Investigation on interaction reaction mechanism between metallic interconnect and electrodes in solid oxide fuel cell

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**INVESTIGATION ON INTERACTION
REACTION MECHANISM BETWEEN METALLIC
INTERCONNECT AND ELECTRODES
IN SOLID OXIDE FUEL CELL**

**ZHEN YONGDA
SCHOOL OF MECHANICAL AND AEROSPACE
ENGINEERING**

2007

Investigation on Interaction Reaction Mechanism between Metallic Interconnect and Electrodes in Solid Oxide Fuel Cell

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ABSTRACT

Solid oxide fuel cell (SOFC) is probably the most efficient energy conversion device with very low greenhouse gas emission. Thus use of SOFC can significantly reduce the atmospheric pollution and minimize the impact of the consumption of fossil fuels on the environment. Recently significant progress has been achieved to lower the operating temperature of SOFC from traditional 1000oC to intermediate temperatures of 600-800oC. The low SOFC operating temperature enables the use of cheap chromia-forming alloys as interconnect materials for SOFC. This study aims to understand the interaction reactions between the metallic interconnect and the cathodes under the SOFC operating conditions.

The interaction reactions between the chromia-forming alloy interconnect and the most promising cathodes, (La,Sr)MnO₃ (LSM) and (La,Sr)(Co,Fe)O₃ (LSCF) cathodes, have been systematically investigated under cathodic polarization conditions at the temperature range of 700-900°C. For the reaction on the LSM cathode, deposition of Cr species preferentially occurs on the yttria stabilized zirconia (YSZ) electrolyte surface, forming distinct deposit rings at the edge of the LSM cathode while on the LSCF cathode, Cr species deposits on the surface of LSCF electrode and little Cr species deposition is inside the bulk of the LSCF electrode and on the gadolinium-doped ceria (GDC) electrolyte surface. The results conclusively demonstrate that the deposition of Cr species at the SOFC cathodes is not an electrochemical reduction reaction of high valent Cr vapor species to solid Cr₂O₃ in

competition with the O_2 reduction reaction. Rather, the deposition of Cr species is essentially a chemical reaction on re-deposition. The deposition process is controlled by the nucleation reaction between the gaseous Cr species and the nucleation agent. At the LSM electrode, the nucleation agent is the Mn^{2+} ions generated under cathodic polarization while at the LSCF electrode, the nucleation agent is the SrO species enriched originally at the LSCF electrode surface. The strong dependence of the Cr deposition process on the nature of the materials is also supported by the chemical interaction between the alloy and the LSM material as well as the constituent oxides of LSM material such as La_2O_3 , SrO and Mn_2O_3 under normal sintering conditions.

For the O_2 reduction reaction on the LSM cathode in the presence of chromia-forming alloy interconnect, the surface diffusion process of oxygen species is strongly inhibited by the gaseous Cr species generated at high temperature while the migration process of oxygen ions into the YSZ electrolyte is limited by the $Cr_2O_3/(Cr,Mn)_3O_4$ solid species deposition on the YSZ electrolyte surface. Such an inhibiting effect results in a rapid performance degradation of LSM cathode for the O_2 reduction reaction.

On the other hand, LSM/YSZ composite and GDC-impregnated LSM cathodes show high tolerance towards the Cr species. The interaction between the chromia-forming alloy and the LSM/YSZ composite as well as the GDC-impregnated LSM cathodes reveals that the composite electrodes show much higher electrochemical activity and performance stability as compared to the pure LSM cathode. The performance degradation caused by the Cr species is much smaller for

the O₂ reduction on the composite cathodes. There is no preferential deposition of Cr species at the electrode and electrolyte interface region for the reaction on the LSM/YSZ composite cathode with high YSZ content (≥ 30 wt%) and a 1.60 mg cm⁻² GDC-impregnated LSM composite cathode. The amount of Cr deposition is also much smaller in comparison to that on the pure LSM cathode. The decrease of Mn²⁺ species generated under cathodic polarization is responsible for the significant reduction of Cr deposition at the composite cathodes.

Finally, an easy and quick electrochemical testing method is developed to evaluate different chromia-forming alloys. Three types of chromia-forming alloys with different Cr content and alloying elements are examined for the potential application as interconnect based on the initial performance of the LSM cathode for the O₂ reduction. The magnitude of performance degradation caused by the gaseous Cr species is related with the microstructure and composition of oxide scale formed on the surface of alloys. The formation of (Cr,Mn)₃O₄ spinels on the alloy surface is effective to reduce the generation of gaseous Cr species and leads to a significant decrease in performance degradation.

