current passage is shown in Fig4.1c. Table 4.1 gives some fitting parameters derived from the impedance spectra for the O_2 reduction reaction on freshly-prepared LSM electrodes under various polarisation conditions at 800°C and in air under open-circuit.

Table 4.1 Fitted impedance parameters from the equivalent circuit for the O₂ reduction on the freshly-prepared and acid-etched LSM electrodes measured under various polarisation conditions at 800°C in air.

Electrode	Extra high-frequency arc				High-frequency arc				Low-frequency arc			
	$R_{H'}$, $\Omega\text{ cm}^2$	$Q_{H'}$, $\Omega^{-1}\text{ cm}^{-2}\text{ s}^n$	n	$\omega_{H'}$	R_H , $\Omega\text{ cm}^2$	Q_H , $\Omega^{-1}\text{ cm}^{-2}\text{ s}^n$	n	ω_H	R_L , $\Omega\text{ cm}^2$	Q_L , $\Omega^{-1}\text{ cm}^{-2}\text{ s}^n$	n	ω_L
LSM, Freshly-prepared	0.144	8.489E-5	1	82 KHz	2.019	5.484E-3	0.9	90.3 Hz	19.08	5.8E-3	0.72	9 Hz
	0.121	6.724E-5	1	123 KHz	0.27	2.2E-3	0.95	1684 Hz	0.156	4.756E-2	0.75	125 Hz
	0.1	4.041E-4	1	25 KHz	1.85	6.384E-3	0.85	85 Hz	18.59	9.636E-3	0.68	5.6 Hz
	0.113	7.902E-5	1	112 KHz	0.223	4.718E-3	0.88	950 Hz	0.072	3.624E-2	0.7	96 Hz
LSM, Acid treated	-	-	-	-	2.431	1.943E-3	0.9	211.7 Hz	0.456	1.176E-3	0.75	1.87 Hz
	-	-	-	-	0.722	1.165E-3	0.98	1190 Hz	0.204	3.716E-2	0.80	132 Hz
	-	-	-	-	1.403	2.511E-3	0.98	284 Hz	5.525	8.156E-3	0.8	22.2 Hz
	-	-	-	-	-	-	-	-	-	-	-	-

- 1. LSM-C: LSM electrode after 3hr cathodic polarisation treatment.
- 2. LSM-C-A: LSM electrode after 6hr sequential cathodic and anodic polarisation treatment.
- 3. LSM-C-A-C: LSM electrode after 9hr sequential cathodic, anodic then cathodic polarisation treatment.

Fig 4.1 Impedance responses (Nyquist plot (a) and Bode plot (b)) and time dependence of R_E and R_{Ω} (c) for the reaction on a freshly-prepared LSM electrode under cathodic current passage at 200 mAcm⁻² and 800°C in air.

For O₂ reduction on freshly-prepared LSM electrode, the impedance arc decreased substantially with the application of cathodic current. The initial R_E was 21.40 $\Omega \text{ cm}^2$ for the reaction on the freshly-prepared electrode, and reduced to 0.97 $\Omega \text{ cm}^2$ after

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cathodic polarisation for 5min, a 22times reduction in R_E . At the end of 3hr cathodic polarisation treatment, R_E reduced to $0.56\Omega\text{cm}^2$. The dramatic decrease of R_E indicates the activation effect of cathodic polarisation on the electrochemical performance of LSM electrode, in particular during the first 5 to 15mins of cathodic current passage. At the same time, R_Ω remained constant regardless of cathodic polarisation treatment. Additional information regarding the mechanism and kinetics for O_2 reduction reaction could be obtained from Bode plots (Fig4.1b). It was found that characteristic frequency originally at $\sim 40\text{Hz}$ for the reaction on freshly-prepared LSM was abruptly shifted to $\sim 400\text{Hz}$ after cathodic current treatment for 5mins. Prolonged cathodic polarisation treatment didnot shift the characteristic frequency any more. It thus could be argued that rate determining step for the O_2 reduction reaction may be changed after cathodic polarisation on the freshly-prepared LSM electrode.

The effect of cathodic polarisation treatment on individual impedance arcs was shown in Fig 4.2. For the reaction on the freshly-prepared LSM, R_{H^+} , R_H and R_L were $0.14\Omega\text{cm}^2$, $2.02\Omega\text{cm}^2$ and $19.08\Omega\text{cm}^2$, respectively, indicating the dominant process associated with the low frequency arc. With the application of cathodic current, both R_H and R_L showed dramatic decreases, whilst R_{H^+} remained more or less stable regardless of cathodic polarisation treatment. It should be pointed out that the reduction in R_L was much more significant than that in R_H . After 3hr of cathodic polarisation, R_L was only $0.16\Omega\text{cm}^2$, smaller than the value of R_H ($0.27\Omega\text{cm}^2$). This suggests that the dominant electrode process has shifted from the low frequencies to the high frequencies. This is consistent with the shift of characteristic frequency on

Fig 4.2 Fitted electrode polarisation resistances of the O_2 reduction reaction on a freshly-prepared LSM electrode as a function of cathodic current passage time at 200 mA cm^{-2} and 800°C in air.

the Bode plot from $\sim 40\text{Hz}$ for the reaction on freshly-prepared LSM to $\sim 400\text{Hz}$ after 3hr cathodic polarisation treatment.

For the solid electrode/electrolyte systems of the type studied here, the interfacial processes show considerable frequency dispersion. Such behaviour is generally analysed by the inclusion of a constant phase element ($Q=Y_0(j\omega)^n$, where Y_0 is the admittance, j the imaginary unit, ω the angular frequency and n is the frequency power). For $n=1$, Q is a pure capacitance and for $n=0.5$, Q is a Warburg-type diffusion impedance. In the case of the extra-high frequency arc ($R_H Q_H$), the frequency power n , was equal to 1 for the O_2 reduction reaction on the LSM electrodes regardless of various polarisation treatments. The electrode process at this extra-high frequency arc

has been discussed previously and is most likely associated with the charge transfer process (Jiang, 2002a and 2000a). It should be noted that the charge transfer process is a very fast process as compared to the surface dissociative diffusion process or the oxygen ion incorporation process at the LSM/YSZ interface (Jiang, 2002a), and in the presence of inductive tail at high frequency part of impedance spectra, the feature of $(R_H \cdot Q_H)$ arc is usually too obscured by the inductive effect to resolve completely. This may explain the fact that, for some LSM electrodes, the $(R_H \cdot Q_H)$ arc cannot be well resolved (see Table 4.1 and Chapter 8). On the other hand, the n values for the high frequency arc ($R_H Q_H$) slightly increased from 0.9 to ~ 1 after cathodic polarisation treatment. This indicates the pure capacitive behaviour of the electrode process associated with the high frequency arc for the reaction on cathodically polarised LSM, which is consistent with the proposed oxygen ion transfer process from the LSM electrode to the YSZ electrolyte at the interface region (Jiang, 2000a). The ready decrease of R_H with cathodic current passage can be related to the microstructural improvement of LSM from large agglomerates to sphere-shaped particles at the LSM/YSZ interface region under cathodic polarisation potential, which would in turn promote the oxygen species diffusion at the vicinity of the three-phase boundary (Jiang, 2003a). For the low frequency arc ($R_L Q_L$), the n values deviate significantly from 1 and approach 0.5, indicating that the electrode processes at the low frequency arc would be a mixed process of the dissociation and surface diffusion of oxygen species. This is also supported by the high Q values for the low frequency arc. The dramatic decrease of R_L with cathodic current passage implies that the cathodic

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polarisation/current passage may have a profound effect on the surface status of LSM.

After cathodic polarisation on the freshly-prepared LSM electrode for 3hr, an anodic current was subsequently applied to the LSM electrode. Fig 4.3 shows the impedance responses and the change of R_E and R_Ω as a function of anodic current passage time at 200mAcm^{-2} and 800°C in air. With the application of anodic current, the impedance arcs increased in size. Correspondingly, R_E increased from $0.55\Omega\text{cm}^2$ for the reaction on cathodically polarised LSM to $1.40\Omega\text{cm}^2$ after anodic current passage for 5mins, and finally to $20.54\Omega\text{cm}^2$ at the end of the 3hr anodic polarisation treatment. The increase of R_E clearly indicates that the electrocatalytic activity of the LSM electrode for the O_2 reduction reaction was reduced after anodic polarisation treatment. However, different from the rapid decrease of R_E with cathodic current passage, the increase in R_E with anodic current passage time was rather gradual and much slower (Fig4.3c). R_E tends to be stable after anodic current passage for 60mins. On the other hand, the very stable values of R_Ω under anodic current passage implies that delamination at the LSM/YSZ interface may not occur in present study. This is confirmed by the fact that, the adhesion of the LSM coating to the electrolyte surface remained good after testing. In the Bode plot, the characteristic frequency was gradually shifted from $\sim 400\text{Hz}$ for the reaction on cathodically polarised LSM to $\sim 40\text{Hz}$ at the end of anodic polarisation. Moreover, an additional impedance shoulder developed at frequencies around 5Hz . Such impedance behaviour suggests that the impedance arc, which is usually observed at low frequency range (below 100Hz) for the O_2 reduction on porous LSM electrodes, might be the combination of two

Fig 4.3 Impedance responses (Nyquist plot (a) and Bode plot (b)) and time dependence of R_E and R_{Ω} (c) for the reaction on the LSM electrode under anodic current passage at 200 mAcm⁻² and 800°C in air.

electrode processes. Given the close characteristic frequencies of these two reaction steps, the separation between the process associated with the characteristic frequency and the other process at the frequency shoulder would be difficult under normal

operation conditions.

Fig 4.4 shows the effect of anodic polarisation on individual impedance arcs. Similar to that observed under cathodic polarisation, the effect of anodic polarisation was primarily on (R_LQ_L) and (R_HQ_H) arcs whilst $R_{H'}$ remained more or less the same. It appears that R_L showed equally high sensitivity on either cathodic or anodic polarisation treatments, as indicated by the much faster increase in R_L with anodic current passage time. As a result, R_L became larger than R_H after 5mins of anodic current passage and remained dominant for prolonged anodic polarisation treatment, an indication of the dominant role of the oxygen surface dissociation/diffusion for the O_2 reduction reactions on porous LSM electrode.

Following the sequential cathodic and anodic polarisation for 6hrs, the LSM

Fig 4.4 Fitted electrode polarisation resistances of the O_2 reduction reaction on the LSM electrode as a function of anodic current passage time at 200mAcm^{-2} and 800°C in air.

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Fig 4.5 Impedance responses (Nyquist plot (a) and Bode plot (b)) and time dependence of R_E and R_Ω (c) for the reaction on the LSM electrode under second round cathodic current passage at 200 mAcm⁻² and 800°C in air.

electrode was treated again with a cathodic current at 200mAcm⁻². Fig 4.5 shows the impedance responses and the change of R_E and R_Ω during the second phase of cathodic polarisation treatment. The stable values of R_Ω again indicate good

Fig 4.6 Fitted electrode polarisation resistances of the O_2 reduction reaction on LSM electrode as a function of cathodic current passage time at 200 mA cm^{-2} and 800°C in air.

interfacial contact between the LSM cathode and the YSZ electrolyte even after sequential cathodic, anodic and cathodic polarisation treatment for 9hrs. Fig 4.6 shows the fitted electrode resistances of individual impedance arcs for the reaction on the LSM electrode as a function of cathodic current passage time at 800°C in air under open circuit. Similar to that observed on the freshly-prepared LSM electrode, the impedance arcs decreased significantly with cathodic current passage and the effect of the cathodic polarisation is mainly on the $(R_H Q_H)$ and $(R_L Q_L)$ arcs. However, the initial decrease in R_L and R_H is not as sharp as that observed on freshly-prepared LSM electrode. This indicates that the electrode processes in respect to the polarisation treatment are not completely reversible. This might be related to the irreversible morphological and topographical changes at the LSM/YSZ interface and within LSM

bulk structure under cathodic and/or anodic polarisation (Jiang, 2003a; Chapter 5 and 6; Wang, 2004). However, the close values of R_E for the reaction on freshly-prepared (Fig4.1c) or anodically polarised LSM (Fig4.3c) eliminates the microstructural improvement as a primary cause for the activation effect of cathodic polarisation. At the end of the second phase cathodic polarisation, the low frequency arc, with R_L as small as $0.07\Omega\text{cm}^2$, almost disappeared. The impedance shoulder at $\sim 5\text{Hz}$ in the Bode plot after second phase cathodic polarisation also disappeared. Similar impedance behaviour, e.g. the disappearance of low frequency arc after cathodic polarisation treatment for 4hr, was reported by Jiang et al. (1999a) for the O_2 reduction on porous $\text{La}_{0.72}\text{Sr}_{0.18}\text{MnO}_3$ electrode.

4.3.2 Relaxation behaviour of freshly-prepared LSM after cathodic polarisation

The cathodic current passage/polarization treatment has significant enhancing effect on the electrochemical activity of LSM electrodes, as shown by the significant reduction in the polarization resistance with cathodic current passage time. On the other hand, the polarisation resistance increases under sequential anodic current passage, indicating a deactivation effect of anodic current passage/polarisation treatment on the electrochemical activity of LSM electrodes. The activation/deactivation effect of cathodic/anodic polarisation has already been elaborated in Section 4.3.1. This section would focus on the relaxation behaviour of LSM electrodes after ceasing the applied cathodic current/polarization potential.

Fig 4.7 Relaxation behaviour of R_E (a) and impedance responses (Nyquist plot (b) and Bode plot (c)) for the reaction on LSM at 700°C after 3hr of cathodic polarisation at 200mAcm⁻² in air. Lines are the linear fitting of the experimental data.

Fig 4.7-4.9 shows the relaxation behaviour of R_E and some impedance responses (Nyquist and Bode plots) of LSM electrodes as a function of relaxation time at different temperatures. For all three LSM electrodes, R_E relax very slowly towards the original values. As compared to the sharp decrease in R_E only after 5mins of cathodic

Fig 4.8 Relaxation behavior of R_E (a) and impedance responses (Nyquist plot (b) and Bode plot (c)) for the reaction on LSM at 800°C after 3hr of cathodic polarisation at 200mAcm⁻² in air. Lines are the linear fitting of the experimental data.

current passage (Fig4.1c), the time scale for the relaxation of R_E (hours) under open-circuit is much larger. For example, R_E for the O₂ reduction on freshly-prepared LSM at 800°C was 17.19Ωcm² which was substantially reduced to 1.50Ωcm² after 3hr of cathodic current treatment at 200mAcm⁻². With ceasing the applied cathodic

Fig 4.9 Relaxation behavior of R_E (a) and impedance responses (Nyquist plot (b) and Bode plot (c)) for the reaction on LSM at 900°C after 3hr of cathodic polarisation at 200mAcm⁻² in air. Lines are the linear fitting of the experimental data.

current, R_E gradually increased to 1.86Ωcm² and 9.81Ωcm² after 10hr and 100hr relaxation, respectively, which were still much lower than the original value (Fig4.8). Such relaxation behaviour of LSM electrodes after cathodic polarisation shows interesting characteristics. Firstly, the relaxation of R_E shows a two-stage

characteristics which is clearly represented by the different slopes of the two fitted lines in Figs 4.7a, 4.8a and 4.9a. This might imply that different processes dominated the O_2 reduction reaction with increasing relaxation time. Secondly, the increase in the size of impedance spectra with relaxation time was much more pronounced at the low-frequency regime, e.g. below 100Hz. Moreover, the characteristic frequency in Bode plot gradually shifted from high frequencies to low frequencies. In the case of LSM electrode tested at 700°C, an additional impedance shoulder even developed at ~1Hz (Fig4.7) after 40hr of relaxation, indicating the increasingly dominant role of the low-frequency process, i.e. the oxygen surface dissociation and diffusion process. Thirdly, the relaxation of R_E shows decreasing kinetics as the testing temperature increased from 700°C to 900°C. For the LSM electrode tested at 900°C, the relaxation of R_E is the slowest among all these three LSM electrodes, and showed some oscillation during the first 20hr of relaxation.

4.3.3 Electrode behaviour of acid-etched LSM

Considering the dramatic effect of cathodic and anodic polarisation treatment on the impedance responses of freshly-prepared LSM, it is of interest to study the electrode behaviour of the LSM cathode under polarisation conditions after surface cleaning by dilute acid etching in HCl solution. Fig 4.10 shows the impedance responses of a LSM electrode after acid etching under a cathodic current passage at 200mAcm⁻² and 800°C in air. The variation of R_E and R_Ω as a function of cathodic current passage time was shown in Fig 4.10c. In the Nyquist plot (Fig4.10a), symbols

Fig 4.10 Impedance responses (Nyquist plot (a) and Bode plot (b)) and time dependence of R_E and R_{Ω} (c) for the reaction on the acid-treated LSM electrode under cathodic current passage at 200 mAcm^{-2} and 800°C in air.

are experimental data and solid lines are fitted results. The equivalent circuit for the fitting is shown in the inset of Fig4.10a, and is composed of two (RQ) circuits in series. The disappearance of the extra-high frequency arc ($R_{H^+}Q_{H^+}$) for the LSM electrode with acid etching is most likely due to the inductive distortion in impedance

spectra at the high frequency range. Some fitting parameters for the reaction on the acid-etched LSM electrode are also listed in Table 4.1.

For O_2 reduction on the acid-etched LSM electrode, the cathodic polarisation/current passage yielded small activation effect. The initial R_E was $2.89\Omega\text{cm}^2$ for the reaction on the LSM electrode after acid etching, and reduced to $1.83\Omega\text{cm}^2$ after cathodic current passage for 5mins. At the end of 3hr of cathodic polarisation, R_E was $0.93\Omega\text{cm}^2$, a ~ 3 times reduction in R_E . In comparison, R_E was $21.40\Omega\text{cm}^2$ for the reaction on freshly-prepared LSM, and reduced to $0.56\Omega\text{cm}^2$ after 3hr of cathodic current passage, a ~ 38 times reduction in R_E (Fig4.1c). Moreover, the abrupt shift of characteristic frequency in the Bode plot that was observed in the case of freshly-prepared LSM was not found on acid-etched LSM. Dramatically different electrode behaviour of freshly-prepared and acid treated LSM electrodes clearly

Fig 4.11 Fitted electrode polarisation resistances of the O_2 reduction reaction on the acid-etched LSM electrode as a function of cathodic current passage time at 200mAcm^{-2} and 800°C in air.

indicates the significant role of the LSM surface on the kinetics of O_2 reduction reactions. Decorse et al. (1999) examined the surface composition of LSM powder and pellet and found strontium enrichment on the LSM surface. Elemental analysis of the etched solution of freshly-prepared LSM coating also showed primarily the presence of elemental Mn and Sr (Jiang, 2001b). Surface segregation of Ca content was also observed on $La_{1-x}Ca_xMnO_3$ powders and the catalytic activity of $La_{1-x}Ca_xMnO_3$ decreases with increase in the Ca content (Isupova, 2001). The correlation between the catalytic activity of $La_{1-x}Ca_xMnO_3$ perovskites and the surface Ca content was explained by the blocking of the surface active sites by the CaO segregated within the surface layer (Isupova, 2001). Similarly, SrO species originally enriched within the surface layer of LSM electrodes could inhibit oxygen surface diffusion by blocking the diffusion path as SrO is an insulator and then significantly contributes to the initially very high polarisation loss of LSM electrodes. Upon etching, the obstructive phases were removed, facilitating the oxygen dissociative adsorption and/or surface transport. As a result, the initial R_E for the reaction on the acid-etched LSM was much smaller than that on the freshly-prepared LSM.

The effect of acid etching on the freshly prepared LSM is further demonstrated by the variation of R_H and R_L under cathodic current passage of $200mAcm^{-2}$ at $800^\circ C$, as shown in Fig 4.11. Different from that of the freshly-prepared LSM, the decrease in R_H and R_L with cathodic current passage time was rather small on the acid treated LSM electrode. Moreover, the initial R_H was much higher than that of R_L , and was dominant during the cathodic polarisation treatment. This is similar to the electrode

behaviour of freshly-prepared LSM after cathodic polarisation for 3hr (Fig4.1). This implies that the cleaning of the surface inhibiting species could also be achieved by the application of a cathodic potential. As the acid etching may only affect the surface layer of LSM particles, this again suggests that the effect of cathodic polarisation treatment could also be mainly on the surface status of the LSM electrodes.

Fig 4.12 Impedance responses (Nyquist plot (a) and Bode plot (b)) and time dependence of R_E and R_O (c) for the reaction on the acid-treated LSM electrode under anodic current passage at 200 mA cm⁻² and 800°C in air.

Following cathodic polarisation, an anodic current of 200mAcm^{-2} was applied on the acid-etched LSM for 3hr. Fig 4.12 shows the impedance responses and change of R_E and R_Ω as function of anodic current passage time at 200mAcm^{-2} and 800°C in air and under open-circuit. Fig 4.13 is the variation of R_H and R_L . With the application of anodic current, R_E increased steadily and became nearly constant after anodic polarisation for 30mins. It is of interest to note that R_E was $6.93\Omega\text{cm}^2$ at the end of anodic polarisation treatment, more than two times higher than that of $2.89\Omega\text{cm}^2$ for the reaction on acid-etched LSM before cathodic current passage. The rather constant value of R_Ω indicates that there is no delamination at the LSM/YSZ interface region. As clearly shown in Fig4.13, the increase in R_E was mainly due to the substantial increase of R_L with anodic current passage. This suggests that, similar to that of cathodic polarisation treatment, the effect of anodic polarisation is also primarily

Fig 4.13 Fitted electrode polarisation resistances of the O_2 reduction reaction on the acid-etched LSM electrode as a function of anodic current passage time at 200mAcm^{-2} and 800°C in air.

related to the surface status of LSM electrodes. Thus, the surface status of the LSM electrode that has been modified by dilute acid etching could, to some extent, be restored by the application of anodic polarisation/current passage. This implies that some inhibiting species, probably SrO, could be pushed from the LSM lattice and segregate again to the surface under the anodic potential. As a result, the oxygen surface dissociation and diffusion process associated with ($R_L Q_L$) arc again dominated the O_2 reduction reaction. However, the impedance arc for the reaction on acid treated LSM after anodic polarisation is still much smaller than that of the freshly-prepared LSM electrode (Fig4.1a). This again indicates the significant inhibiting effect of surface enriched SrO species on the O_2 reduction on the freshly-prepared LSM.

4.4 Discussion

It has been known that the initial polarisation loss and electrode interface resistance for O_2 reduction on freshly-prepared LSM electrodes could be significantly reduced with the application of cathodic polarisation/current passage. The origin of the activation effect of cathodic polarisation was generally explained based on the generation of oxygen vacancies under cathodic potential (*Jiang, 1998; Lee, 1995*). It is considered that manganese ions at the LSM lattice and interstitial sites can be reduced with concomitant generation of oxygen vacancies on the LSM electrode surface under cathodic polarisation conditions, according to:

where $O_{O,LSM}^x$ and $O_{O,YSZ}^x$ are the O^{2-} ions in LSM and YSZ lattice sites, respectively; $V_{O,LSM}^{\bullet\bullet}$ and $V_{O,YSZ}^{\bullet\bullet}$ stand for oxygen vacancies; $Mn_{Mn,LSM}^{\bullet}$, $Mn_{Mn,LSM}^x$ and $Mn_{Mn,LSM}'$ are Mn^{4+} , Mn^{3+} and Mn^{2+} ions respectively. The formation of oxygen vacancies increases the active sites on the LSM surface, enhancing the dissociative adsorption and diffusion of oxygen on the electrode surface. On the other hand, under oxidation environment, e.g. anodic polarisation potential or gas phase O_2 , the oxygen vacancies formed could be consumed by the recombination reaction, i.e., the reversed reactions of Eq(4.1) and Eq(4.2), leading to significantly reduced electrochemical activity for O_2 reduction. However, there are limitations in the explanation based on the formation of oxygen vacancies. One expected consequence of this explanation is that cathodic polarisation would have more or less the same activation effect on both freshly-prepared and acid-etched LSM electrodes. The observed fairly small activation effect of cathodic polarisation after dilute acid etching indicates the manganese ion reduction and concomitant generation of oxygen vacancies could not be the sole cause for the activation effect of cathodic polarisation treatment.

As shown by numerous thermodynamic defect models (Nowotny, 1998; Poulsen, 2000; Mizusaki, 2000a), $La_{1-x}Sr_xMnO_{3\pm d}$ can display both oxygen-excess (superstoichiometry) and oxygen-deficient (substoichiometry) non-stoichiometry as a function of partial pressure of oxygen. In fact, LSM maintains a nearly full perovskite stoichiometry at P_{O_2} above $\sim 10^{-10}$ atm and becomes superstoichiometric at high P_{O_2} ($> 10^{-3}$ atm). Since the close-packed ABO_3 perovskite structure cannot accommodate an excess of oxygen as an interstitial oxygen ion due to its large radius,

it is considered that cation vacancies appear at the oxygen excess region, according to (Nowotny 1998):

where $V_{La}^{\bullet\bullet}$ and $V_{Mn}^{\bullet\bullet}$ are cation vacancies on LSM lattice sites. Neutron powder diffraction (NPD) studies (Mitchell, 1996; van Roosmalen, 1994; Alonso, 1997) have all indicated the presence of cation vacancies in (La,Sr)MnO₃ perovskites. The charge neutrality in these compounds is achieved by the oxidation of Mn ions from 3+ to 4+. Such cation vacancies could occupy the active sites for oxygen dissociative adsorption and diffusion on LSM surface, leading to substantially high polarisation resistance for O₂ reduction (Yasumoto, 2001). However, it should also be noted that the A/B cation vacancy is disproportional. As pointed out by Mitchell et al. (1996) on the NPD study of La_{1-x}Sr_xMnO_{3+δ}, cation vacancies most likely occur on the La/Sr site, rather than on the Mn site.

Considering the dominant defect in LSM as cation vacancies under fuel cell operating conditions, Chen et al. (2004b) suggested that the reduction of $Mn_{Mn,LSM}^{\bullet}$ to $Mn_{Mn,LSM}^x$ occurs with the concomitant removal of cation vacancies on A and B sites at the initial stage of cathodic polarisation, according to:

Further reduction of manganese ions and the generation of oxygen vacancies, as illustrated in Eq(4.1) and (4.2), can take place only after all the metal vacancies are consumed. The oxygen vacancies formed would then propagate from the LSM/YSZ

interface region to the LSM surface under cathodic potential. With ceasing the cathodic polarisation potential/current or the sequential application of anodic polarisation/ current, the oxygen vacancies will be consumed in the presence of gaseous O_2 with the concomitant Mn ion oxidation. Thereafter, the concentration of cation vacancies gradually increases, resulting in the superstoichiometric structure of LSM. Both the decrease in oxygen vacancies and the increase in cation vacancies would have a deactivating effect on the electrochemical performance of LSM electrodes.

Nevertheless, one question to be raised on the above mechanism is where the released cations (La or Sr on A site, and Mn on B site) are after the formation of cation vacancies within the LSM lattice under normal sintering environments. The surface enrichment of Sr and/or Mn, detected separately by Decorse et al. (1999) and Jiang et al. (2001b) might provide one possibility. Such inhibiting species can be removed by either acid etching or cathodic polarisation treatment. As shown in Fig4.1 and Fig4.10, the acid-etched LSM had a much smaller initial impedance, nearly identical to that of an unetched LSM that had been cathodically polarised for several hours. It thus can be argued that the surface enriched Sr and/or Mn species could be incorporated into the lattice of $LaMnO_3$ under cathodic polarisation. Cook et al. (1999), on the study of the correlation between the creep behaviour and defect chemistry of $(La_{1-x}Sr_x)_{1-y}MnO_{3+\delta}$, proposed a defect model in which the substitution of La^{3+} with Sr^{2+} ions was compensated by the oxidation of Mn at high P_{O_2} and by the creation of oxygen vacancies at low P_{O_2} , according to:

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where $Sr'_{La,LSM}$ represents Sr ions introduced into La sites in the LSM lattice. The incorporation/segregation of constituent elements in perovskite oxides under reducing/oxidizing atmosphere was also reported on $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_3$ (BSCF) ceramic membrane reactor for methane conversion (*Shao, 2001*). It was found that the Co and Fe metallic species originated during reduction were reincorporated into the perovskite structure after subsequent oxidation.

Therefore, a modified defect model of $La_{1-x}Sr_xMnO_3$ based on the above considerations can be derived. For freshly-prepared LSM, the dominant defects are the cation vacancies (La/Sr site and/or Mn site) and surface enriched Sr and/or Mn species. Under cathodic polarisation potential, the SrO can be incorporated into the LSM lattice structure, according to:

This process, i.e. the incorporation of SrO, should be thermodynamically favoured as the existence of cation vacancies in the LSM lattice structure, and could be even facilitated with the application of cathodic polarisation potential. The dramatic inhibiting effect of SrO species on the oxygen surface dissociation/diffusion was clearly demonstrated by the much smaller R_E value ($2.89\Omega\text{cm}^2$) for the reaction on acid-etched LSM as compared to that on freshly-prepared LSM ($21.40\Omega\text{cm}^2$). This explains that the cathodic polarisation treatment could result in rapid reduction

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(~38times) in R_E during the first 5 to 15mins of cathodic current passage (Fig4.1) whilst such a dramatic effect of cathodic polarisation disappeared after acid etching (Fig4.10). Further cathodic polarisation will cause the reduction of Mn ions and the generation and propagation of oxygen vacancies, according to

However, it should be pointed out that the activation effect of the generation and propagation of oxygen vacancies seems to be limited, as indicated either by the gradual decrease in R_E after the first 5 to 15mins of cathodic current passage (Fig4.1) or by the fairly small activation effect of cathodic polarisation after removal of surface enriched SrO species with dilute acid etching (Fig4.10).

The two-stage activation processes under cathodic polarisation were also supported by the observation in the Bode plot, in which the characteristic frequency was shifted from ~40Hz for the reaction on freshly-prepared LSM to ~400Hz after cathodic current passage for 5mins (Fig4.1). Additional evidence may be found in the reoxidation behaviour of LSM electrodes at low P_{O_2} under cathodic and anodic polarisation conditions. Chen et al. (2004b) reported that three potential stages, which were ascribed to three respective electroredox reactions, were observed in the potential response curve after the cathodic current on porous $La_{0.85}Sr_{0.15}MnO_3$ electrode was stepped from $400mAcm^{-2}$ to zero at $900^\circ C$ and with oxygen partial pressure of 0.001atm. Similar redox behaviour was reported by Hammouche et al.

(1991) on $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ at 960°C with an oxygen partial pressure of 10^{-4}atm .

Under anodic polarisation, the formed oxygen vacancies can be consumed by the recombination reactions, followed by the re-segregation of Sr and/or Mn species on the LSM surface with the concomitant generation of cation vacancies in the LSM lattice structure. It should be noted that the consummation of oxygen vacancies might be a fast process under anodic potential and cannot be the primary cause for the deactivation effect of anodic polarisation on the O_2 reduction reactions on LSM electrodes. This seems to be supported by the much large R_E ($6.93\Omega\text{cm}^2$) after sequential anodic polarisation, as compared to the initial value ($2.89\Omega\text{cm}^2$) for the reaction on acid-etched LSM (Fig 4.12). Thus, the increase in R_E for the O_2 reduction reactions on LSM electrodes under anodic polarisation (Figs 4.3 and 4.12) could be an indicator for the kinetic characteristics of the Sr re-segregation process, which might involve the escape of Sr ions from La site and thereafter the generation of cation vacancies in the LSM lattice structure. Such a process cannot be thermodynamically favoured, and would result in the rather gradual and much smaller increase in R_E with anodic current passage (Fig4.3), as compared to the rapid reduction of R_E with cathodic current passage.

In the case of relaxation conditions, i.e., exposure of LSM electrodes in air under an OCV after 3hr of cathodic polarisation, the oxygen vacancies would also be consumed in the presence of gaseous phase O_2 , followed by the re-segregation of Sr species and the concomitant generation of cation vacancies in LSM lattice structure, according to:

Based on the defect models proposed by Nowotny et al. (1998), the dominant ion defect in LSM should be cation vacancies under present relaxation conditions. Thus the relaxation of cathodically polarised LSM electrodes under OCV and in air involves a change in concentration and transport of oxygen and cation vacancies. This might occur concurrently with the escape of Sr ions from the LSM lattice structure and thereafter the diffusion to the surface layer. It is of significance to note that cation defects have much slower diffusion kinetics as compared to that of anion defect. For perovskite-type oxides, migration energy of cation vacancies ranges from ~4eV for La vacancies to ~7.7eV for Mn vacancies (*de Souza, 1999*), which is much higher than that of oxygen vacancies (~0.7eV) (*Cherry, 1995*). This explains the two distinct stages in the relaxation behaviour of R_E , as shown in Fig4.7-4.9. It can be argued that the increase in R_E during the first 10-20hr of relaxation might result from the disappearance of oxygen vacancies and hence the reduction of the active sites for O_2 reduction reactions on the LSM surface. Further increase in R_E during prolonged relaxation experiments might be due to the severe blocking effect of SrO species on the surface active sites. It can also be seen in Fig4.7-4.9 that the increase in R_E caused by the disappearance of oxygen vacancies is still much smaller in magnitude than that caused by the Sr re-segregation and the formation of cation vacancies. This again confirms the dominant influence of surface enriched SrO species on the inhibition of the oxygen surface dissociation and diffusion process.

The transition of the dominant defect structures in the LSM lattice under cathodic and anodic polarisation conditions would also essentially influence not only the kinetics but also the reaction mechanism and the corresponding limiting reaction steps for the O_2 reduction. For freshly-prepared or anodically polarised LSM, the dominant ionic defect would be cation vacancies with concomitant surface enriched Sr species, both of which could significantly inhibit the oxygen surface dissociation and diffusion processes. Accordingly, the O_2 reduction on these two LSM electrodes is primarily limited by the electrode process associated with the low-frequency arc, as shown in Fig4.2 and Fig4.4. Under cathodic polarisation condition, the inhibiting SrO species originated on the LSM surface can be incorporated into the LSM lattice structure with concomitant disappearance of cation vacancies, leading to significantly enhanced electrochemical activity of the LSM electrode. The dominant ionic defects on cathodically polarised LSM are oxygen vacancies which could also act as active sites on the LSM surface for oxygen dissociative adsorption or oxygen species diffusion. As a result, the magnitude of low frequency process for the O_2 reduction is reduced, leading to the change of limiting reaction step to a high frequency process. Likewise, the Sr-free LSM surface can be achieved on acid-etched LSM, in which the O_2 reduction reaction is no longer limited by the oxygen surface dissociation and diffusion process.

4.5 Conclusion

The effect of cathodic and anodic polarisation on the electrochemical behaviour

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of porous LSM electrodes has been investigated at 800°C in air. The dramatic activation effect of cathodic polarisation and deactivation effect of anodic polarisation on the electrochemical performance of the LSM electrode are confirmed in the present work. Three electrode steps are identified for O₂ reduction reactions, namely, oxygen surface dissociation and diffusion (low-frequency process), oxygen ion migration and incorporation into the YSZ electrolyte (high-frequency process), and charge transfer (extra high-frequency process).

A comparative study was carried out on acid-etched LSM where cathodic polarisation was found to yield very little activation effect whilst anodic polarisation still showed a significant deactivation effect on the electrode performance. A modified defect model is therefore suggested for LSM electrodes. The surface enriched SrO species and cation vacancies are the dominant ion defects in the LSM lattice structure, and are considered to be the main cause for the initially very high electrode polarisation resistance for O₂ reduction. With the application of cathodic polarisation, the inhibiting SrO species is believed to be re-incorporated into the LSM lattice structure with the concomitant disappearance of cation vacancies, followed by the reduction of Mn ions and the generation of oxygen vacancies. Under anodic polarisation or relaxation conditions at OCV, the Sr ions may escape from the LSM lattice sites and segregate to the surface layer, resulting in the formation of cation vacancies and hence the reduced electrochemical activity for the O₂ reduction reaction.

CHAPTER 5.

Effect of Polarisation on the LSM Microstructure

5.1 Introduction

Sr-doped LaMnO_3 (LSM) is the most common cathode material for solid oxide fuel cells due to its good stability and high electrocatalytic activity for O_2 reduction at high temperatures. However, as shown recently there is a complex relationship between the microstructure and electrochemical polarisation performance for the O_2 reduction reaction on LSM electrodes (Jiang, 2003a). The relationship between the microstructural and electrode behaviour involves continuous change and evolution under fuel cell operation conditions. Tsukuda et al. (1994) studied the effect of cathodic current passage on the electrode properties of $\text{La}_{0.9}\text{Sr}_{0.1}\text{MnO}_3$, and found that microstructure changes occurred at the LSM/YSZ interface after cathodic polarisation. This was ascribed to the flux of oxygen vacancies from the YSZ electrolyte to LSM side under cathodic potential. Mizusaki et al. (1996) studied the O_2 reduction on dense LSM films and observed the formation of grains of submicrometer size with clear grain boundaries on originally dense and smooth LSM films after cathodic polarisation, an indication of morphological change induced by polarisation treatment.

Our recent studies showed that cathodic polarisation causes the microstructural change not only at the LSM/YSZ interface but also in the LSM electrode bulk (Jiang, 2003b).

In this chapter, additional results of electrode behaviour and microstructural observation for LSM electrodes under various current passage/polarisation conditions are presented. The results of electrochemical impedance spectroscopy (EIS) and scanning electron microscopy (SEM) indicate that either cathodic or anodic polarisation treatment will result in the microstructural change at the electrode/electrolyte interface and in the LSM electrode bulk. Such microstructural change has significant effect on the polarisation performance of LSM electrodes.

5.2 Experimental details

A-site deficient $(\text{La}_{0.8}\text{Sr}_{0.2})_{0.9}\text{MnO}_3$ (LSM) cathode material and YSZ electrolyte substrate were used in this chapter. Details of sample preparation and testing cell arrangement can be found in Chapter 3.

All polarisation treatments were performed under a constant current density of 200mA cm^{-2} at 800°C in air. Polarisation treatments selected in this study were (a) cathodic for 3 hrs, (b) consecutive cathodic and anodic for 6 hrs each, (c) anodic for 3 hrs, and (d) consecutive cathodic, anodic and cathodic for 9 hrs each. Duration for each individual polarisation section was set as 3 hrs. The polarisation was interrupted from time to time to conduct electrochemical impedance spectroscopy (EIS) measurement using a Solartron 1260 frequency response analyser in combination with

a Solartron 1287 electrochemical interface. The frequency range of EIS was from 0.1Hz to 100kHz and signal amplitude was 10mV. EIS measurements were performed in a three-electrode arrangement at open circuit. Electrode ohmic resistance (R_{Ω}) was measured from the high frequency intercept and electrode interface (polarisation) resistance (R_E) was obtained directly from the difference between the high-frequency and low frequency intercepts on impedance curves.

Microstructure of the LSM electrode before and after various polarisation treatments was examined by scanning electron microscopy (SEM, Leica S360). At least two samples were tested for each current/polarisation treatment to confirm the reproducibility of the microstructural change and electrode behaviour. The average particle size of LSM electrodes after various current passage treatments was directly estimated from SEM pictures taken at different areas of the electrodes.

5.3 Results

5.3.1 Polarisation behaviour

Fig 5.1 shows the impedance responses and the change of electrode polarisation resistance (R_E) of a freshly-prepared LSM electrode as a function of cathodic current passage time at 200 mAcm^{-2} and 800°C in air for 3 hrs. The absolute value of R_E depended on individual LSM electrodes. However, the trend of the change of R_E with the cathodic current passage time was the same. R_E shows a very sharp decrease during the first 5min of cathodic polarisation after which the decrease in R_E was much smaller with the current passage time. The initial R_E value was $18.5 \text{ }\Omega\text{cm}^2$ before

Fig 5.1 Initial (a) impedance responses and (b) electrode polarisation resistance (R_E) of freshly-prepared LSM electrode as a function of cathodic current passage time at 200 mAcm^{-2} and 800°C in air.

cathodic current passage and was reduced significantly to 3.5 $\Omega \text{ cm}^2$ after 5min of current passage. At the end of 3hr cathodic polarisation treatment, R_E was reduced to 0.75 $\Omega \text{ cm}^2$. This indicates that the activation process of cathodic polarisation on the polarisation performance of LSM electrodes is rather rapid and is most effective at first 5 to 15 minutes of cathodic current passage under present test conditions.

Fig 5.2 shows the impedance responses and electrode polarisation resistance of a

Fig 5.2 Impedance responses of freshly-prepared LSM electrode with (a) cathodic and then (b) anodic current passage time at 200mAcm^{-2} and 800°C in air. The change of electrode polarisation resistance (R_E) as a function of different current passage time is shown in (c).

freshly prepared LSM electrode after 3 hr cathodic current passage followed by another 3 hr anodic current passage at 200 mAcm^{-2} and 800°C . Similar to that shown in Fig5.1, a rapid reduction in R_E was observed with cathodic current passage. After the cathodic current passage treatment, R_E increased with the anodic current passage. However, different from the rapid reduction of R_E with the cathodic current passage, the increase in R_E with anodic current passage time was rather gradual and much slower (Fig5.2c). The increase of R_E with the anodic current passage is an indication of deactivation effect of anodic polarisation on the O_2 reduction reactions on LSM electrodes. At the end of anodic current passage treatment for 3 hrs, R_E was $23 \text{ } \Omega\text{cm}^2$, still much smaller than the initial R_E of $43.6 \text{ } \Omega\text{cm}^2$ before the cathodic current passage. This indicates that activation effect of cathodic polarisation and deactivation effect of anodic polarisation are not completely reversible in respect to the polarisation behaviour of LSM electrodes.

The effect of anodic polarisation was also studied on a freshly-prepared LSM electrode, as shown in Fig 5.3. Change of R_E with anodic current passage time can be characterised by two distinct regions: R_E increased very quickly with anodic current passage, followed by a region where R_E showed a gradual decrease (Fig5.3b). R_E was $19 \text{ } \Omega\text{cm}^2$ before anodic current passage. After 5min of anodic current passage, R_E increased significantly to $39.5 \text{ } \Omega\text{cm}^2$. Further anodic current passage treatment led to the monotonous decrease of R_E . After anodic polarisation for 3 hrs, R_E was reduced to $32 \text{ } \Omega\text{cm}^2$, which was still higher than the initial value of $19 \text{ } \Omega\text{cm}^2$ before anodic polarisation. Such polarisation behaviour of the freshly-prepared LSM electrode with

Fig 5.3 Initial (a) impedance responses and (b) electrode polarisation resistances (R_E) of freshly-prepared LSM electrode as a function of anodic current passage time at 200mAcm⁻² and 800°C in air.

anodic current passage was quite different from that observed on the cathodically polarised LSM electrode (see Fig5.2).

Fig 5.4 shows the impedance responses and change of electrode polarisation resistance as a function of sequential cathodic, anodic and then cathodic current passage treatments at 200 mAcm⁻² and 800°C in air. The activation effect of cathodic polarisation and deactivation effect of anodic polarisation were again observed and the rate of increase in R_E with anodic polarisation was much smaller than the rate of

decrease in R_E with the cathodic polarisation, similar to that described above (Fig5.2).

Moreover, the activation effect of cathodic polarisation on anodically-polarised LSM electrode is almost identical to that on freshly-prepared LSM electrodes, indicated by the rapid reduction in R_E .

Fig 5.4 Impedance responses of freshly-prepared LSM electrode with (a) cathodic, (b) anodic and finally (c) cathodic current passage time at 200 mA cm^{-2} and 800°C in air. The change of electrode polarisation resistance (R_E) as a function of different current passage time is shown in (d).

5.3.2 Microstructure observation

Fig 5.5 shows the SEM pictures of fractured cross-sections of LSM electrodes in the bulk and at the electrode/electrolyte interface region before and after cathodic polarisation treatment at 200 mA cm^{-2} and 800°C for 3 hrs in air. The microstructure of

Fig 5.5 SEM pictures of fractured cross-section of freshly-prepared LSM electrode (a&c) before cathodic current passage and (b & d) after cathodic current passage of 200mAcm^{-2} at 800°C for 3hr in air. (a) and (b) shows the bulk and (c) and (d) are the interface region.

the freshly-prepared LSM electrode is characterised by large agglomerates with no clear grain boundaries between LSM particles (Fig5.5a). The bonding between LSM agglomerates and YSZ electrolyte appears to be good, indicated by the continuity between LSM electrode and YSZ electrolyte phases (Fig5.5c). After cathodic current passage treatment, large agglomerates of LSM electrodes disappeared and the microstructure of the LSM electrode was characterised by much smaller and well-defined granular-shaped particles with clear grain boundaries (Fig5.5b). This is similar to the microstructural change induced by cathodic polarisation on LSM electrodes with a different composition (Jiang, 2003b). However, such change in the microstructure of LSM electrode does not seem to affect the good bonding between

LSM particles and YSZ electrolyte. This is indicated by the continuity at the LSM and YSZ interface (Fig 5.5d). There is also significant increase in small pores due to the microstructural change of the LSM cathode after cathodic current passage.

Fig 5.6, 5.7 and 5.8 are the respective SEM pictures of freshly-prepared LSM electrode in the bulk and at the electrode/electrolyte interface region after various polarization/current passage treatments, i.e., consecutive cathodic and anodic polarisation (Fig 5.6), anodic polarisation (Fig 5.7) and consecutive cathodic, anodic and cathodic polarisation (Fig 5.8). It is clear that the microstructural change at the

Fig 5.6 SEM pictures of the fractured cross-section of freshly-prepared LSM electrode (a) in the bulk and (b) the interface region after cathodic and anodic current passage for 6 hrs at 200mAcm^{-2} and 800°C in air.

LSM/YSZ interface is similar to that observed in the bulk. Similar to those after cathodic polarisation (see Fig5.5b&5.5d), the microstructure of the freshly-prepared LSM electrode after cathodic and anodic polarisation was characterised by well-defined sphere-shaped particles (Fig5.6). This indicates that the morphology change caused by the cathodic current passage treatment cannot be reversed with subsequent anodic current passage treatment. The microstructural change was also observed on freshly-prepared LSM electrode after anodic current passage (Fig5.7). The morphology change induced by anodic current passage was similar to that after

Fig 5.7 SEM pictures of the fractured cross-section of freshly-prepared LSM electrode (a) in the bulk and (b) the interface region after anodic current passage for 3 hrs at 200 mAcm⁻² and 800°C in air.

Fig 5.8 SEM pictures of the fractured cross-section of freshly-prepared LSM electrode (a) in the bulk and (b) the interface region after cathodic, anodic and cathodic current passage for 9 hrs at 200mAcm^{-2} and 800°C in air.

cathodic current passage treatment on the freshly-prepared LSM sample (see Fig5.5). This shows that the morphology and microstructure change of freshly-prepared LSM electrode can take place either under cathodic or under anodic polarisation conditions. Similar morphological change was also observed after sequential cathodic, anodic and finally cathodic current passage for total 9 hrs (Fig5.8). However, it appears that LSM particles grew after such sequential polarisation treatment. After cathodic current passage for 3 hrs, average LSM particle size was estimated to be $0.76 \pm 0.18 \mu\text{m}$ (Fig5.5b). After anodic current passage for 3 hrs, average particle size of LSM was

Fig 5.9 Average particle size of LSM electrodes after cathodic current passage for 3 hrs, anodic current passage for 3 hrs, cathodic and anodic (C-A) current passage for 6 hrs, and cathodic, anodic and cathodic (C-A-C) current passage for 9 hrs at 200 mAcm^{-2} and 800°C .

$0.67 \pm 0.19 \text{ } \mu\text{m}$ (Fig5.7), slightly smaller than that after cathodic current passage treatment. On the other hand, LSM particles grew to $0.89 \pm 0.29 \text{ } \mu\text{m}$ after cathodic and anodic current passage for 6 hrs (Fig5.6) and to $1.04 \pm 0.29 \text{ } \mu\text{m}$ after cathodic, anodic and finally cathodic current passage for 9 hrs (Fig5.8). Fig 5.9 compares the average particle size of LSM electrodes after various current passage treatments. The LSM particles after alternative cathodic, anodic and cathodic current passage for 9 hrs was 37% larger than that after cathodic current passage for 3 hrs. It appears that the increase in the LSM grains is quite significant with alternative cathodic and anodic current passage/polarisation.

5.4 Discussion

Cathodic current passage/polarisation has a significant effect on the polarisation behaviour of the O_2 reduction reaction on LSM electrodes. As discussed in Chapter 4, the incorporation of surface inhibiting SrO species and the removal of cation vacancies would occur during the first stage of cathodic polarisation, after which the oxygen vacancies could be generated at the electrode/electrolyte interface region with charge compensation by the reduction of Mn ions. Oxygen vacancies formed at the LSM/YSZ interface region would propagate, extending the reactive sites for the O_2 reduction reaction (*Lee, 1995*). The electrochemical improvement in activity is thus believed to result from the favorable broadening of the active reaction zone as a result of the removal of surface inhibiting SrO species and the formation of oxygen vacancies (*Hammouche, 1991; Siebert, 1994, Chapter 4*).

The polarisation behaviour of LSM electrodes under anodic current passage appears to be dependant on the electrochemical history of individual LSM electrodes, e.g. freshly-prepared or cathodically polarised. As shown in Fig5.2 and 5.4, R_E increased with the anodic current passage time on the cathodically-polarised LSM electrodes, which could be ascribed to the transition of the dominant ionic defect from oxygen vacancies to cation vacancies, and the re-segregation of inhibiting SrO to the LSM surface under anodic potential (*Chapter 4*). However, in the case of the freshly-prepared LSM electrode, a very sharp increase of electrode polarisation resistance (R_E) was observed after applying anodic polarisation for 5 min and this was

followed by a gradual decrease in R_E with anodic current passage time (Fig5.3). Nevertheless, after anodic current passage for 3 hrs, R_E was still higher than the initial R_E value of the freshly-prepared LSM electrode before the current passage treatment.

There may exist two possible effects of anodic current passage on the electrode behaviour of freshly-prepared LSM electrodes. Under anodic polarisation conditions, LSM is in the oxidation environment and would exhibit apparent oxygen excess nonstoichiometry. According to the defect model suggested by Yasumoto et al. (2001), charge compensation for the excess oxygen would be met by the oxidation of the B-site Mn ions with the concomitant increased concentration of cation vacancy, which would significantly retard the electrode reactions. The application of anodic potential could also cause much more severe SrO segregation from the perovskite structure to the LSM surface layers, likewise contributing to the increase in the electrode polarisation resistance for the O_2 reduction reaction. On the other hand, microstructure and morphology of LSM electrodes also changes under anodic current passage, similar to that observed under cathodic current passage (Fig5.7). The transition from large agglomerates to sphere-shaped particles increases the three phase boundary (TPB) area between gas, LSM electrode and YSZ electrolyte, resulting in the reduction of the polarisation resistance for the O_2 oxidation reaction. The subsequent decrease in R_E with the anodic current passage time (Fig5.3b) indicates that the positive effect of morphology improvement became predominant, compensating the negative effect of the increase in the cation vacancies and/or the content of surface inhibiting SrO species on LSM electrodes. As the morphological

change induced either by cathodic current passage or by anodic current passage is not reversible (see Fig5.6), the beneficial effect of morphology improvement induced by anodic polarisation for the O_2 reduction reaction on prior cathodically-polarised LSM electrode is therefore no longer operative. Thus, the polarisation resistance would monotonously increase with the increase of anodic current passage time until the pressure of O_2 generated at the interface is high enough to cause the delamination at the electrode/electrolyte interface (Yamashita, 1994). The very fast initial increase of R_E for the reaction on freshly-prepared LSM electrode as compared to that on the prior cathodically-polarised LSM electrode could be the magnified effect of the increase in cation vacancies and/or the severe segregation of inhibiting SrO under anodic potential on originally large and plate-like agglomerates with very low three phase boundary areas.

It should be pointed out here that delamination at the LSM electrode/YSZ electrolyte interface may not occur in the present studies. This is indicated by the very stable electrode ohmic resistance before and after various current passage treatments. SEM examination of LSM electrode at the electrode/electrolyte interface region after 3 hours of anodic polarisation showed no evidence for delamination. However, after anodic current treatment at 200mA cm^{-2} and 800°C for more than 25 hours, LSM electrode coating was observed to be completely delaminated from the YSZ electrolyte. Yamashita et al. (1994) studied the effect of cathodic and anodic polarisation on the electrode performance of $\text{La}_{0.9}\text{Sr}_{0.1}\text{MnO}_3$, and found that the LSM electrode adhered well with YSZ electrolyte after anodic current treatment at 300

mAcm^{-2} for 5 hours but delaminated after ~ 10 hours of anodic current treatment. The delamination is most likely caused by the high oxygen pressure generated at the electrode/electrolyte interface due to the oxygen oxidation reaction.

As shown by the SEM studies of freshly-prepared LSM electrodes (Figs 5.5 & 5.7), the change in microstructure and morphology can be induced by either cathodic or anodic current passage. The microstructural change of LSM electrodes under polarisation is clearly irreversible as shown by the stability of sphere-like morphology of LSM electrodes after repetitive current passage treatments (Fig 5.6). The microstructural changes induced by cathodic current passage could be explained by the generation and migration of oxygen vacancies and Mn ions under cathodic polarisation conditions. As shown recently by Miyoshi et al. (2003), the lattice of LSM perovskites expanded under a reducing environment at low partial pressure of oxygen. This is due to the fact that when oxygen vacancies are introduced (i.e. an increase of oxygen nonstoichiometry) due to reduced partial pressure of oxygen, the charge neutrality in the LSM structure would be maintained by the reduction of transition metal ions in LSM B-site to the lower valence state according to Eq(4.1) and (4.2), leading to an increase of the average ionic radius of the cation and thus lattice expansion. The effect of increase in B-site radius could be partially offset by the increase in the crystallographic distortion (Miyoshi, 2003). Lattice expansion upon reduction has also been studied on LaCrO_3 -based interconnect materials (Zuev, 2000; Mori, 2001). Similar to that under reducing environment at low partial pressure of oxygen, lattice expansion and crystallographic distortion of LSM perovskite structure

could also occur under cathodic current passage/polarisation conditions. It is known that manganese species such as Mn^{3+} and Mn^{2+} ions are also mobile under fuel cell operating conditions as shown by the extensive Cr deposition on the YSZ electrolyte surface which has been shown to be initiated by the Mn^{2+} ions migrated from LSM electrodes (Jiang, 2000a and 2001a). Weber et al. (1996) studied the microstructural change of $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ cathodes operated at 950°C for ~ 2000 hrs and observed the migration of Mn out of the cathode and into the zirconia electrolyte in addition to the significant grain growth and densification. Lattice expansion, crystallographic distortion and cation migration could all weaken the contacts between particles of the agglomerates, leading to the disintegration of the agglomerating structure into sphere-shaped particles. Diffusion of oxygen vacancies generated under cathodic polarisation is most likely through diffusion on the LSM surface (Carter, 1992). Therefore, morphological change from the agglomerating structure to sphere-shaped particles induced by the cathodic polarisation would promote the O_2 reduction reaction, as the surface diffusion path of oxygen would be shorter on sphere-shaped particles, as compared to that on larger agglomerates. However, morphological change induced by prolonged cathodic polarisation can cause the pore formation and increase the porosity of LSM electrodes, leading to the performance degradation (Jorgensen, 2000). On the other hand, prolonged sintering at 1000°C under open circuit conditions in air has little effect on the microstructure and performance of LSM electrodes (Jorgensen, 2000).

Similar to that observed under cathodic current passage, large agglomerates in

freshly-prepared LSM electrodes changed to sphere-like particles with clear grain boundaries after anodic current passage treatment at 200 mAcm^{-2} and 800°C for 3 hrs (Fig5.7). As discussed above, under anodic current passage/polarisation or oxidation conditions, LSM perovskites could incorporate excess oxygen with the valence increase of the transition metal ions in LSM B-site and the creation of cation vacancies, leading to the lattice shrinkage, similar to that observed on $\text{LaMnO}_{3.8}$ (Töpfer, 1997; Hauback, 1996). Thus, the morphology and microstructure change of the freshly-prepared LSM electrode under anodic current passage/polarisation is most likely related to the shrinkage of unit cells of LSM under oxidation environment. This appears to be supported by the slightly smaller grain size of the LSM electrode after anodic current passage at 200 mAcm^{-2} and 800°C for 3 hrs ($0.67 \pm 0.19 \mu\text{m}$) as compared to that ($0.76 \pm 0.18 \mu\text{m}$) after cathodic current passage under the same conditions. LSM lattice expansion and shrinkage under cathodic and anodic polarisation could be the reason for the observed relatively fast grain growth of LSM electrodes after consecutive cathodic and anodic current passage treatment (Fig5.9). The irreversibility in the microstructure and morphology change under cathodic or anodic current passage explains the partial irreversibility of the initial LSM polarisation behaviour observed on the freshly-prepared LSM electrodes (Jiang, 1999a; Lee, 1995).

5.5 Conclusion

Effect of polarisation has been studied on freshly prepared LSM electrodes at

800°C in air under different polarisation conditions. Cathodic current passage/polarisation was found not only to enhance the polarisation performance of the LSM electrode, but also to improve the microstructure and morphology of the LSM electrode. The generation and migration of oxygen vacancies and Mn ions and lattice expansion and crystallographic distortion under cathodic current passage could all contribute to the microstructural changes. Similar to that observed under cathodic current passage, anodic current passage also induced microstructure and morphology improvement on freshly-prepared LSM electrode, which is most likely due to the lattice shrinkage under oxidation environment.

Performance of freshly-prepared LSM electrodes for O₂ reduction reactions is improved significantly under cathodic current passage/polarisation. In addition to the microstructure enhancement, cathodic polarisation could reduce the content of passivation species such as SrO on the LSM surface layers (*Chapter 4*) and promote the generation of oxygen vacancies (*Lee, 1995*), leading to the broadening of the three phase boundary areas for the O₂ reduction. In the case of freshly-prepared LSM electrodes, anodic polarisation would lead to the increase of both cation vacancies and surface passivation species due to the increased oxygen excess nonstoichiometry under oxidation conditions and at the same time enhance the microstructure of the LSM electrode. The microstructure change from large agglomerate to sphere-like particles with clear grain boundaries increases the three phase boundary regions for the O₂ reduction. This explains the observed initial increase and then gradual decrease in R_E of the freshly-prepared LSM electrode with anodic current passage time.

CHAPTER 6.

Effect of Polarisation on LSM/YSZ Interface

6.1 Introduction

The O_2 reduction reaction on a Sr-doped $LaMnO_3$ (LSM) cathode is one of the most important electrode reactions in solid-oxide fuel cells (SOFC) and has been extensively investigated. Increasing the reaction sites or areas between the LSM and YSZ electrolyte is critical to enhance the electrode performance of the LSM cathodes. However, there are still considerable discrepancies in the exact reaction sites for the O_2 reduction reactions in the LSM/YSZ system. Mizusaki et al. (1991) reported a proportional relationship between the rate of the O_2 reduction reaction and the length of the three-phase boundary (TPB) where electrode, electrolyte and O_2 gas meet on $La_{0.6}Ca_{0.4}MnO_3$ electrodes. A similar relationship between the LSM electrode performance and TPB length was also reported by Fukunaga et al. (1996). By using LSM powders sintered at different temperatures, van Heuveln et al. (1997a) observed that the electrochemical performance of LSM cathodes depends on the TPB zone and the extension of the TPB zone at the LSM electrode and YSZ electrolyte interface was estimated to be in the range of 0.03 to 0.07 μm . Horita et al. (1998) used

secondary-ion mass spectrometry (SIMS) to study oxygen transport in $\text{La}_{0.9}\text{Sr}_{0.1}\text{MnO}_3$ and found that the active sites for O_2 reduction were spots around the $\text{O}_2/\text{LSM}/\text{YSZ}$ three-phase boundary. The rationale behind the critical role of the TPB in the O_2 reduction reactions is the very low oxygen ion conductivity of LSM materials, which was estimated to be in the range of 10^{-7} to 10^{-6} Scm^{-1} at 1000°C (Carter, 1992; Yasuda, 1996). This is also consistent with the observation that the polarisation performance of a dense LSM electrode is much poorer than that of porous LSM electrodes (van Herle, 1996; Endo, 1996). On the other hand, Odgaard et al. (1996) found that the polarisation resistance of $\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_3$ electrode decreased with increases in the LSM/YSZ contact area. Brichizin et al. (2000) studied the geometry dependence of the cathode potential on a well-defined thin LSM microelectrode and found that the polarisation resistance varied inversely with the electrode area rather than the TPB length. This suggests that the rate-determining step of the reaction could be related to the surface area of the LSM or the LSM/electrolyte two-phase area. The limiting step associated with bulk diffusion of oxygen was also suggested for the reaction on porous $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ electrode at 950°C (Kuznecov, 2003). The significant dependence of the electrochemical behaviour on the polarisation for the reaction on LSM electrodes also complicates the issue of the reaction sites (Ghargabe, 1994; Siebert, 1995; Jiang, 1999a).

In this chapter, we employed the atomic force microscopy (AFM) technique to examine the morphology/topography changes at an LSM/YSZ interface under both cathodic and anodic polarisation conditions. The AFM results clearly indicate that

polarisation has a significant effect on the morphology and topography of the three-phase boundary at the LSM/YSZ interface, an invaluable indication of the reaction sites for the O₂ reduction and oxidation reactions in the LSM electrode and YSZ electrolyte cell.

6.2 Experimental details

The details of sample preparation, testing cell arrangement and the various polarisation treatments could be found in Chapter 3 and Chapter 5, respectively. The morphology and topography changes at the LSM/YSZ interface before and after various polarisation treatments were examined by scanning electron microscopy (SEM, Leica S360) and atomic force microscopy (AFM, Nanoscope IIIA, Digital Instruments). In order to examine the LSM/YSZ interface, the LSM electrode coatings were removed after testing by hydrochloric acid treatment in an ultrasonic bath at room temperature. As shown by Mitterdorfer and Gauckler (1998), such acid treatment will not remove YSZ or secondary phases formed on the YSZ electrolyte surface. Thereafter, the specimen was cleaned with ethanol and distilled water and dried before the SEM and AFM examination.

6.3 Results and Discussion

Fig 6.1 summarises the electrode polarisation resistance (R_E) of freshly prepared LSM under various polarisation treatments at 200mAcm^{-2} and 800°C in air. The electrode behaviour of LSM under various polarisation conditions has been presented

Fig 6.1 Electrode polarisation resistance of freshly-prepared LSM electrodes as a function of polarisation treatment time at 200 mA cm^{-2} and 800°C . (a) cathodic current for 3 hrs, (b) cathodic current for 3 hrs followed by anodic current for 3 hrs, (c) cathodic, anodic and cathodic current for a total of 9 hrs and (d) anodic current for 3 hrs. Electrode polarisation resistance was measured by EIS at open circuit.

and discussed in previous chapters, and will not be repeated here.

Fig 6.2 shows the SEM pictures of the YSZ electrolyte surface in contact with the LSM coating before and after cathodic current treatment at 200 mA cm^{-2} and 900°C for 4 hrs. The LSM coating was removed by HCl acid treatment. The contact marks between LSM particles and YSZ electrolyte can be clearly seen and such SEM pictures are commonly used to estimate the three-phase boundary length and electrode/electrolyte contact areas (*van Heuveln, 1997a; Chen, 2004c; Kuznecov, 1999*). However, as shown by the SEM pictures, the change in the morphology of the

Fig 6.2 SEM pictures of YSZ electrolyte surface in contact with LSM cathode (a) before and (b) after polarisation treatment at 200mAcm^{-2} and 900°C for 4 hrs.

interface contact between the LSM electrode and the YSZ electrolyte before and after cathodic current polarisation is not clearly distinguishable.

Fig 6.3 shows the AFM images of the original YSZ electrolyte surface with no LSM contact. Smooth YSZ surface with clear grain boundary of average size around $1.5\mu\text{m}$ in length can be seen.

Fig 6.4 shows the AFM images of the YSZ surface in contact with the LSM electrode before polarisation treatment. After removing the LSM electrode coating by

Fig 6.3 AFM images of pure YSZ electrolyte surface.

HCl acid treatment, rings or dents approximately 0.5-1.0 μm in diameter can be clearly seen on the YSZ surface. They grew out of the YSZ electrolyte, forming convex-shape rings on the YSZ surface. The rings had sharp boundaries and the depth of the rings was in the range of 90 to 140 nm. These rings locate either on the smooth surface of YSZ grains or at the grain boundary area (Fig6.4b). This indicated that the rings are the contact points between LSM particles and the YSZ surface. The size of the rings is related to the size of LSM grains in contact with YSZ electrolyte. Mitterdorfer and Gauckler (1998), in the study on the inter-reaction between $\text{La}_{0.85}\text{Sr}_{0.15}\text{Mn}_y\text{O}_3$ cathodes and YSZ electrolyte, also reported the formation of evenly-distributed Mn-doped YSZ rings at the LSM/YSZ interface region during the early sintering period of the LSM coating, which was most likely due to the Zr^{4+} ions diffusing along the YSZ surface towards the TPB. Square islands of the inter-reaction

Fig 6.4 AFM images of YSZ electrolyte surface in contact with LSM coating before polarisation treatment. (a) and (b) have different magnification

product $\text{La}_2\text{Zr}_2\text{O}_7$ was found to form on top of the convex rings after prolonged sintering at 1200°C (Mitterdorfer, 1998). However, the sharp boundaries of the convex rings showed in Fig 6.4 indicate that there is no formation of $\text{La}_2\text{Zr}_2\text{O}_7$ under the experimental conditions in this work. The reason for Zr^{4+} ion surface diffusion may be that the region near the TPB of unsintered LSM grains on YSZ surface is highly curved, and decreasing the curvature of the contact decreases the free surface energy (Mitterdorfer, 1998).

Fig 6.5 shows AFM images of the YSZ electrolyte surface in contact with the LSM coating after various polarisation treatments at 200mA cm^{-2} and 800°C in air. Despite the difference in the polarisation treatments, the changes in the morphology and topography of the convex rings are similar. After polarisation treatment, the sharp edge of the YSZ rings disappeared and the rings grew outwards. The circumference of the rings became a two-dimensional boundary area. The width of the rings was in the

See following page

(d)

Fig 6.5 AFM images of YSZ electrolyte surface in contact with LSM electrodes after (a) cathodic current treatment for 3 hrs, (b) cathodic and anodic current treatment for 6 hrs, (c) cathodic, anodic and cathodic current treatment for a total of 9 hrs and (d) anodic current treatment for 3 hrs at 200 mAcm^{-2} and 800°C in air. Note that two different magnifications were used for each sample.

range of 0.08 to $0.23 \mu\text{m}$ and the average ring width was $0.15 \pm 0.05 \mu\text{m}$. The significant change in the topography of the convex rings indicates that microstructure and morphology changes occur not only in the bulk of the LSM electrode (*Chapter 5; Jiang 2003a*) but also at the LSM/YSZ interface. It is noted that such interfacial changes induced by cathodic polarisation are not reversible under subsequent anodic polarisation, as shown in Fig6.5b and Fig6.5c. Moreover, the anodic current treatment on a freshly-prepared LSM electrode also induced the change in LSM/YSZ interface topography in a similar manner to the cathodic current treatment (Fig6.5d). This indicates that the initial LSM/YSZ interface formed by the thermal treatment of the system is morphologically unstable. Either cathodic or anodic current passage has a significant effect on the interface morphology and topography between the LSM electrode and the YSZ electrolyte. It can also be seen that the topography at the

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LSM/YSZ interface after 9 hrs of polarisation (Fig6.5c) is similar to that after only 3 hrs of either cathodic (Fig6.5a) or anodic current treatment (Fig6.5d). This shows that the broadening or flattening of the convex rings at the LSM/YSZ interface may not be a significant function of polarisation time.

The area within the convex rings is an indication of the two-phase LSM/YSZ contact area and the flattened circumference of the ring is an indication of the three-phase boundary area. Thus, the two-phase contact areas between the LSM electrode and YSZ electrolyte and the three-phase boundary areas can be estimated from the contact diameter (d) and ring width (δ) of the convex rings, respectively. Fig 6.6 shows the dependence of the two-phase area and three-phase boundary areas as a function of the contact diameter for the LSM electrodes after various polarisation treatments at 200mAcm^{-2} and 800°C . In both cases, the two-phase area and the three-phase boundary area increased proportionally with the LSM contact diameter or the LSM grain size. This shows that if the three-phase boundary is taken as a two dimensional area rather than a one dimensional line, the dependence of the electrode polarisation resistance on the three-phase boundary areas would be similar to that on the two-phase contact area (*van Heuveln, 1997a; Brichzin, 2000*). This indicates that a simple proportional dependence of the electrode polarisation resistance or conductivity on the two-phase contact area or on the three-phase boundary area may not be a sufficient evidence to determine the reaction sites of O_2 reduction reactions in the LSM/YSZ system. The broadening of the convex ring under various polarisation treatments is probably clear evidence that the three-phase boundary is not a one

Fig 6.6 Plots of two-phase contact area and three-phase boundary areas as a function of the contact diameter for the LSM electrodes after various polarisation treatments at 200 mAcm^{-2} and 800°C as shown in Fig6.5.

dimensional line.

The sensitivity of the electrode polarisation resistance of LSM cathodes with polarisation treatment has been discussed in detail in Chapter 4 and Chapter 5. The significant effect of polarisation treatment on the electrode impedance and polarisation behaviour has been explained by migration and removal of passivation species such as strontium oxides on the LSM electrode surface under the influence of cathodic polarisation (Jiang, 2001b; Chapter 4), the removal of cation vacancies (Chen, 2004b), formation of oxygen vacancies and enlargement of the TPB (Odgaard, 1996; Lee, 1995; Siebert, 1994), and morphological and microstructural changes in

Chapter 6. Effect of Polarisation on LSM/YSZ Interface

LSM (*Chapter 5; Jiang, 2003a*). The AFM results presented in this study show that polarisation treatment also has a significant effect on the topography and morphology of the interface contact between the LSM electrode and YSZ electrolyte. The topography changes at the LSM/YSZ interface could shed light on the reaction sites for O₂ reactions on LSM electrodes. Horita et al. (*1998 and 2000*) studied the reaction sites for O₂ reduction at the LSM/YSZ interface by secondary-ion mass spectrometry (SIMS). The high concentration of ¹⁸O at the O₂/LSM/YSZ three phase boundary region indicates that TPB is the main reaction site for O₂ reduction reactions even though O₂ can diffuse through the LSM under high polarisation potentials. The width of the TPB was estimated to be less than 0.95 µm. Further study showed that convex parts of the YSZ electrolyte surface have significantly higher concentrations of manganese as compared to that of the flat boundary between LSM and YSZ and the convex boundaries are also found to be the oxygen diffusion paths (*Horita, 2002*). According to Lee et al. (*1995*), Mn²⁺ ions are generated under cathodic polarisation conditions with concomitant formation of oxygen vacancies. Similar to oxygen vacancies, Mn²⁺ ions are also mobile. Therefore, under cathodic polarisation conditions, Mn²⁺ ions could migrate from the LSM electrode surface to the YSZ electrolyte surface, dissolve in the YSZ electrolyte and/or diffuse along the YSZ electrolyte surface. Yokokawa et al. (*1991*) reported that manganese can dissolve up to 11.4% (2.1% as Mn³⁺ and 9.3% as Mn²⁺) in (ZrO₂)_{0.85}(Y₂O₃)_{0.15} at 1300°C in air. Although the temperature used in present work was relatively low e.g. 800°C, the applied cathodic potential may be favourable for manganese diffusion (*Jiang, 2000b*).

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The convex rings at the O₂/LSM/YSZ interface could provide the short diffusion paths for oxygen incorporation and/or manganese dissolution. The significant topography change of the convex rings after cathodic polarisation is most likely due to the incorporation of oxygen and/or manganese and interdiffusion processes between the LSM and the YSZ electrolyte. Anodic polarisation will enhance the oxygen activity at the O₂/LSM/YSZ interface. The significant topography changes in the convex rings at the O₂/LSM/YSZ interface region under anodic polarisation treatment indicate that the oxygen evolution reaction most likely occurs via oxygen interdiffusion at the O₂/LSM/YSZ three-phase boundary areas. The flattening of the convex rings may be partly responsible for the small decrease of the R_E with the anodic polarisation on freshly-prepared LSM electrodes due to the increased reaction area (Fig 6.1b). Similar changes in the morphology and topography of the convex rings at the O₂/LSM/YSZ interface region under both cathodic and anodic polarisation conditions indicate that the convex ring areas are the reaction sites for oxygen incorporation and evolution between the LSM electrode and the YSZ electrolyte. The broadening or flattening of the convex rings reduces surface energy and thus stabilises the reaction sites at the interface.

The broadening or flattening of the convex rings as observed in the present work also shows that TPB is a two-dimensional area and not a one-dimensional line. Based on the AFM images, the TPB width has been estimated to be $0.15 \pm 0.05 \mu\text{m}$. This is higher than the value of 0.03-0.07 μm estimated from electrochemical performance measurements but lower than 0.95 μm estimated by SIMS techniques (*van Heuveln*,

1997a; Horita, 2002). As shown in Fig6.6, the three-phase boundary area and the LSM/YSZ two-phase boundary are proportional to the LSM contact diameter or the LSM particle size. The similar dependence of both contact areas on the LSM particle size could partly explain the discrepancies in the reaction sites for the O₂ reduction reactions in the LSM/YSZ systems as reported in the literature.

6.4 Conclusion

The electrode polarisation resistance and interface morphology and topography between LSM electrodes and the YSZ electrolyte were studied by EIS, SEM and AFM under various polarisation conditions. Thermal treatment of the LSM electrode at 1150°C caused formation of convex rings with sharp edges at the LSM/YSZ interface. Under cathodic or anodic polarisation conditions, the edge of the convex rings became broadened and flattened. The similar change in the morphology and topography of the convex rings under cathodic and anodic polarisation treatments indicates that the convex ring areas are most likely the reaction sites for the O₂ incorporation/diffusion between LSM and YSZ electrolyte. The width of the convex ring was estimated as $0.15 \pm 0.05 \mu\text{m}$.

CHAPTER 7.

SINTERING BEHAVIOUR OF LSM CATHODES UNDER CATHODIC POLARISATION

7.1 Introduction

In solid oxide fuel cells (SOFCs), the stability and sintering behaviour of electrode materials such as Sr-doped LaMnO_3 (LSM) and $\text{Ni/Y}_2\text{O}_3\text{-ZrO}_2$ (Ni/YSZ) cermet is a major concern for the long-term performance at SOFC operation temperatures (*Iwata, 1996; Antonucci, 1998; Ioselevich, 1997; Vaßen, 2001; Wilkenhoener, 1999; Simwonis, 2000*). In the case of Ni/YSZ cermet electrodes, the sintering behaviour is dominated by the agglomeration and grain growth of Ni particles and critically related to the content of Ni and YSZ phases in the cermet (*Jiang, 2003e*). An agglomeration of Ni particles in the cermet can lead to a significant reduction in the three-phase boundary areas and to an increase in the electrode polarisation resistance for the H_2 oxidation reaction (*Iwata, 1996*). Optimization of the phase distribution between Ni and YSZ is critical for the inhibition of agglomeration and sintering of the Ni particles and for an improvement of the performance stability of SOFC (*Simwonis, 2000; Jiang, 2003e; Itoh, 1997*). In

the case of LSM cathodes, the sintering behaviour is found to be related to the strontium dopant level and stoichiometric composition of $(\text{La,Sr})_x\text{MnO}_3$. It has been shown that LSM with an A-site deficient composition ($x < 1$) sinters more readily than their B-site deficient counterparts ($x > 1$) (Meixner, 2002; van Roosmalen, 1993). In SOFCs based on YSZ electrolyte, the A-site deficient composition is often preferred to reduce the formation of resistive phases such as $\text{La}_2\text{Zr}_2\text{O}_7$ or SrZrO_3 at the interface between LSM and YSZ (Mitterdorfer, 1998).

Jørgensen et al. (2000) investigated the performance and microstructure stability of LSM/YSZ composite cathodes under a cathodic current of 300mAcm^{-2} at 1000°C for 2000hr. The overpotential losses were doubled and there was an increase of the porosity at the interface between the composite electrode and YSZ electrolyte interface. On the other hand they did not observe such structural changes for the composite cathodes sintered under open circuit conditions. As shown in Chapter 5, the morphology of LSM changes significantly under cathodic and/or anodic polarisation which can be related to the lattice expansion or shrinkage under either cathodic or anodic polarisation (Miyoshi, 2003; Hauback, 1996). Therefore an interesting question would be the sintering behaviour of LSM electrodes under cathodic polarisation as this is important for the fundamental understanding of the structural and performance stability of LSM-based cathodes under SOFC operation conditions.

In this chapter, a comparative study was conducted on the grain growth and sintering behaviour of LSM cathodes as a function of A-site stoichiometry with and without application of a constant cathodic current load at 1000°C . The results indicate

that the sintering behaviour of LSM cathodes is hindered under cathodic polarisation conditions as compared to those sintered under open circuit conditions.

7.2 Experimental details

3mol% $\text{Y}_2\text{O}_3\text{-ZrO}_2$ (TZ3Y) electrolyte substrate and $(\text{La}_{0.8}\text{Sr}_{0.2})_x\text{MnO}_3$ powder with $x=1.0$ (LSM-A), 0.9 (LSM-B) and 0.8 (LSM-C) were used. Details on sample preparation and testing cell arrangement can be found in Chapter 3.

The sintering of the LSM electrodes under open-circuit was carried out in a tube furnace at 1000°C in open air for 1600 h. To study the sintering behaviour under polarisation, the LSM cathodes were cathodically polarised under a constant current load of 500mA cm^{-2} at 1000°C in open air for 1600 h. The current was interrupted from time to time to measure the overpotential by the galvanostatic current interruption (GCI) technique. The details of GCI technique can be found in Chapter 3. The overpotential was directly measured from the potential decay on the GCI curves.

A stability test was also carried out on a 50×50 mm cell with Ni (50vol%) /YSZ (50vol%) cermet anode and $(\text{La}_{0.80}\text{Sr}_{0.20})_{0.9}\text{MnO}_3$ (LSM-B) cathode at 1000°C under a constant current of 250 mAcm^{-2} for 2543 h. The YSZ electrolyte was prepared by tape-casting and the thickness was $194\text{ }\mu\text{m}$. The Ni/YSZ cermet anode and the LSM cathode were applied to the YSZ electrolyte by screen-printing, followed by sintering at 1400°C and 1150°C , separately. The cell configuration is illustrated in Fig 7.1. In this arrangement, electrode geometries were symmetric with reference electrodes located at the side of the working electrodes. The distance between the

Fig 7.1 Schematic diagram of cell configuration

reference electrode and working electrode was about 5 mm. The dimensions of air and fuel electrodes were 34mm×32mm giving an effective electrode area of about 10.9cm², while the reference electrodes were strip-type with dimensions of 34mm×3mm on both sides. The fuel composition at the anode side was 96%H₂/4%H₂O and air was used as the oxidant gas. The flow rate of the H₂ fuel and air was 1000sccm. Pt mesh was used as current collector on the cathode and Ni mesh on the anode.

The microstructure of the LSM electrode before and after various polarisation treatments was examined by scanning electron microscopy (SEM, Leica S360) equipped with X-ray energy dispersive spectroscopy (EDS, Oxford). The cross section of the LSM electrodes was examined on polished samples. The average grain size of LSM electrodes before and after the polarisation and sintering tests was directly estimated from SEM pictures taken at different parts of the electrodes. In this

method, the scanning electron micrograph was mapped with a scaled transparent paper and the size of each individual particle was manually measured.

7.3 Results

Fig 7.2 shows SEM micrographs of the electrode surface of LSM with different A-site stoichiometry before the polarisation and sintering tests. The average particle size of the LSM-A electrode was $0.35 \pm 0.11 \mu\text{m}$ and for LSM-B and LSM-C, the particle size was $0.78 \pm 0.29 \mu\text{m}$ and $0.79 \pm 0.26 \mu\text{m}$, respectively. The particle size of the A-site stoichiometry LSM electrode (LSM-A) is much smaller than that of the A-site deficient or non-stoichiometric LSM (LSM-B and LSM-C). This is consistent with the observed high sinterability of A-site deficient LSM (Meixner, 2002; van Roosmalen, 1993).

Cross-sections of polished LSM samples with different A-site stoichiometry before the polarisation and sintering tests are presented in Fig 7.3. The large particle size of the A-site non-stoichiometric LSM (LSM-B and LSM-C) was apparent as compared to that of A-site stoichiometric LSM (LSM-A). However, as the A-site non-stoichiometry increased to 0.2, isolated dark particles were observed (Fig7.3c), indicating the formation of a second phase. As LSM is a line compound and has a limited ability to increase the A- or B-site vacancies beyond a narrow range (Cherapanov, 1997), A-site deficient compositions are expected to contain B_3O_4 compounds while B-site deficient compositions contain A_2BO_4 phases in addition to the LSM perovskite phase. EDS analysis shows that the dark particles contain a

Fig 7.2 SEM pictures of the electrode surface of (a) LSM-A, (b) LSM-B and (c) LSM-C electrodes before the polarisation and sintering tests. Scale bar applies to all SEM pictures.

Fig 7.3 The polished cross sections of (a) LSM-A, (b) LSM-B and (c) LSM-C electrodes before the polarisation and sintering tests.

significantly high amount of manganese, indicating that the second phases are Mn rich and probably Mn_3O_4 .

Fig 7.4 shows SEM pictures of the surface of LSM electrodes sintered at 1000°C in air with and without a cathodic current passage of 500mA cm^{-2} for 1600 h. The particles of the LSM electrodes sintered under a constant cathodic current load were

Fig 7.4 SEM pictures of the electrode surface of (a) LSM-A, (b) LSM-B and (c) LSM-C electrodes sintered under a current load of 500 mA cm^{-2} and (d) LSM-A, (e) LSM-B and (f) LSM-C electrodes sintered under no current load at 1000°C in air for 1600 h. Scale bar applies to all SEM pictures.

Fig 7.5 Plots of the particle size of LSM electrode coating sintered at 1000°C in air with and without a current load of 500mAcm⁻² as a function of A-site stoichiometry composition.

significantly smaller than those sintered under no current load (i.e., at open circuit). For example, for the $(\text{La}_{0.8}\text{Sr}_{0.2})_{0.9}\text{MnO}_3$ (LSM-B) electrode, the particle size of the LSM grains was $0.88 \pm 0.30 \mu\text{m}$ after sintering at 1000°C under a current load of 500mAcm⁻² for 1600 h. In the case of LSM-B coating sintered at open-circuit under the same conditions, the LSM particles grew to $1.17 \pm 0.25 \mu\text{m}$, which is 33% larger than that sintered under current load. The same trend was observed for the LSM electrodes with different compositions (see Fig 7.5). The grains of LSM electrodes, when sintered at 1000°C, grew less under current load as compared to the ones sintered under open-circuit conditions.

Fig 7.6 shows the polarisation losses of the LSM cathodes for the O₂ reduction reaction under a constant current load of 500mAcm⁻² at 1000°C in air. The

Fig 7.6 The overpotentials (polarisation losses) of the LSM cathodes for the O_2 reduction reaction under a constant current load of 500 mA cm^{-2} at 1000°C in air

reproducibility of the absolute performance (i.e., the overpotential values) for the LSM electrodes with different A-site stoichiometry was not particularly good and varied with the individual samples. For example, for the LSM-C electrode, the overpotential measured over 7 samples was $104 \pm 44 \text{ mV}$ at 500 mA cm^{-2} and 1000°C . Similar variation in the performance was also found for LSM with other compositions. This may be largely related to the complex effect of the morphology of the starting LSM powder and the activation effect of the polarisation on the final performance of the LSM electrode (Jiang, 1999a). The initial high polarisation losses (e.g., 453 mV for LSM-A) again indicate the significant activation effect of the cathodic polarisation on the electrocatalytic activities of the freshly prepared LSM electrodes. Nevertheless, the LSM electrodes showed reasonable stability over the period studied. This is

generally consistent with the observed relatively slow grain growth of the LSM electrodes under polarisation conditions (Fig7.4).

The stability of LSM cathode with A-site deficient composition was also tested on 50×50mm cells at 1000°C under typical SOFC operating conditions. Fig 7.7 shows the performance of a 50×50mm cell with Ni (50vol%)/YSZ (50vol%) anode and LSM-B cathode under current density of 250mA cm⁻² in 96%H₂/4%H₂O and air at 1000°C. The overall cell performance deteriorated 70mV over 2500 h. The overpotential values for the anode and cathode were not measured for this cell. However, the cell performance indicates that the overpotential losses due to the anode and cathode should be low. Fig 7.8 is the SEM micrograph of the LSM-B electrode after the testing. Two features can be seen from the cross-section of the electrode after the long-term polarisation test. Isolated dark particles appeared in the electrode,

Fig 7.7 Cell performance of a 50×50 mm cell with Ni (50 vol%)/YSZ (50 vol%) anode and LSM-B cathode under a current density of 250 mA cm⁻² in 96%H₂/4%H₂O and air at 1000°C

Fig 7.8 SEM picture of the cross section of the LSM-B electrode after the fuel cell testing as shown in Fig7.7.

similar to those of the LSM-C electrode before the polarisation testing. This indicates the formation of the Mn rich probably Mn_3O_4 phase inside the LSM-B electrode after the cathodic polarisation at 500mAcm^{-2} for 2543 h. The formation of Mn rich region in the LSM electrode is most likely due to the observed significant diffusion and migration of manganese species under the cathodic polarisation conditions (*Jorgensen, 2000; Jiang, 2001c*). The second feature is the appearance of voids at the LSM electrode and YSZ electrolyte. The formation of voids at the LSM/YSZ interface region was also observed by Kuznecov et al. (2003).

7.4 Discussion

The sintering behaviour of LSM materials under static conditions with no current load is considered to be governed by two main factors: the ionic radius of the

diffusing species and the defect chemistry induced by the substitution of strontium for lanthanum with subsequent oxygen non-stoichiometry (Meixner, 2002; van Roosmalen, 1993; Poirson, 1997). Considering that the difference between the radii of La^{3+} (0.132 nm) and Sr^{2+} (0.140 nm) is very small, the sinterability of LSM materials is mainly affected by the defect chemistry. Sr-doped LaMnO_3 is a p-type semiconductor, exhibiting both Mn^{3+} and Mn^{4+} ions. Their corresponding ratio depends on the partial pressure of oxygen. The charge neutrality condition for Sr-doped LaMnO_3 may be expressed as (Badwal, 2001):

$$[\text{Sr}'_{\text{La}}] + 3[V'''_{\text{La}}] + 3[V'''_{\text{Mn}}] + n = 2[V''_{\text{O}}] + p \quad (7.1)$$

where Sr'_{La} denotes Sr^{2+} ions introduced into La^{3+} lattice sites, V'''_{La} and V'''_{Mn} are cation vacancies, V''_{O} oxygen vacancy and n and p are the concentration of electrons and electron holes, respectively. Under normal sintering environment (i.e., in air), the dominant defects in the A-site non-stoichiometric compositions of LSM materials are cation vacancies as significant interstitial species are not expected in these compositions (van Roosmalen, 1993). Oxygen vacancies become dominant only at much lower oxygen partial pressures ($\ll 10^{-5}$ Pa) (Nowotny, 1998). As shown in Fig7.2, the particle size of A-site non-stoichiometry LSM electrodes (LSM-B and LSM-C) was significantly larger than that with A-site stoichiometry (LSM-A). Nevertheless, the difference in the particle size between the LSM electrodes with A-site stoichiometry of 0.9 and 0.8 (LSM-B and LSM-C) is very small. Meixner and Cutler (2002) studied the sintering behaviour of LSM in a wide range of A/B ratios. A-site deficiency improves the sinterability and there is sharp transition for A/B=1.

They concluded that the limiting step in LSM sintering is the cation diffusion on the A-site. The observed significant grain growth and sintering of the LSM with A-site deficient compositions (LSM-B and LSM-C) as compared to that of the A-site stoichiometric composition (LSM-A) in this study are consistent with the sintering mechanism proposed by Meixner and Cutler (2002).

Under cathodic polarisation or current load, O_2 reduction reaction occurs and the oxygen activity inside the LSM electrode and at the LSM/YSZ interface region in particular would be much lower as compared to that of the gas phase. Thus, under O_2 reduction reaction conditions, two factors should be considered: On the one hand, the vanishing of cation vacancies and hence the generation of oxygen vacancies under cathodic polarisation will lead to the formation of Mn^{2+} ions at the same time (Lee, 1995). The formation of Mn^{2+} is also confirmed indirectly by the observed grain growth under the cathodic polarisation (see Chapter 5). This will lead to a decrease in the concentration of the Mn^{4+} ions at the B-site. Decreasing the Mn^{4+} content would improve the sinterability as shown by the shifting of the sintering curve to lower temperature in nitrogen atmosphere in comparison to that sintered in air (Poirson, 1997). On the other hand, the dominant ionic defects would be oxygen vacancies due to the significantly low partial pressure of oxygen under O_2 reduction conditions and cation vacancies on the A-sites would disappear completely (Nowotny, 1998). This would in turn inhibit the cation diffusion at the A-sites. As shown in Figs 7.4 and 7.5, the particles of LSM coating sintered in air with no current load were significantly larger than those sintered at a constant current load of $500mAcm^{-2}$ under the same

conditions. This indicates that the sintering rate of an LSM electrode under cathodic polarisation is actually lower than that under open circuit conditions. The driving force for the sintering process is the reduction of surface energy by the formation of larger particles. This is achieved by cation diffusion. Thus, the hindrance of sintering under cathodic polarisation is most likely due to the reduced cation diffusion at the A-sites. The results of this study indicate that the Mn^{4+} concentration and the cation diffusion at the A-sites are both important for the sintering processes of LSM. However, the prime driving force for the LSM sintering is most likely the cation diffusion at the A-site (Meixner, 2002; van Roosmalen, 1993; Stevenson, 1995). This conclusion is also consistent with atomistic simulation results of the formation and diffusion of cation defects in LSM perovskites (de Souza, 1999).

As demonstrated in the stability test on the 50×50mm cell for over 2500 h (Fig7.7), LSM materials with A-site deficient composition show quite reasonable performance stability, considering that the electrode materials for both anode and cathode were not in the optimized stage. The formation of dark particles in the LSM-B electrode after long-term polarisation indicates a phase segregation for the A-site deficient compositions. Such a phase segregation appears to have little effect on the performance stability under the conditions studied. However, the phase segregation may have a detrimental effect on the long-term structural and compositional stability of the cathode. The formation of voids at the LSM electrode and YSZ electrolyte interface region is interesting and could have significant implications for the long-term performance stability though at this stage the reasons

for the void formation are not clear. Oxygen vacancy and cation diffusion has been suggested to be responsible for such void formation at the interface (*Kuznecov, 2003*).

7.5 Conclusion

LSM electrodes with A-site deficient (LSM-B and LSM-C) showed a much higher sinterability than an electrode with A-site stoichiometric composition (LSM-A). Polarisation has a significant effect on the sintering behaviour of LSM electrodes for both A-site stoichiometric and A-site deficient compositions. Under a constant cathodic current density of 500mAcm^{-2} at 1000°C in air, the grain growth of LSM electrodes was significantly smaller than under the open circuit conditions at the same temperature for all the compositions studied. The hindrance of sintering under cathodic polarisation has been attributed to the elimination of cation vacancies at the A-sites, thus increasing the sintering resistance. The results of this study indicate that the sintering process of the LSM electrode is kinetically limited by cation diffusion at the A-sites and the effect of the Mn^{4+} concentration on the sintering behaviour would be relatively small.

The most important observation in the present study is the reduced sinterability and grain growth of the LSM electrodes under cathodic polarisation conditions, which explains the observed stable performance of LSM-based cathodes in SOFC cells and stacks under SOFC operation conditions (*Badwal, 1998; Tietz, 2004*).

CHAPTER 8.

HIGH PERFORMANCE LSM CATHODES FOR IT-SOFC

8.1 Introduction

Sr-doped LaMnO_3 (LSM) is a material of choice for the SOFC operating at high temperatures (900-1000°C) due to its high activities for the O_2 reduction reactions, good stability and thermal compatibility with the YSZ electrolyte at the SOFC operation temperature. However, the negligible oxygen transport ability of LSM (Carter, 1992; de Souza, 2000) would limit the O_2 reduction reactions at or near the triple phase boundaries (TPB) between electrode, electrolyte and O_2 gas. This poses practical limitations and restrictions on the application of LSM based systems as potential cathodes for the intermediate temperature SOFC or IT-SOFC.

Various strategies have been developed to improve the electrocatalytic activities of the LSM-based cathodes. Murray and Barnett (1998 and 2001) showed that adding YSZ or GDC phases to the LSM significantly reduced the electrode polarisation resistance, and the lowest electrode polarisation resistance was $0.49 \Omega\text{cm}^2$ at 750°C for the reaction on the LSM/GDC composite cathodes. This is considerably lower than $3.5 \Omega\text{cm}^2$ measured on the pure LSM cathode at the same temperature. Xia et al. (2003) studied the LSM/GDC composite cathodes fabricated by the sol-gel process.

The sol-gel derived composite cathodes showed very low electrode polarisation resistance, $0.16 \Omega\text{cm}^2$ at 750°C , lower than that obtained by the slurry coating technique (Xia, 2002). Using functionally-graded structure can also reduce the electrode polarisation resistance of the LSM-based cathode, as shown by Hart et al. (2001) on cathodes consisting of five prints of LSM/YSZ composite electrodes and five prints of $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ electrodes. Recently, Liu et al. (2004a and 2004b) used a combustion CVD (CCVD) process to fabricate functionally-graded LSM/LSC/GDC electrodes and achieved an electrode polarisation resistance of $0.43\Omega\text{cm}^2$ at 700°C . The high electrocatalytic activity of the LSM-based cathode fabricated by combustion CVD has been attributed to the functionally-graded and nanostructured interface. This indicates that through the proper composition optimization and materials engineering of the electrode structure, LSM-based electrodes could be used for the intermediate temperature SOFC.

Ion impregnation has been shown to be a very effective method to introduce nano-sized electrocatalytic phases into the porous electrode structure. Gorte et al. (Gorte, 2002; Cracium, 1999) developed Ni-free Cu/YSZ cermet anodes by the impregnation of porous YSZ structure with Cu salt solutions. Impregnation of lanthanide additives has been found to have a significant effect on the electrocatalytic activity of the Cu/YSZ cermet anodes for the direct oxidation of hydrocarbon fuels (McIntosh, 2002). Our investigation shows that the performance of conventional Ni/YSZ cermet anodes and LSM cathodes can be significantly improved by the ion impregnation of mixed conducting oxides such as Sm- and Gd-doped CeO_2 (SDC and GDC) (Jiang, 2002b, 2003b and 2004; Wang, 2004b). In the case of Ni/YSZ cermet anodes, impregnation of YSZ and SDC nitrate solutions reduced the sintering of the Ni phase in the cermet, leading to significant enhancement of the reactive sites for the

electrochemical oxidation of H_2 (Jiang, 2002b). With the impregnation of 1.7 mgcm^{-2} GDC (8.5 vol% GDC) in the Ni anode, the electrode polarisation resistance was $0.71 \Omega\text{cm}^2$ at 800°C , which is close to $0.24 \Omega\text{cm}^2$ reported on good Ni/YSZ cermet anodes at the same temperature (Jiang, 2002b and 2004). GDC-impregnation is equally effective in the reduction of the electrode polarisation resistance for the O_2 reduction reaction on the LSM cathodes. Our recent results showed that after impregnation of 5.8 mgcm^{-2} GDC in the porous LSM cathode, the electrode polarisation resistance is drastically reduced to $0.21 \Omega\text{cm}^2$ at 700°C , which is 56 times smaller than that of the pure LSM cathode at the same temperature. The electrochemical activity of the GDC-impregnated LSM electrode is similar to that reported on the mixed ionic and electronic conducting $(\text{La,Sr})(\text{Co,Fe})\text{O}_3$ cathodes (Jiang, 2002a).

In this chapter, the fabrication and electrode behaviour of the GDC impregnated LSM cathodes have been investigated. The results indicate that the impregnation of the GDC phase not only substantially improves the performance of the LSM cathodes but also has significant electrocatalytic effect on the mechanism and kinetics of the O_2 reduction reaction.

8.2 Experimental details

YSZ electrolyte substrate and A-site deficient $(\text{La}_{0.8}\text{Sr}_{0.2})_{0.9}\text{MnO}_3$ (LSM) cathode were used in this chapter. Details on the sample preparation and testing cell arrangement can be found in Chapter 3. After preparation of testing cells, the ion impregnation treatment was carried out with $3\text{M Ce}_{0.8}\text{Gd}_{0.2}(\text{NO}_3)_x$ solution which was prepared from $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.9%, Aldrich) and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.9%, Aldrich). The pH value of as-prepared $\text{Ce}_{0.8}\text{Gd}_{0.2}(\text{NO}_3)_x$ solution was ~ 1.6 . No

neutralisation was done thereafter. Generally ion impregnation of the electrode coating was conducted by placing a drop of the solution on top of the LSM coating and letting the solution soak into the porous coating in open air. Then, the surface of the electrode coating was wiped with a soft tissue and dried again in air. The sample was fired at 850°C in air for 1 h to decompose $\text{Ce}_{0.8}\text{Gd}_{0.2}(\text{NO}_3)_x$ nitrate solution, forming $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_2$ -type oxide phase. The mass of the electrode coating before and after the impregnation treatment was measured to estimate the impregnated oxide loading. The loading of the oxide phase was increased by repeating the impregnation process.

The electrochemical activities of the impregnated LSM cathodes were characterised by electrochemical impedance spectroscopy (EIS) between 700 and 850°C in increments of 50°C and at the oxygen partial pressure between 0.001 atm and 1 atm. The impedance responses were analysed by the equivalent circuit method. To stabilise the electrode behaviour, LSM electrodes were polarised at 850°C with a constant current density of 200mA cm^{-2} for 180 min before the electrochemical testing. The electrochemical behaviour of pure and GDC-impregnated LSM electrodes was also studied in the presence of gaseous Cr species. Gaseous Cr species were introduced by using a chromia-forming alloy interconnect (25w/o Cr, 73w/o Fe, 0.7w/o Mn, negligible Si) in contact with the LSM electrodes. It has been shown that the gaseous Cr species can be used effectively to diagnose the surface and bulk diffusion process of the O_2 reduction through the inhibition of the oxygen surface diffusion on the LSM electrode (Jiang, 2001a). The details of the set-up of the LSM electrode with the Cr alloy metallic interconnect coupon can be found elsewhere (Jiang, 2001a). The microstructure of the electrodes was examined by scanning electron microscopy (SEM, Leica S360) equipped with X-ray energy dispersive

spectroscopy (EDS, Oxford). The porosity of the electrode coating was estimated from the SEM images of the cross-section of the electrode samples. From the porosity difference between the LSM electrodes with and without GDC-impregnation, the volume percentage of the impregnated GDC phase in the LSM electrode was obtained.

An anode-supported YSZ cell with Ni (50vol%) / YSZ (50vol%) cermet anode and $(\text{La}_{0.8}\text{Sr}_{0.2})_{0.9}\text{MnO}_3$ cathode was fabricated for a stability test on GDC-impregnated LSM. The YSZ electrolyte powder was co-pressed with Ni/YSZ anode powder, followed by co-firing at 1400°C for 2 hr. The thickness of YSZ electrolyte was $\sim 60 \mu\text{m}$. The LSM cathode was applied to the YSZ electrolyte by slurry coating, followed by sintering at 1150°C for 2 hr. The GDC impregnated treatment was then done on the LSM cathode. Humidified H_2 (97% H_2 /3% H_2O) was used as fuel on the anode and air as oxidant gas on the cathode. The flow rates of H_2 fuel and air were 100sccm. Pt mesh was used as current collector on the cathode and Cu mesh on the anode.

8.3 Results

The GDC loading of the impregnated LSM electrode was 0.72 mg cm^{-2} after one impregnation treatment, and increased to 1.68 mg cm^{-2} and 3.05 mg cm^{-2} after two and three times impregnation treatments, respectively. The maximum loading of GDC was 5.8 mg cm^{-2} after repeating the impregnation processes 6 times. The porosity of the pure LSM electrode was 37.2% and it was 34.1% for the 0.72 mg cm^{-2} GDC-impregnated LSM electrode. Thus the volume loading of the impregnated GDC for the 0.72 mg cm^{-2} GDC-impregnated LSM electrode was 3.1vol%. In the case of the LSM electrode with the impregnation of 5.8 mg cm^{-2} GDC, the porosity of the

impregnated LSM electrode was almost zero, indicating that volume loading of the GDC was 37vol%. The GDC volume loading can also be calculated from the weight of impregnated GDC and the measured coating thickness. For example, based on the density of 7.132gcm^{-2} of CeO_2 and the measured coating thickness, the volume percentage of the 0.72mgcm^{-2} GDC-impregnated LSM electrode was calculated to be 4.3vol%. The calculated volume loading is generally higher than that measured from the SEM images. This can be explained by the observation that there was a precipitation of GDC particles on the LSM surface. Thus the GDC volume loading measured from the SEM cross-section images should be closer to the real situation. Table 8.1 shows the GDC loading and porosity of the GDC-impregnated LSM

Table 8.1 Porosity and GDC loading of the impregnated LSM electrodes

Impregnation cycle	0	1	2	3	6
Porosity	37.2%	34.1%	22.6%	12%	~0%
Loading in weight (mg cm^{-2})	0	0.72	1.68	3.05	5.8
Loading in volume%	0	3.1	14.6	27.2	37.2

electrodes.

Fig 8.1 shows the SEM pictures of the surface and fractured cross-section of pure and GDC-impregnated LSM electrodes after the fuel cell testing. Fig 8.2 is the EDS patterns of the surface of the selected LSM electrodes. For pure LSM, well-defined

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Fig 8.1 SEM pictures of (a) surface and (b) fractured cross section of pure LSM; (c) surface and (d) fractured cross section of 0.72mgcm^{-2} GDC impregnated LSM; (e) surface and (f) fractured cross section of 1.68mgcm^{-2} GDC impregnated LSM; (g) surface and (h) fractured cross section of 3.05mgcm^{-2} GDC impregnated LSM, and (i) surface and (j) fractured cross section of 5.8mgcm^{-2} GDC impregnated LSM.

and granular-shaped particles with clear grain boundaries were observed (Figs 8.1a&8.1b). The LSM grains were in the range of 0.7 to $1.2\mu\text{m}$. EDS pattern

Fig 8.2 EDS patterns of (a) pure LSM, (b) 1.68 mg cm^{-2} GDC impregnated LSM, and (c) 3.05 mg cm^{-2} GDC impregnated LSM.

reveals the presence of the constituent elements of LSM, La, Sr and Mn (Fig8.2a). After the ion impregnation with $\text{Ce}_{0.8}\text{Gd}_{0.2}(\text{NO}_3)_x$ solution, very fine particles were formed around LSM grains (Figs8.1c&8.1d). The size of $(\text{CeGd})\text{O}_2$ oxide particles was in the range of 100-200nm, as estimated from the enlarged SEM pictures. The fine particles were most likely $(\text{CeGd})\text{O}_2$ oxides as identified by the EDS patterns (Figs8.2b&8.2c). Clearly the impregnated GDC particles are much smaller than that

of LSM particles. The distribution of the nano-sized GDC particles appears to be isolated. With the increase in the GDC loading, there was significant increase in the coverage of the LSM particles by the nano-sized GDC particles. This is indicated by the disappearance of the smooth and well-defined morphology of the LSM grains (see Fig8.1f). The pores were gradually filled with fine GDC particles and the porosity of the LSM electrodes decreased considerably with the increase in the impregnated GDC loading. In the case of the 5.8 mgcm^{-2} GDC-impregnated LSM electrodes, the pores were almost completely filled by the GDC phase, forming a rather dense structure.

Fig 8.3 shows the initial impedance responses of the pure and GDC-impregnated LSM electrodes as a function of cathodic current passage at 200 mA cm^{-2} and 700°C in air. For the pure LSM, the initial electrode interface (or polarisation) resistance (R_E) was $72.8 \text{ } \Omega\text{cm}^2$, and reduced significantly with cathodic current passage (Fig8.3a). After the cathodic current treatment for 180 min, R_E was $11.7 \text{ } \Omega\text{cm}^2$, more than 6 times smaller than the initial R_E value. The rapid reduction in the electrode polarisation resistance for the O_2 reduction on the freshly-prepared LSM electrodes is related to the significant activation effects of the cathodic polarisation and could be ascribed to the microstructural improvement of the LSM electrode (Wang, 2004a), removal of the surface passive species such as SrO (Jiang, 2001b), the generation of the oxygen vacancies (Jiang, 1998) or the removal of the cation vacancies under the cathodic polarisation (Chen, 2004b). After the GDC impregnation treatment, the LSM electrodes behaved very different (Figs8.3b&8.3c). Firstly, the initial R_E values for the O_2 reduction reaction on the impregnated LSM electrodes were decreased significantly with the increase in the impregnated GDC loading. For example, R_E was $9.5 \text{ } \Omega\text{cm}^2$ for the 0.72 mgcm^{-2} GDC-impregnated LSM. In the case of the 5.8 mg/cm^2 GDC-impregnated LSM electrodes, it was $0.21 \text{ } \Omega\text{cm}^2$, 56 times smaller than that of

Fig 8.3 Initial electrochemical impedance responses of the freshly-prepared (a) pure LSM, (b) 0.8mgcm⁻² GDC-impregnated LSM, and (c) 5.8 mgcm⁻² GDC-impregnated LSM electrodes as function of cathodic current passage at 200mA cm⁻² and 700°C in air.

the pure LSM electrode at the same temperature. The very low electrode polarisation resistance achieved on the GDC-impregnated LSM electrodes is clearly related to the deposition of the nano-sized oxygen conducting (Gd,Ce)O₂ particles in the LSM electronic conducting network (Fig8.1). Secondly, the change of the impedance responses with the cathodic current passage was very small. For example, for the

Fig 8.4 Initial electrode polarisation resistance (R_E) of the freshly-prepared LSM electrodes with and without the GDC-impregnation treatment under a cathodic current passage of 200 mAcm^{-2} at (a) 850°C and (b) 700°C.

LSM electrode impregnated with 0.72 mg cm^{-2} GDC, R_E was decreased to $7.5 \text{ } \Omega \text{ cm}^2$ after the cathodic current passage for 120 min, which is close to the initial value of $9.5 \text{ } \Omega \text{ cm}^2$ (Fig8.3b). This might be related to the removal of surface inhibiting SrO species as the pH value of impregnation solution is ~ 1.6 .

Similar initial impedance behaviour was also observed for the O_2 reduction reaction on the freshly-prepared pure and GDC-impregnated LSM electrodes at other temperatures. Fig 8.4 shows the dependence of the R_E for the O_2 reduction on the freshly-prepared LSM electrodes with and without the GDC-impregnation as a function of the cathodic current passage time at 850°C and 700°C . The cathodic current was 200 mA cm^{-2} . This clearly indicates that the activation effect of the cathodic polarisation is no longer effective for O_2 reduction on the GDC-impregnated LSM electrodes.

Fig 8.5 shows the effect of the impregnated GDC loading on the electrode

Fig 8.5 Plots of R_E of GDC-impregnated LSM electrodes measured at different temperatures.

polarisation resistance for the O_2 reduction reaction at different temperatures. The R_E was measured after the initial cathodic polarisation activation at 200 mA cm^{-2} and 850°C for 180 min. R_E of the LSM electrode decreased significantly with increase in the impregnated GDC loading. The reduction in the R_E is particularly effective for the GDC-impregnated LSM electrodes at low temperatures (e.g. 650°C). With the impregnated GDC loading of 5.8 mg cm^{-2} , R_E was $0.75 \Omega \text{ cm}^2$ at 650°C . The impregnation of the nano-sized ionic conducting GDC phase in the predominantly electronic conducting LSM porous network could substantially enhance the three phase boundaries for the O_2 reduction. This would be similar to the effect of YSZ and GDC phases in the LSM/YSZ and LSM/GDC composite electrodes on the promotion of the O_2 reduction reaction rate (Jorgensen, 2001b; Murray, 1998 and 2001; Xia, 2003).

Fig 8.6 shows the polarisation performance of the pure and 5.8 mg cm^{-2} GDC-impregnated LSM electrodes measured at different temperatures in air. For the

Fig 8.6 Polarisation curves of pure and 5.8 mg cm^{-2} GDC-impregnated LSM electrodes measured at different temperatures in air. Performance of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ (LSCF) at 700°C was taken from (Jiang, 2002a).

purpose of comparison, the performance of the $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ (LSCF) electrode on GDC electrolyte measured at 700°C in air (Jiang, 2002a) is also given in the figure. Pure LSM shows reasonable performance at high temperatures. For example at 900°C, η for the O_2 reduction at 200mAcm^{-2} was 120mV. However, as the temperature decreased to 700°C η increased rapidly to 800mV at the same current. This indicates that the LSM electrode is not suitable for the IT-SOFC. However, with the GDC impregnation treatment, the polarisation performance of the LSM cathodes was significantly enhanced. At 700°C and under a current density of 150mAcm^{-2} , η was 33mV for the O_2 reduction on the 5.8mgcm^{-2} GDC-impregnated LSM, even smaller than 97mV obtained on the pure LSM electrode at 900°C under the same conditions. This indicates that the operational temperature for the O_2 reduction reaction on the 5.8mgcm^{-2} GDC-impregnated LSM is reduced by more than 200°C as compared to that on the pure LSM electrode. Moreover, the polarisation performance of the 5.8mgcm^{-2} GDC-impregnated LSM was the same as that of the LSCF electrode at 700°C (Jiang, 2002a). The high polarisation performance of the GDC-impregnated LSM electrodes clearly demonstrates the usefulness of the impregnation method in the enhancing performance of conventional LSM electrodes.

The stability of GDC-impregnated LSM cathode was also tested on an anode-supported cell at 800°C under typical SOFC operation conditions. Fig 8.7 shows the performance of a single cell with Ni (50vol%) / YSZ (50vol%) cermet anode and 1.3mgcm^{-2} GDC-impregnated LSM cathode under a constant current of 500mAcm^{-2} in 97% H_2 /3% H_2O and air at 800°C for an operation period of 65 hr. The overall cell performance shows an improvement of ~120 mV during the first 20 hr operation, after which the cell voltage remained stable under the operation conditions. No visible degradation of the cell performance was observed. This indicates that the

Fig 8.7 Cell performance of a single cell with Ni (50vol%)/YSZ (50vol%) anode and 1.3mgcm^{-2} GDC-impregnated LSM cathode under a current density of 500mAcm^{-2} in $97\%\text{H}_2/3\%\text{H}_2\text{O}$ and air at 800°C

nano-sized GDC particles are stable in the LSM structure under the present operation conditions.

Fig 8.8 shows the impedance curves of the pure and GDC-impregnated LSM electrodes measured at 850°C as a function of partial pressure of oxygen. The symbols are experimental data and the solid lines are fitted results. The fitting of the equivalent circuit to the experimental data is quite reasonable. The equivalent circuit used to fit the experimental data is shown in Fig8.8e. In the circuit, L, Q and R denote inductance, constant phase element (CPE) and electrode resistance, respectively. R_0 is the ohmic resistance between cathode and reference electrode and subscript H and L correspond to the high and low frequency arcs. Table 8.2 gives the typical fitting impedance parameters evaluated by the equivalent circuit from the impedance spectra for the O_2 reduction reaction on the GDC-impregnated LSM electrodes measured at

Fig 8.8 Impedance spectra of (a) pure LSM, (b) 0.72 mg cm^{-2} GDC-impregnated LSM, (c) 1.68 mg cm^{-2} GDC-impregnated and (d) 3.05 mg cm^{-2} GDC-impregnated LSM electrodes as function of oxygen partial pressure at 850°C . The equivalent circuit is shown in (e). The symbols are experimental data and solid lines are fitted data.

700°C and in air under open circuit. For all the LSM electrodes, with or without ion impregnation treatment, two impedance arcs were visible at high and low frequency regimes. Additional impedance arcs were also identifiable at high frequencies ($R_H \cdot Q_H$) and low frequencies ($R_L \cdot Q_L$) in some cases. The additional low frequency arc

appeared when the oxygen partial pressure was lower than 0.05atm. This is particularly the case for the reaction on the LSM electrode with high GDC loading (e.g., the 3.05 mgcm^{-2} GDC-impregnated LSM electrode, see Fig8.8d). As shown in Fig8.1 and Table 8.1, the increase in the GDC-impregnation led to the reduction in the porosity of the electrodes. The dominance and the appearance of the additional low frequency impedance arc are consistent with the significant reduction in the porosity of the GDC-impregnated LSM structure. Thus, the additional low-frequency arc at the low partial pressure of oxygen is most likely associated with the oxygen gas diffusion through the pores of the LSM electrode. An additional arc was also observed at frequencies higher than 10kHz for the oxygen reduction on the LSM electrodes at reduced temperatures, i.e. 700°C . However it disappeared as the temperature increased.

As discussed in Chapter 3, the CPE in the equivalent circuit (Fig 8.8e) is a Warburg-type diffusion impedance in the case of $n=0.5$, and a pure capacitor in the case of $n=1$. For the additional high frequency arc, the frequency power, n_H , was equal to 1 for the reaction on the LSM electrodes regardless of the GDC-impregnation treatment. This is similar to what was observed on pure LSM electrodes under polarisation conditions at 800°C (see Chapter 4). Meanwhile, the Q components of the additional high frequency arc ($R_H Q_H$) ranged from 7.2 to $15 \mu\text{Fcm}^{-2}$, which is similar in magnitude to that observed for the charge transfer reaction of H_2 oxidation on the Ni/YSZ cermet anodes (Jiang, 1999b). All these clearly suggest that the electrode process at this additional high frequency arc is most likely associated with the charge transfer process.

The behaviour of high frequency arc ($R_H Q_H$) and low frequency arc ($R_L Q_L$) show similar characteristics with that of pure LSM electrodes measured at 800°C , in which

Table 8.2 Fitted impedance parameters form the equivalent circuit for the O₂ reduction on pure and GDC-impregnated LSM electrodes measured at 700°C under open circuit and P_{O_2} =0.21atm.

Electrode	Additional high-frequency arc				High-frequency arc				Low-frequency arc			
	R_{H^+} , $\Omega\text{ cm}^2$	Q_{H^+} , $\Omega^{-1}\text{ cm}^{-2}\text{ s}^n$	n	$R\times Q$, $\tau_{L^+}\text{ s}^n$	R_{H^+} , $\Omega\text{ cm}^2$	Q_{H^+} , $\Omega^{-1}\text{ cm}^{-2}\text{ s}^n$	n	$R\times Q$, $\tau_{L^+}\text{ s}^n$	R_{L^+} , $\Omega\text{ cm}^2$	Q_{L^+} , $\Omega^{-1}\text{ cm}^{-2}\text{ s}^n$	n	$R\times Q$, $\tau_{L^+}\text{ s}^n$
Pure LSM	0.75	7.22E-6	1	5.42E-6	2.67	1.26E-3	0.95	3.36E-3	40.88	1.87E-3	0.7	0.08
0.72mg cm ⁻² GDC impregnated LSM	-	-	-	-	3.5	7.0E-4	0.93	2.45E-3	23.02	2.20E-3	0.7	0.05
1.68mg cm ⁻² GDC impregnated LSM	-	-	-	-	1.9	2.06E-3	0.9	3.9E-3	8.48	3.41E-3	0.8	0.03
3.05mg cm ⁻² GDC impregnated LSM	0.22	1.5E-5	1	3.3E-6	1.82	9.26E-4	0.85	1.7E-3	1.75	4.32E-3	0.8	0.008

Fig 8.9 Plots of electrode conductivity of electrode processes at (a) high frequency arc (σ_H), (b) low frequency arc (σ_L) and (c) additional low frequency arc ($\sigma_{L'}$) of pure and GDC-impregnated LSM electrode at 850°C.

n_H is very close to 1 and n_L deviates significantly from 1 and approaches to 0.5. It is indicated that the electrode processes at ($R_H Q_H$) and ($R_L Q_L$) can be related to the oxygen ion transfer process at the LSM/YSZ interface and a mixed process of the dissociation and surface diffusion of oxygen species, respectively.

Fig 8.9 shows the plots of the electrode conductivity (σ is the reciprocal of electrode polarisation resistance) of the electrode processes at high and low frequencies ($\sigma_H = 1/R_H$ and $\sigma_L = 1/R_L$) for O_2 reduction reaction on pure and GDC-impregnated LSM electrodes at 850°C. In comparison, the electrode conductivity of the additional low frequency arc ($\sigma_{L'} = 1/R_{L'}$) is also given in the figure. Only two $\sigma_{L'}$ values were available due to the disappearance of the additional low frequency arc at high oxygen partial pressure. The reaction order of $\sigma_{L'}$ with respect to P_{O_2} was estimated from the limited data, which was ~ 1 for pure and GDC-impregnated LSM electrodes. The reaction order of the electrode process at the additional low frequency arc with respect to the oxygen partial pressure is independent of the GDC-impregnation. σ_H was independent of the oxygen partial pressure regardless of the GDC impregnation treatment while the σ_L for the reaction on the LSM electrodes decreased with the decrease in the P_{O_2} and appeared to depend on the GDC loading. The reaction orders of σ_H and σ_L with respect to P_{O_2} were also evaluated for the reaction at other temperatures. However, it was found that the reaction orders for both high and low frequency arcs did not show particular dependence on the temperature. Fig 8.10 shows the reaction orders of the σ_H and σ_L with respect to P_{O_2} as a function of the GDC loading. The reaction orders in the figure are the average of the values evaluated at the temperature range of 700-850°C. For the pure LSM, σ_L is found to be approximately proportional to $P_{O_2}^{0.5}$, which is close to that

Fig 8.10 Reaction orders of the electrode conductivity of high and low frequency arcs (σ_H and σ_L) of the LSM electrodes with respect to P_{O_2} as a function of the GDC loading.

reported on the LSM electrodes in the literature (Jiang, 2002c). In the case of the GDC-impregnated LSM electrodes, the reaction order ranges from 0.23 to 0.34, which is lower than that on the pure LSM electrodes. This indicates that the impregnated GDC has electrocatalytic effect on the electrode process at the low frequency arc for the reaction on the LSM electrodes.

Fig 8.11 shows the activation energy plots of σ_H and σ_L of the pure and GDC-impregnated LSM electrodes in air. For the reaction on pure LSM, σ_H is significantly higher than σ_L in the temperature range studied (Fig8.11a), indicating the dominant electrode process associated with the low frequency arc. With the impregnation of GDC phase, σ_L increased significantly while the increase in σ_H was much smaller. Thus, the difference between σ_L and σ_H was getting smaller as the loading of the impregnated GDC increased. When the impregnated GDC loading

Fig 8.11 Activation energy plots of σ_H and σ_L of (a) pure LSM, (b) 0.72mgcm^{-2} GDC-impregnated LSM, (c) 1.68mgcm^{-2} GDC-impregnated and (d) 3.05mgcm^{-2} GDC-impregnated LSM electrodes measured at 0.21atm.

increased to 3.05 mgcm^{-2} , σ_H was actually lower than σ_L (Fig8.11d). This suggests that the dominant electrode process has shifted from the low frequencies to the high frequencies. The activation energy was calculated from the slopes of the curves. Fig 8.12 shows the dependence of the activation energy of the electrode conductivity of the low and high frequency arcs on the GDC loading. The activation energy of σ_H is $\sim 100\text{ kJmol}^{-1}$, and is independent of the impregnated GDC loading. For the reaction on the pure LSM electrode, the activation energy of σ_L was $\sim 170\text{ kJmol}^{-1}$. High

Fig 8.12 Dependence of the activation energy of the electrode conductivity of low and high frequency arcs on the GDC loading. The activation energy values were obtained from Fig8.10.

activation energies for the electrode processes at the low frequency arc on LSM electrodes were frequently reported in the literature (*Jiang, 2002c; Chen, 2003; Youngblood, 1993*). With the impregnation of nano-sized GDC phase in the LSM electrodes, the activation energy of the electrode process at the low frequency arc was reduced to $\sim 140 \text{ kJ mol}^{-1}$. The change in the reaction order and the activation energy of σ_L after the GDC-impregnation treatment indicates a significant electrocatalytic effect of the impregnated GDC phase on the O_2 reduction reaction process.

Fig 8.13 shows the polarisation potential (E_{cathode}) and overpotential (η) for the O_2 reduction in air on the pure and GDC-impregnated LSM electrodes under a cathodic current passage of 200 mA cm^{-2} in the absence and presence of Cr alloy. E_{Cathode} was measured between the LSM cathode and the Pt air reference electrode and the electrode ohmic resistance (R_Ω) and electrode polarisation resistance (R_E) were

Fig 8.13 Polarisation potential curves of pure LSM (a) in the absence of Cr alloy at 800°C, (b) in the presence of Cr alloy at 900°C, and (c) 5.8mgcm⁻² GDC-impregnated LSM electrode at 900°C in the presence of Cr alloy. The cathodic polarisation current was 200mAcm⁻².

measured by the EIS at open circuit. For the O_2 reduction on the pure LSM in the absence of Cr alloy, the E_{cathode} decreased rapidly with the cathodic current passage, from 815mV initially to 556mV after 5 min of the cathodic current passage at 800°C. The reduction in E_{cathode} was mainly due to the reduction in η , as R_{Ω} remained almost the same with the current passage. The polarisation behaviour is in a good agreement with the impedance behaviour as shown in Fig8.3a. On the other hand, the presence of Cr alloy completely changed the polarisation behaviour of the pure LSM electrode. Instead of a rapid decrease, E_{cathode} for O_2 reduction on the pure LSM in the presence of Cr alloy increased very quickly with cathodic current passage time, followed by a region where the increase in E_{cathode} was much smaller. The very different behaviour of E_{cathode} with cathodic current passage in the absence and presence of Cr alloy has been discussed previously and is a clear indication of the significant inhibiting effect of the Cr species on the surface dissociation and diffusion processes for the O_2 reduction at the LSM electrodes (*Jiang, 2003d, 2001a and 2000a*).

For the O_2 reduction on the 5.8mgcm⁻² GDC-impregnated LSM electrode in the presence of Cr alloy, the change in the E_{Cathode} with the cathodic current passage was much smaller as compared to that on the pure LSM electrode. The relative increase of the cathode potentials ($\Delta E_{\text{cathode}}$) after the cathodic current passage for 60min was ~15mV for the reaction on GDC-impregnated LSM, much smaller than ~270mV measured on the pure LSM electrode (Figs8.13b&8.13c). The slight decrease in the E_{cathode} with the cathodic current passage during the first 15min might be due to the small decrease of R_{Ω} in this case. Such small increase in the cathodic potential with the current passage for the reaction on the GDC-impregnated LSM electrode in the presence of Cr alloy is almost identical to that observed on the (La,Sr)(Co,Fe)O₃ (LSCF) cathodes (*Jiang, 2002a*).

Fig 8.14 compares the electrode polarisation resistance of the GDC-impregnated LSM electrodes in this study with those of the pure LSM, LSM/YSZ, LSM/GDC and selected MIEC cathodes reported in the literature. Electrode polarisation resistance (R_E) was generally measured from the impedance curves under open circuit in air. Without specification, cathodes were tested on the YSZ electrolyte. For the O_2 reduction reaction on the pure LSM electrodes, R_E varied greatly from 9 to $54 \Omega\text{cm}^2$

Fig 8.14 A comparison of the electrode polarisation resistance (R_E) of GDC impregnated LSM electrodes in this study with those of the pure LSM, LSM/YSZ, LSM/GDC and selected MIEC electrodes reported in the literature. R_E was measured by EIS in air and without specification, cathodes were tested on YSZ electrolyte. Lines are for the guide only.

at 700°C (Murray, 1998; Jiang, 2000a). With the addition of 50 % YSZ phase in the LSM electrode, R_E of the LSM/YSZ composite cathode was reduced to $2.5 \Omega\text{cm}^2$ at 700°C (Murray, 1998). R_E was further reduced to $1.1 \Omega\text{cm}^2$ at 700°C by substituting YSZ with high ionic conducting GDC phase in the LSM/GDC composite electrode (Murray, 2001). For the O_2 reduction on the 5.8mgcm^{-2} GDC impregnated LSM electrode, R_E was $0.21 \Omega\text{cm}^2$ at 700°C, significantly lower than that of both LSM/YSZ and LSM/GDC composite cathodes (Murray, 1998 and 2001; Leng, 2004; Choi, 2001; Kim, 2001). Most significantly, the electrode polarisation performance of the 5.8 mgcm^{-2} GDC-impregnated LSM is comparable to that of LSCF and $\text{Gd}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ (GSC) electrodes. LSCF is known to be a very good mixed ionic and electronic conductor with high electrocatalytic activity for the O_2 reduction reactions (Jiang, 2002a). The oxygen ion conductivity of LSCF is $\sim 0.2 \text{ Scm}^{-1}$ at 900°C (Teraoka, 1991). Ralph et al. (2001) compared the electrode polarisation resistance of different MIEC electrodes including LSCF, $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$, $\text{Sm}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ and $\text{Gd}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$. $\text{Gd}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ electrode showed the lowest electrode polarisation resistance (Ralph, 2001). The electrode polarisation resistance of the functionally-graded LSM/LSC/GDC electrodes prepared by CCVD achieved $0.43 \Omega\text{cm}^2$ at 700°C (Liu, 2004a and 2004b). However, the 5.8mgcm^{-2} GDC-impregnated LSM electrodes reported in this study show compatible performance with those of the MIEC conducting electrodes and the functionally-graded LSM-LSC-GDC by the CCVD method (Liu, 2004a and 2004b; Jiang, 2002a; Ralph, 2001).

8.4 Discussion

The results in this chapter demonstrate that impregnation of oxygen ion conducting GDC phase in the LSM electrodes not only enhances the electrocatalytic

activity of the LSM electrodes (Figs 8.5 & 8.14) but also changes the electrode behaviour (Figs 8.10 & 8.12). It has been known that incorporation of ionic conducting phases such as YSZ or GDC to the predominant electronic conducting LSM materials is effective in improving the electrode performance (Murray, 1998 and 2001; Leng, 2004; Kim, 2001). However, the performance of the LSM/YSZ composite cathode is strongly influenced by the particle size of LSM and YSZ (Østergård, 1995; Chen, 2003). As the TPB is the critical area for the O₂ reduction reaction in SOFC, the electrodes based on the concept of the functionally-graded structure and nanoparticles are considered to be the next generation materials for the SOFC for applications in the temperature range of 600-800°C (Liu, 2004c). However, the preparation of conventional composite cathodes normally includes mechanical mixing of LSM and YSZ or GDC powders followed by high temperature sintering at 1100-1200°C. Kim et al. (2001) studied the microstructure and performance of LSM/YSZ composite cathodes. High temperature sintering caused significant grain growth of the YSZ phase, leading to a substantial reduction in the porosity and the electrode polarisation conductivity. The grain size of YSZ in the LSM/YSZ composite cathodes prepared by the ceramic mixing route is typically in the range of 0.5-1 µm (Leng, 2004). On the other hand, as shown in this chapter, the microstructure of the GDC-impregnated LSM electrodes is characterized by the porous LSM network covered by the very fine and uniformly distributed GDC particles (Fig 8.1). The size of the impregnated GDC oxides is in the range of 100-200 nm, significantly smaller than that observed on the LSM composite cathodes prepared by the conventional method. This would substantially enhance the active sites for the O₂ reduction reaction on the GDC-impregnated LSM as confirmed by the extremely low electrode polarisation resistance (0.21 Ωcm² at 700°C) of the 5.8 mgcm⁻² GDC impregnated LSM electrode

as compared to that of the LSM/GDC composite electrodes tested under similar conditions (Fig8.14). The uniform coverage of the nano-sized GDC particles on the LSM surface may have some inhibiting effect on the sintering and grain growth of the LSM phase under the fuel cell operation conditions. Nevertheless, the long-term stability of the GDC-impregnated LSM electrodes is important and deserves further studies in the future.

Previous investigation of the O_2 reduction reaction on the LSM electrodes indicates that the reaction is most likely limited by two reaction steps, corresponding to the impedance arcs at high and low frequencies (*Jiang, 2000a and 2002c*). The electrode process at high frequencies is characterized by the activation energy of $70\text{--}90\text{kJmol}^{-1}$ and its electrode conductivity is independent of the partial pressure of oxygen and the dc bias. On the other hand, the reaction order of the electrode conductivity of the low frequency arc with respect to the partial pressure of oxygen is in the range of 0.6-0.8 and has high activation energy of 180kJmol^{-1} . The high activation energy is considered to be related to the high activation energy process of the oxygen diffusion in the LSM electrodes. This indicates that the electrode process associated with the high frequency arc most likely corresponds to the oxygen ion migration from the LSM electrode to the YSZ electrolyte at the TPB region while the low frequency arc is related to the dissociation and diffusion of oxygen on the LSM electrode surface.

Impregnation of oxygen ion conducting GDC phase in the LSM electrodes has significant influence on the electrode behaviour (Figs8.10&8.12). However, the effect of the GDC-impregnation is far more pronounced on the electrode process associated with low frequencies as compared to that with high frequencies. The activation energy of the electrode process at high frequencies for the O_2 reduction on the

GDC-impregnated LSM is $\sim 100 \text{ kJ mol}^{-1}$ and the σ_H is essentially independent of the P_{O_2} (Figs 8.10 & 8.11), similar to that for the reaction on the pure LSM. Similar electrode behaviour for the high frequency process was also observed on the LSM/YSZ (Murray, 1998; Wang, 1998) and LSM/GDC (Murray, 2001) composite cathodes. The observed independence of σ_H on P_{O_2} implies the dominant role of the electrolyte on the high frequency process. This appears to be supported by the fact the activation energy of the σ_H ($80\text{--}100 \text{ kJ mol}^{-1}$) is close to $\sim 80 \text{ kJ mol}^{-1}$ of the oxygen ion conductivity of the YSZ electrolyte materials (Ciacchi, 1994). This indicates that the electrode process at high frequencies is most likely the oxygen migration and incorporation reaction between the GDC-impregnated LSM electrode and YSZ electrolyte. On the other hand, the effect of the GDC impregnation treatment on the electrode process at the low frequency arc is significant. The reaction order of σ_L with respect to partial pressure of oxygen is in the range of 0.23–0.34, lower than 0.5 observed for the reaction on the pure LSM. Esquirol et al. (2004) studied the electrode behaviour of LSCF for the O_2 reduction reaction and identified two impedance arcs, the high frequency arc at normal partial pressure of oxygen and the low frequency arc at very low partial pressure of oxygen. This is consistent with the observation that under normal P_{O_2} , the O_2 reduction reaction on LSCF electrodes is characterized by a single impedance arc (Jiang, 2002a). The reaction order of σ_H with respect to P_{O_2} is 0.23 while for σ_L it is much higher, 1.42. They concluded that the high frequency arc is most likely related to the oxygen dissociation and diffusion on the LSCF electrode and the electrode process of the low frequency arc is the gas diffusion in the electrode pore. The gas diffusion was also observed for the O_2 reduction on the GDC-impregnated LSM electrode, indicated by the appearance of the additional low

frequency arc at low P_{O_2} and its high reaction order of ~ 1 . The ionic conductivity of GDC is 0.1 Scm^{-1} at 800°C (Steele, 2001), similar to that of LSCF (Teraoka, 1991). The reaction order of the low frequency arc for the reaction on the GDC-impregnated LSM is 0.23-0.34, similar to that of the high frequency arc for the reaction on the LSCF electrodes. Thus, considering that the low frequency arc for the reaction on the LSCF electrode only occurred at reduced P_{O_2} , the electrode process at low frequency arc of the GDC-impregnated LSM is most likely the oxygen dissociation and diffusion, similar to that of the high frequency arc reported on the LSCF electrodes. However, the impregnation of nano-sized GDC greatly accelerates the oxygen dissociation and diffusion process. This is supported by the significant reduction in the electrode resistance and the reduced activation energy of the electrode process associated with the low frequency arc. The activation energy of σ_L for the reaction on the GDC-impregnated LSM is 140 kJmol^{-1} , also lower than $\sim 170\text{-}200 \text{ kJmol}^{-1}$ for the reaction on the pure LSM (Jiang, 2002c). The low activation energy of the reaction on the GDC-impregnated LSM is probably related to the low activation energy of 74.3 kJmol^{-1} for the ionic conductivity process on GDC (Steele, 2000a).

The electrocatalytic effect of the impregnated GDC on the electrode behaviour of the LSM electrode is also indicated by the much higher tolerance of the GDC-impregnated LSM electrode to gaseous Cr species as compared to that of the pure LSM electrode (see Fig8.13). Under SOFC operating conditions, volatile Cr species such as CrO_3 produced from chromium-based alloy could readily occupy the active sites on LSM surface and effectively block the path for O_2 surface dissociation and diffusion process, resulting dramatically increased E_{cathode} and R_E (Jiang, 2003d, 2001a and 2000a). The much lower increase in the cathodic potential (E_{cathode}) for the O_2 reduction on the GDC-impregnated LSM electrodes indicates the enhanced bulk

diffusion processes as observed on the mixed ionic and electronic conducting electrodes such as LSCF as compared to that on the dominant electronic conducting LSM and Pt electrodes (Jiang, 2001a). Thus, GDC-impregnation not only enhances the electrochemical catalytic activity of the LSM electrodes but also substantially increases the bulk diffusion of oxygen in the LSM electrodes. GDC is known to have a high surface exchange property for oxygen. Therefore, in addition to the effective electronic and ionic pathways within impregnated LSM, there might be synergistic processes involving the injection of the mobile charge oxygen surface species into the GDC ionic carrier, pointed out by Steele et al. (2000). This appears to be supported by the fact that there was significant improvement in the electrode activity for the O_2 reduction on the GDC-impregnated LSM electrodes in the case of low GDC loading even though in the case of low GDC loading (e.g., 0.72mgcm^{-2} GDC), the distribution of GDC particles seems to be isolated and there is no continuous GDC ionic conducting phase (Fig8.2c&8.2d).

8.5 Conclusion

The fabrication and performance of GDC-impregnated LSM electrodes were investigated. The microstructure of the GDC-impregnated LSM electrode was characterized by the continuous and porous LSM network with the deposition of nano-sized GDC particles. Very high electrochemical activity has been achieved for the O_2 reduction on the GDC-impregnated LSM cathodes. For example, on the 5.8mgcm^{-2} GDC-impregnated LSM electrode, extremely low electrode polarisation resistance of $0.21\Omega\text{cm}^2$ at 700°C was obtained despite the dense of the GDC-impregnated LSM structure.

The impregnation of oxygen ion conducting GDC phase in the LSM electrode not

only enhance the electrode activity but also has significant electrocatalytic effect on the O_2 reduction reactions. However, the electrocatalytic effect of the GDC impregnation is primarily on the electrode process associated with the low frequency arc. Two limiting steps, i.e., dissociation/adsorption of O_2 and transfer of oxygen ions into YSZ electrolyte were identified on the pure and impregnated LSM electrodes. Impregnation of fine GDC oxide particles significantly enhance the O_2 dissociation/adsorption process, probably due to the effective ionic diffusion pathway along GDC film or an injection effect of mobile charged oxygen species into GDC ionic carrier. On the contrary, the transfer of oxygen ions to YSZ electrode was limited by the electrolyte side, and was much less affected by the GDC-impregnation treatment.

CHAPTER 9.

GDC-IMPREGNATED Ni ANODES FOR DIRECT UTILIZATION OF METHANE

9.1 Introduction

Solid oxide fuel cells (SOFC) offer significant advantages over other types of fuel cells with respect to the high fuel flexibility. Other than pure hydrogen, SOFC can be fed with the more readily available hydrocarbon fuels such as methane, which would eliminate the need for pre-reformer and greatly reduce the complexity, size and cost of the overall SOFC system. However, primarily due to the severe carbon deposition caused by cracking of methane, the conventional Ni-based anode is generally considered not appropriate for the direct oxidation of hydrocarbons. Various strategies have been adopted, either by exploitation of new electrode materials or by continuous modification/improvement of existing Ni-based cermets, to develop alternative anode materials for the direct oxidation of hydrocarbon fuels. By partial substitution (Kim, 2002; Lee, 2004) or complete replacement (Park, 2000; Gorte, 2000 and 2003) of Ni with Cu, Gorte et al. demonstrated the feasibility to use Cu-ceria cermet anodes for the direct methane oxidation in SOFC. Other materials

such as LaCrO_3 -based perovskite (Tao, 2003; Sfier, 2003) or doped ceria (Mogensen, 1994; Marina, 1999) were reported to have high stability in methane atmosphere whilst their low electrical conductivity would pose special challenge in the design of the current collector.

On the other hand, it has been shown recently that ion impregnation is a very effective method to introduce nano-sized electrocatalytic phases into porous SOFC electrode structure (Chapter 8; Jiang, 2002b and 2004). After impregnation treatment of LSM electrodes with $\text{Ce}_{0.8}\text{Gd}_{0.2}(\text{NO}_3)_x$ solution, the electrode polarisation resistance decreased from the original $26.4 \Omega\text{cm}^2$ for pure LSM electrode to $0.72 \Omega\text{cm}^2$ for the O_2 reduction at 700°C , a reduction in the electrode polarisation resistance by 36 times (Chapter 8). In the case of Ni/YSZ cermet anodes, impregnation of YSZ and SDC nitrate solutions reduced the sintering of the Ni phase in the cermet, leading to significant enhancement of the reactive sites for the electrochemical oxidation of H_2 (Jiang, 2002b). With the impregnation of 1.7mgcm^{-2} GDC (8.5vol% GDC) in the Ni anode, a novel structured mixed conducting anode was developed in which the Ni grains were covered by fine (100-300nm) and uniformly distributed GDC oxide particles (Jiang, 2004). The electrode polarisation resistance for H_2 oxidation at 700°C was substantially reduced from $10.75\Omega\text{cm}^2$ on pure Ni anode to $4.72\Omega\text{cm}^2$ on 0.52mgcm^{-2} GDC-impregnated Ni and $1.37\Omega\text{cm}^2$ on 1.7mgcm^{-2} GDC-impregnated Ni. This suggests that such GDC-impregnated Ni anodes may be useful for the direct methane oxidation as the underlying Ni can form an electronic conducting network while the fine GDC particles on Ni surface can act

as an electrocatalyst for methane oxidation and protect Ni from direct exposure to the methane, reducing the deposition of carbon.

In this chapter, a preliminary study on the application of GDC-impregnated Ni anode for the direct utilization of methane in SOFCs was carried out. The electrode behaviour of GDC-impregnated Ni anode in weakly humidified ($\sim 3\% \text{H}_2\text{O}$) methane was investigated under open circuit or low current load conditions at 800°C . The results clearly indicate that the incorporation of nano-GDC into Ni anodes not only improves the kinetics of methane oxidation reactions but also significantly suppresses the degradation of Ni anodes caused by carbon deposition in methane.

9.2 Experimental details

Electrolyte substrates were prepared by die pressing of 8 mol% $\text{Y}_2\text{O}_3\text{-ZrO}_2$ powder (TZ8Y, Tosoh, Japan), followed by sintering at 1500°C for 4 hrs in air. Electrolyte thickness and diameter were 1mm and 19mm, respectively. NiO (J.T. Baker) powders were pre-coarsened at 600°C for 2hr in air to reduce the powder shrinkage and to improve the coating quality, followed by ballmilling in propanol for 5hr. The NiO electrode coating was applied to the YSZ electrolyte by slurry painting and sintered at 1400°C for 2hr. Electrode coating thickness was $\sim 30\mu\text{m}$ and electrode area was 0.5cm^2 . The pre-coarsened NiO powder was also ball-milled with 20mol% Gd_2O_3 -doped CeO_2 (GDC) powder with composition of 70vol% Ni and 30vol% GDC for 20hr. Ni/GDC cermet anode was also prepared by slurry coating.

The ion impregnation of $\text{Ce}_{0.8}\text{Gd}_{0.2}(\text{NO}_3)_x$ nitrate solution was described in

Chapter 8. The mass of the electrode coating before and after the impregnation treatment was measured to estimate the impregnated oxide loading. The loading of the oxide phase was 10vol% or 1.42mg per cm^{-2} of the anode surface after one impregnation treatment.

A three-electrode arrangement was used for the electrochemical measurement. The electrode arrangement can be found in Chapter 3, and the working electrode (WE) hereby is Ni or Ni/GDC cermet anodes. Hydrogen and methane humidified at room temperature ($\sim 3\% \text{H}_2\text{O}$) were used as fuel while the counter and reference electrodes were exposed in static air. The flow rate of fuel gases was set to 200sccm/min. Electrochemical performance of Ni and Ni/GDC cermet anodes was characterized by electrochemical impedance spectroscopy (EIS) technique and steady-state polarisation curve. EIS was carried out on a frequency response analyzer (Solartron 1260) in combination with an electrochemical interface (Solartron 1287) with frequency range of 0.1 Hz to 100 kHz. The electrode polarisation resistance (R_E) was determined by the difference between high and low frequency intercepts in impedance spectra.

All the anodes were evaluated with the same testing procedure. The Ni or Ni/GDC cermet anodes were reduced in-situ in 97% H_2 /3% H_2O when the temperature raised from room temperature to 800°C. A constant anodic current at 200mAcm⁻² was applied at 800°C for around 1hr, after which the fuel gas was changed to 97% CH_4 /3% H_2O , and the anodic current was kept at 200mAcm⁻² until the anodic potential was stable. The anodes were then exposed in 97% CH_4 /3% H_2O under open circuit (OCV) or low current load (20mAcm⁻²) conditions at 800°C for 3hr, during

which the impedance responses for the methane oxidation were monitored from time to time and current-voltage characteristic was measured in the end. After testing, the fuel gas was changed back to H_2 and the specimen was quenched in H_2 ; afterwards, the anodes were examined either by visual inspection or by scanning electron microscopy (SEM, Leica S360).

9.3 Results and discussion

Fig 9.1 compares the impedance curves of pure Ni, Ni/GDC cermet and GDC-impregnated Ni anodes measured at 800°C and under OCV as a function of exposure time in 97% CH_4 /3% H_2O . The electrode polarisation resistance (R_E) is summarised in Fig 9.2. It can be seen that pure Ni anode has very poor electrocatalytic activity for methane oxidation (Fig9.1a). R_E was as high as $31.8\Omega\text{cm}^2$ initially, and increased substantially to $40\Omega\text{cm}^2$ 15mins later and further to $52.1\Omega\text{cm}^2$ after exposed to wet CH_4 for 3hr at OCV. The dramatic increase in R_E is not surprising as Ni tends to catalyze reforming reactions as well as methane decomposition. The deposited carbon from cracking of methane would occupy the active site on Ni anode surface, leading to degradation of electrochemical activity. This is confirmed by the fact that after testing, a large amount of carbon was found on specimen surface and the Ni anode was completely spoiled.

On the contrary, Ni/GDC cermet anode shows reasonable stability under the same testing conditions, as shown in Fig9.1b. The initial R_E was $3.05\Omega\text{cm}^2$ for the methane

Fig 9.1 Impedance curves of (a) pure Ni anode, (b) Ni/GDC cermet, and (c) 1.42mg cm^{-2} GDC impregnated Ni anodes as function of exposure time in 97% CH_4 /3% H_2O under OCV at 800°C

oxidation on Ni/GDC cermet anode and slightly increased to $3.45\Omega\text{cm}^2$ 15mins later and further to $3.73\Omega\text{cm}^2$ after 150mins of exposure time. Much better stability and electrocatalytic activity in wet CH_4 were demonstrated on Ni anode with

Fig 9.2 Comparison of electrode polarisation resistance (R_E) measured on pure Ni, Ni/GDC cermet and 1.42mg cm^{-2} GDC-impregnated Ni under OCV and under constant current load of 20mAcm^{-2} in $97\%\text{CH}_4/3\%\text{H}_2\text{O}$ at 800°C .

impregnation treatment of $(\text{Ce}_{0.8}\text{Gd}_{0.2})(\text{NO}_3)_x$ solution. Fig9.1c shows the impedance responses of GDC-impregnated Ni anode exposed in $97\%\text{CH}_4/3\%\text{H}_2\text{O}$ under OCV at 800°C . The initial R_E for the methane oxidation on GDC-impregnated Ni was only $1.29\Omega\text{cm}^2$, ~ 25 times smaller than that of pure Ni and ~ 2 times smaller than that of Ni/GDC cermet anode under the same testing condition. Furthermore, the R_E values showed nearly negligible increase in exposing in methane. R_E was $1.35\Omega\text{cm}^2$ and $1.41\Omega\text{cm}^2$ after 15mins and 3hrs of exposure time in methane respectively, indicating that GDC impregnation treatment could greatly suppress carbon deposition on Ni anode in methane atmosphere.

In the Cu-ceria system proposed by Gorte et al. (2000 and 2003; Kim, 2002; Lee,

2004; Park, 2000), Cu which is almost inactive to C-H bond breaking, worked primarily as a current collector, while ceria was thought to act as an electrocatalytic material for direct oxidation of methane. However, as pointed out recently by Mogensen et al. (2003), direct electrochemical oxidation of methane may not occur with a reaction rate as that reported in the literature (Gorte, 2000 and 2003; Kim, 2002; Lee, 2004; Park, 2000). Instead, the conversion of hydrocarbon in Cu-ceria system is most likely based on the cracking of hydrocarbons followed by electrochemical oxidation of hydrogen and/or carbon. In this study, the existence of Ni in the anode structure seems to make the carbon deposition unavoidable. However, the rather stable impedance behaviour of GDC-impregnated Ni or Ni/GDC cermet anode may indicate that GDC oxide could effectively oxidize methane steam or the cracking products of methane because of the presence of mobile lattice oxygen (Steele, 1990; Metcalfe, 1992). The much higher electrocatalytic activity observed on GDC-impregnated Ni anode suggests that the impregnated nano-sized GDC particles might be much more effective in aiding in the combustion of deposited carbon as compared to the counterpart in Ni/GDC cermet anode. This could be related to the particularly high active surface areas of impregnated nano-sized GDC for methane oxidation reactions.

The stability of GDC-impregnated Ni anode in wet CH₄ can be further improved when anodic current passage was applied after 3hr of exposure time under OCV condition. Fig 9.3 shows the impedance responses for the reaction on GDC-impregnated Ni anode in 97%CH₄/3%H₂O under constant current load of

Fig 9.3 Impedance curves of 1.42 mg cm^{-2} GDC impregnated Ni anode under constant current load of 20 mA cm^{-2} as function of exposure time in $97\% \text{ CH}_4/3\% \text{ H}_2\text{O}$ at 800°C

20 mA cm^{-2} at 800°C . The anodic current passage appeared to improve the electrochemical performance of GDC-impregnated Ni anode for the methane oxidation. R_E was $1.20 \Omega \text{ cm}^2$ after 2mins of anodic current passage and was gradually decreased to $1.15 \Omega \text{ cm}^2$ and $0.9 \Omega \text{ cm}^2$ 30mins and 180mins later, respectively. Similar improved electrode performance after long-term operation in methane under anodic polarisation potential at 0.5 V was reported on Cu-Ni cermet anode and was attributed to enhanced electronic conductivity of the electrode due to moderate level of carbon deposition (Kim, 2002). In the case of Ni/YSZ cermet anode operated in methane, the electrical load at 200 mA cm^{-2} was found to effectively remove the deposited carbon originated previously under open circuit condition (Koh, 2002). As we will present below, despite the stable electrode performance in methane, a small amount of carbon deposition was found on the surface of GDC-impregnated Ni anode after testing.

Obviously, the carbon deposition was likely to occur during exposure in methane under OCV (Fig9.1c). The sequential application of anodic current load could facilitate the continuous supply of oxygen ions from the cathode side to the electrolyte, and finally to the anode surface by the aid of fine GDC oxide particles, which would promote the electrochemical oxidation of hydrogen/methane steam and deposited carbon. It is worth noting that the current load (20mAcm^{-2}) used to suppress carbon deposition in present work was much lower than the previous reported on Ni-based anodes, e.g. from 200mAcm^{-2} to 1Acm^{-2} (Koh, 2002; Sumi, 2004; Gunji, 2004). As the SOFC systems generally operate at a current load of 200mAcm^{-2} or higher, much better performance of GDC-impregnated Ni anodes could be expected.

The suppressing effect of anodic current load on carbon deposition can be represented again by the polarisation performance of GDC-impregnated Ni and Ni/GDC cermet anodes for methane oxidation reactions at 800°C , as shown in Fig 9.4. It should be noted that the GDC-impregnated Ni was exposed to methane under OCV for 3hr and another 3hr under anodic current load before the current-voltage characterisation. It is found that GDC-impregnated Ni has better polarisation performance only at low current regime. When the current is higher than $\sim 150\text{mAcm}^{-2}$, Ni/GDC cermet showed better performance. This is quite different from the electrode impedance behaviour in which GDC-impregnated Ni showed much higher electrocatalytic activity for methane oxidation than Ni/GDC cermet anode (Figs 9.1b&9.1c). The relatively low GDC loading in impregnated Ni anode, e.g. 10vol% in GDC-impregnated Ni whereas 30vol% in Ni/GDC cermet anode, should be taken

Fig 9.4 Polarisation curves of 1.42mgcm⁻² GDC impregnated Ni anode and 70vol%GDC/30vol% Ni cermet anode in 97%CH₄/3%H₂O at 800°C

into account with respect to the dramatic difference between current-voltage characteristic and impedance behaviour. During I-V test, the much higher GDC content in Ni/GDC cermet anode could provide more oxygen ion supply to Ni surface especially under high current load conditions (>150mAcm⁻²), leading to better polarisation performance. In this sense, increased polarisation performance could be expected for the GDC-impregnated Ni with higher GDC loading.

After testing, the GDC-impregnated Ni anode was examined by visual inspection and SEM technique. A thin layer of carbon was found on the anode surface which could be easily blown off. The underlying Ni coating remained undamaged by carbon deposition. Fig 9.5 shows the SEM pictures on the surface and fractured cross-section

Fig 9.5 SEM pictures of (a) surface of pure Ni anode before testing, (b) surface and (d) fractured cross-section of 1.42mgcm⁻² GDC-impregnated Ni anode after testing, and EDS of the GDC-covered Ni particles on the surface (c) and in the bulk (e) of the anode coating.

of GDC-impregnated Ni anode with corresponding EDS patterns on GDC-covered Ni grains after testing. For comparison, the SEM picture on the surface of freshly prepared NiO coating prior to testing is also shown in Fig9.5. The SEM observation and EDS analysis clearly revealed the presence of fine GDC particles deposited around Ni grains not only on the surface but also in the bulk of Ni anode coating.

Continuous Ni coating with good bonding could also be observed. It was reported that carbon deposited on the Ni surface could dissolve into the bulk metal followed by precipitation as graphite on the Ni surface again which would cause the materials to fracture (*Baker, 1989*). This might be the case of the pure Ni anode after exposure in methane for 3hr. The presence of nano-sized GDC particles in the impregnated Ni anode might prevent the deposited carbon from dissolving into the Ni phase by electrochemical oxidation of the carbon. Sumi et al. (*2004*) also reported that the catalytic activity of Ni/scandia-stabilised zirconia cermet anode for the oxidation of methane could be kept for long operation periods more than 200hr, regardless of the formation of whisker-shaped crystalline graphite on the anode surface.

9.4 Conclusion

The suppressing effect of GDC impregnation treatment on carbon deposition on the Ni anode in a methane atmosphere may stem from the presence of mobile lattice oxygen in ceria which would electrochemically oxidize the deposited carbon, as well as the particularly high surface area of impregnated nano-sized GDC particles. The application of anodic current passage facilitates the continuous oxygen ion supply from the cathode side to the anode side, leading to the removal of deposited carbon probably originated under OCV, and the improved electrode performance. More studies may be necessary on the long-term stability of GDC-impregnated Ni anodes in methane.

CHAPTER 10

CONCLUSIONS AND RECOMMENDATIONS

10.1 Conclusions

The subject of this thesis is to get a better understanding on activation process of Sr-doped LaMnO_3 (LSM) cathodes under cathodic and/or anodic polarisation conditions, and to develop LSM-based cathodes for intermediate temperature SOFCs. Of particular interest is the significant effect of polarisation on the electrode behaviour of LSM, such as the initial polarisation performance, the microstructure and morphology changes within the LSM electrode and at the LSM/YSZ interface region, and the sintering behaviour of LSM cathodes. High performance LSM cathodes for intermediate temperature SOFC were developed by ion impregnation of GDC oxide. The ion impregnation method was also applied on the anode side, demonstrating novel structured Ni anodes with much improved electrochemical activity and stability for the direct utilization of methane. Based on the results in this thesis, following conclusions can be drawn.

1. The activation effect of cathodic polarisation and deactivation effect of anodic

polarisation on the electrochemical properties of LSM electrodes were studied in this work. It was found that the application of cathodic and anodic polarisation caused the limiting reaction step for O_2 reduction shift between low frequency process (for freshly prepared and anodically polarised LSM) and high frequency process (for cathodically polarised LSM). Comparative study on freshly prepared and acid etched LSM indicates that the changes of electrode behaviour of LSM electrodes could be correlated to the alternation on the surface status and defect chemistry of LSM under cathodic and/or anodic polarisation conditions. A modified defect model is therefore suggested for LSM electrodes. The surface enriched SrO species and cation vacancies are the dominant defects in LSM lattice structure, and are considered to be the main factors for the initially very high electrode polarisation resistance for O_2 reduction. With the application cathodic polarisation, the inhibiting SrO species is believed to be re-incorporated into LSM lattice structure with the concomitant disappearance of cation vacancies, followed by the reduction of Mn ions and the generation of oxygen vacancies. Under anodic polarisation or relaxation conditions at OCV, the Sr ions may escape from LSM lattice sites and segregate to the surface layer, resulting in the formation of cation vacancies and hence the reducing electrochemical activity for O_2 reduction.

2. Both cathodic and anodic polarisation treatments have dramatic effect on the microstructure and morphology of LSM electrode, e.g. large agglomerates existed in the freshly-prepared LSM change to sphere-like particles with clear grain

- boundaries under cathodic/anodic polarisation. Microstructural changes under cathodic polarisation could be related to the pronounced diffusion and migration of oxygen vacancies and Mn ions on LSM surface and lattice expansion while the lattice shrinkage under oxidation is most likely contributing to the structural changes under anodic polarisation. Such morphological changes were irreversible and were found to be beneficial to the performance of the LSM electrodes.
3. The interface morphology and topography between LSM electrodes and the YSZ electrolyte were studied by atomic force microscopy (AFM) under various polarisation conditions. Thermal treatment of the LSM electrode at 1150°C caused formation of convex rings with sharp edges at the O₂/LSM/YSZ interface. Under cathodic or anodic polarisation conditions, the edge of the convex rings became broadened and flattened. The similar change in the morphology and topography of the convex rings under cathodic and anodic polarisation treatments indicates that the convex ring areas are most likely the reaction sites for the O₂ incorporation/diffusion between LSM and YSZ electrolyte. The width of the three phase boundary, i.e., the convex rings, was estimated as $0.15 \pm 0.05 \mu\text{m}$.
 4. LSM electrodes with A-site non-stoichiometry showed a much higher sinterability than an electrode with A-site stoichiometric composition. Polarisation at 500mAcm^{-2} at 1000°C can significantly suppress the grain growth of LSM electrodes, which can be attributed to the elimination of cation vacancies at the A-sites, thus increasing the sintering resistance. The reduced sinterability and grain growth of the LSM electrodes under cathodic polarisation conditions

- explains the observed stable performance of LSM-based cathodes in SOFC cells and stacks under SOFC operation conditions. The results of this study indicate that the sintering process of the LSM electrode is kinetically limited by cation diffusion at the A-sites and the effect of the Mn^{4+} concentration on the sintering behaviour would be relatively small.
5. Novel structured mixed ionic and electronic conducting cathode was developed based on LSM electronic conducting structure impregnated with GDC ionic conducting phase. The microstructure of the GDC-impregnated LSM electrode was characterized by the continuous and porous LSM network with the deposition of nano-sized GDC particles. Very high electrochemical activity has been achieved for the O_2 reduction on the GDC-impregnated LSM cathodes. For example, on the 5.8 mgcm^{-2} GDC-impregnated LSM electrode, extremely low electrode polarisation resistance of $0.21 \Omega \text{cm}^2$ at 700°C was obtained despite the dense of the GDC-impregnated LSM structure. Mechanism study on the O_2 reduction on pure and GDC-impregnated LSM electrodes reveal that impregnation of fine GDC oxide particles significantly enhance the O_2 dissociation/adsorption process at low frequencies, probably due to the effective ionic diffusion pathway along GDC film or an injection effect of mobile charged oxygen species into GDC ionic carrier, while the transfer process of oxygen ions to YSZ electrode at high frequencies was limited by the electrolyte side, and was much less affected by the GDC-impregnation treatment.
6. GDC-impregnated Ni anode is found to be very stable when exposed in weakly

humidified ($\sim 3\% \text{H}_2\text{O}$) methane under open circuit at 800°C , as compared to Ni and Ni/GDC cermet anodes. The stability of GDC-impregnated Ni in wet methane is further improved when an anodic current load at 20mAcm^{-2} was applied. The suppressing effect of GDC impregnation treatment on carbon deposition on Ni anode in methane atmosphere may stem from the presence of mobile lattice oxygen in ceria which would electrochemically oxidize the deposited carbon, as well as the particularly high surface area of impregnated nano-sized GDC particles. The application of anodic current passage facilitates the continuous oxygen ion supply from cathode side to the anode side, leading to removal of deposited carbon probably originated under OCV and improved electrode performance.

10.2 Major achievements

The major achievements of this work are listed as follows:

- Proposed a new mechanism of activation processes of LSM electrodes.

The activation process of LSM electrodes under cathodic polarisation/current passage has been frequently reported. The previous explanations of this activation process are generally based on the classic defect models of LSM which usually concentrate on the ionic defects such as cation vacancies and oxygen vacancies in LSM lattice. Nevertheless, comparative study on the electrode behaviour of freshly-prepared and acid etched LSM under polarisation conditions, as well as the relaxation behaviour of LSM electrodes after cathodic polarisation, clearly

indicate the limitation of the classic defect models. On the other hand, the modified model proposed in this work takes the surface segregation of SrO species into consideration, which might be the main factor for the initially very high electrode polarisation resistance of LSM for O₂ reduction.

Under cathodic polarisation, the SrO can be incorporated into LSM lattice structure, according to:

followed by the reduction of Mn ions and the generation and propagation of oxygen vacancies, according to:

Under sequential anodic polarisation, the formed oxygen vacancies can be consumed by the recombination reactions, followed by the re-segregation of SrO species on LSM surface with the concomitant generation of cation vacancies in LSM lattice structure, i.e., the revised reaction of Eq (4.2), (4.1) and (4.7). Under open circuit condition, segregation of SrO species to the LSM surface could still occur probably due to the electrical neutrality requirement of oxygen excess,

This mechanism well explains the electrode behaviour of LSM cathodes, either freshly-prepared or acid etched, under polarisation (cathodic/anodic) and relaxation conditions.

- Completed a comprehensive investigation of the effect of cathodic and anodic polarisation on the morphology and topography of the interface between LSM cathode and YSZ electrolyte.

The polarisation treatment was found to have a significant effect not only on the electrocatalytic activities of LSM electrode but also on the topography and morphology of LSM/YSZ interface. The formation of a convex ring on the YSZ electrolyte surface and its subsequent broadening under various polarisation treatments indicate that O_2 reduction and oxidation reactions most likely occur at the O_2 /LSM/YSZ three phase boundary areas.

- Developed LSM-based novel mixed ionic and electronic conducting cathodes for intermediate temperature SOFC.

Primarily due to the negligible oxygen ion conductivity, LSM is generally excluded from the candidate cathode materials for IT-SOFC, despite the fact that LSM may have the best structural and chemical compatibility with the commonly used YSZ electrolyte among the available cathode materials. However, with impregnation treatment with oxygen ion conducting GDC phase, LSM-based cathode can achieve much better electrode performance than that of both LSM/YSZ and LSM/GDC composite cathodes. For the O_2 reduction on the pure LSM electrodes, R_E varies from 9 to $54\Omega\text{cm}^2$ at 700°C . With the addition of 50%YSZ phase in the LSM electrode, R_E was reduced to $2.5\Omega\text{cm}^2$ at 700°C , and could be further reduced to $1.1\Omega\text{cm}^2$ at 700°C by substituting YSZ with GDC. For the O_2 reduction on the 5.8mgcm^{-2} GDC impregnated LSM electrode, R_E was

$0.21\Omega\text{cm}^2$ at 700°C , significantly lower than that of both LSM/YSZ and LSM/GDC composite cathodes. The electrode polarisation performance of GDC impregnated LSM is even comparable to that of LSCF which is known to be a very good mixed ionic and electronic conductor. The results in this work clearly demonstrate that through the proper composition optimization and materials engineering of the electrode structure, LSM-based cathode materials could be used for IT-SOFC.

- Demonstrated the feasibility of GDC impregnated Ni-based anodes for natural gas fuel based SOFC.

In this work, Impregnation method was also applied on Ni anodes GDC phase. Excellent stability of GDC impregnated Ni anode was observed when exposed in weakly humidified ($\sim 3\%\text{H}_2\text{O}$) methane, which can be further improved by the application of anodic current load. Such results indicate the feasibility of the application of Ni-based anodes for IT-SOFC or SOFC with natural gas fuel.

10.3 Recommendations

1. Although impressively good electrochemical performance was achieved on both LSM-based cathodes and Ni-based anodes after impregnation treatment with oxygen ion conducting oxides, the studies in this work were primarily based on half-cell testing, which might somewhat deviate from the practical SOFC operating conditions. Another issue regarding to ion impregnation method is the long term stability of impregnated LSM cathodes and Ni anodes, as the originally

nano-sized oxygen ion conducting particles might grow to large grains under operating temperatures. Thus, cells based on impregnated LSM cathode and Ni anode should be built and subjected to long term stability testing. Also, microstructure tailoring can be conducted to optimize the distribution of oxygen ion conducting particles within the matrix of LSM and/or Ni.

2. The modified defect model proposed in this work for LSM cathodes (Chapter 4) was mostly based on the experimental results of the electrode behaviour of LSM. Further thermodynamic calculation may be still necessary to verify this model.
3. It is generally accepted that direct feeding of natural gas into SOFC is critical for the commercialization of SOFC technology. Promising result was shown in Chapter 9 with respect to the possibility of using GDC-impregnated Ni anodes for the direct conversion of weakly humidified methane in SOFC. However, it still needs more verification especially under long term operation conditions. Moreover, the mechanism of methane oxidation, e.g. internal reforming or direct electrochemical oxidation or the cracking of methane followed by the oxidation of the decomposition products, is still unclear. It should be noted that demands on the anode materials for the methane direct conversion differ significantly with different reaction mechanisms. Thus, it is important to get a better understanding on this issue, so as to tailor the properties of existing anode materials or to exploit alternative materials.

LIST OF PUBLICATIONS

Journal Paper

1. **W. Wang** and S.P. Jiang, 2004, "Effect of polarization on the electrode behavior and microstructure of (La,Sr)MnO₃ electrodes of solid oxide fuel cells", *J. Solid State Electrochem.*, 8, 914-922.
2. S.P. Jiang and **W. Wang**, 2005, "Effect of polarization on the interface between (La,Sr)MnO₃ electrode and Y₂O₃-ZrO₂ electrolyte", *Electrochem. Solid-State Lett.*, 8, A115-A118.
3. S.P. Jiang and **W. Wang**, 2005, "Sintering and grain growth of (La,Sr)MnO₃ electrodes of solid oxide fuel cells under polarization", *Solid State Ionics*, 176, 1185-1191.
4. S.P. Jiang and **W. Wang**, 2005, "Novel structured mixed ionic and electronic conducting cathodes of solid oxide fuel cells", *Solid State Ionics*, 176, 1351-1357.
5. S.P. Jiang, **W. Wang** and Y.D. Zhen, 2005, "Performance and electrode behavior of nano-YSZ impregnated Ni anodes of solid oxide fuel cells", *J. Power Sources*, 147, 1-7.
6. S.P. Jiang and **W. Wang**, 2005, "Fabrication and performance of GDC-impregnated (La,Sr)MnO₃ cathodes for intermediate temperature solid oxide fuel cells", *J. Electrochem. Soc.*, 152, A1398-A1408.
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8. **W. Wang** and S.P. Jiang, 2006, "A mechanistic study on the activation process of (La,Sr)MnO₃ electrodes of solid oxide fuel cells", *Solid State Ionics*, in press.
9. **W. Wang**, S.P. Jiang, A.I.Y. Tok and L.H. Luo, 2006, "GDC-impregnated Ni anodes for direct utilization of methane in solid oxide fuel cells", *J. Power Sources*, in press.

Conference paper

1. S.P. Jiang and **W. Wang**, 2003, "An interface study on O₂ reduction between (La,Sr)MnO₃ and Y₂O₃-ZrO₂ electrolyte", *2nd Guangzhou Fuel Cell Conference*, 18-21 November, 2003, Guangzhou, China.
2. **W. Wang** and S.P. Jiang, 2004, "A mechanism study of O₂ reduction reactions on novel mixed ionic and electronic conducting cathodes", in *Solid State Ionic Device IV*, Electrochem. Soc., 3-8 October, 2004, Hawaii, USA
3. S.P. Jiang and **W. Wang**, 2005, "Effect of polarization on the activation process of (LaSr)MnO₃ electrodes of solid oxide fuel cells", *Solid Oxide Fuel Cells IV*, p1545-1548.
4. **W. Wang** and S.P. Jiang, 2005, "Novel (Ce,Gd)O₂-impregnated LSM Cathodes for Anode-supported Solid Oxide Fuel Cells", in *3rd International Conference on Materials for Advanced Technologies (ICMAT)*, 3-8 July, 2005, Singapore.
5. **W. Wang**, S.P. Jiang and W.W. Ho, 2006, "Characterization of the Cathode/Electrolyte Interface in Solid Oxide Fuel Cells", to be presented in *3rd Guangzhou Fuel Cell Conference*, 20-23 June, 2006, Guangzhou, China.
6. S.P. Jiang and **W. Wang**, 2006, "An Investigation of Methane Oxidation Reaction on GDC-Impregnated (La_{0.75}Sr_{0.25})(Cr_{0.5}Mn_{0.5})O₃ Anodes", to be presented in *7th European SOFC Forum*, 3-7 July, 2006, Lucerne, Switzerland.

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