Keywords: Solid oxide fuel cell, metallic interconnect, Cr deposition, (La,Sr)MnO₃, (La,Sr)(Co,Fe)O₃, cathode, O₂ reduction reaction

LIST OF PUBLICATIONS

Journal paper:

- [1]. S.P. Jiang, Sam Zhang, Y.D. Zhen and A.P. Koh, Performance of GDC-impregnated Ni anodes of solid oxide fuel cells, *Electrochemical and Solid-State Letters*, 7 (9): A282-A285 (2004)
- [2]. S.P. Jiang, Sam Zhang and Y.D. Zhen, Early interaction between Fe-Cr alloy metallic interconnect and Sr-doped LaMnO₃ cathodes of solid oxide fuel cells, *Journal of Materials Research*, 20 (3): 747-758 (2005)
- [3]. S.P. Jiang, Sam Zhang, Y.D. Zhen, A fast method for the investigation of the interaction between metallic interconnect and Sr-doped LaMnO₃ of solid oxide fuel cells, *Materials Science and Engineering B*, 119: 80-86 (2005)
- [4]. San Ping Jiang, Sam Zhang, Yong Da Zhen, and Wei Wang, Fabrication and performance of impregnated Ni anodes of solid oxide fuel cells, *Journal of American Ceramic Society*, 88 (7): 1779-1785 (2005)
- [5]. S.P. Jiang, W. Wang, Y.D. Zhen, Performance and electrode behavior of nano-YSZ impregnated nickel anodes used in solid oxide fuel cells, *Journal of Power Sources*, 147: 1-7 (2005)
- [6]. Y.D. Zhen, San Ping Jiang, Sam Zhang, Vincent Tan, Interaction between metallic interconnect and constitute oxides of (La,Sr)MnO₃ coating of solid oxide fuel cells, *Journal of the European Ceramic Society*, 26 (2006): 3253-3264
- [7]. San Ping Jiang, Sam Zhang, and Y.D. Zhen, Deposition of Cr species at (La,Sr)(Co,Fe)O₃ cathodes of solid oxide fuel cells, *Journal of the Electrochemical Society*, 153(1): A127-A134 (2006)
- [8]. S.P. Jiang, Y.D. Zhen, Sam Zhang, Interaction between Fe-Cr metallic

- interconnect and (La,Sr)MnO₃/YSZ composite cathode of solid oxide fuel cells, *Journal of the Electrochemical Society*, 153 (8): A1511-A1517 (2006)
- [9]. San Ping Jiang, Y.D. Zhen, Sam Zhang, Alfred Ling Yoong Tok, and Ping Wu, An electrochemical method to assess the chromium volatility of chromia-forming metallic interconnect for SOFCs, *Journal of the Electrochemical Society*, 153 (11): A2120-A2125 (2006)
- [10]. Y.D. Zhen, San Ping Jiang, Transitional behavior for O₂ reduction reaction on (La,Sr)MnO₃/YSZ composite cathodes of solid oxide fuel cells, *Journal of the Electrochemical Society*, 153 (12): A2245-A2254 (2006)
- [11]. Y.D. Zhen, Jian Li, San Ping Jiang, Oxygen reduction reaction on Sr-doped LaMnO₃ cathodes in the absence and presence of a Fe-Cr alloy interconnect, *Journal of Power Sources*, 162 (2006): 1043-1052

Conference Paper:

- [12]. San Ping Jiang, Sam Zhang, Yong Da Zhen and Vincent Tan, Performance of LSM/YSZ composite cathodes for metallic interconnect of SOFC, *The Sixth European Solid Oxide Fuel Cell (SOFC) Forum*, Edited by M. Mogenson, Lucerne, Switzerland, p1341 (2004)
- [13]. Y.D. Zhen, S.P. Jiang and S. Zhang, Interaction between Fe-Cr alloy metallic interconnect and Sr-doped LaMnO₃ cathodes of solid oxide fuel cell at early stages, *9th International Symposium on Solid Oxide Fuel Cells (SOFC IX)*, S.C. Singhal and J. Mizusaki, Editors, The Electrochemical Society Proceeding Series. PV 2005-07: 1598-1606 (2005)
- [14]. Y.D. Zhen, S.P. Jiang, Sam Zhang, Evaluation of Fe-Cr alloys as interconnect for solid oxide fuel cell, in *World Hydrogen Technology Conference 2005 (WHTC 2005)*, Singapore, Oct.3-5, 2005

LIST OF ABBREVIATIONS

ASR	Area Specific Resistance
CPE	Constant Phase Element
EDS	Energy Dispersive Spectroscopy
EIS	Electrochemical Impedance Spectroscopy
GDC	Gadolinium-doped Ceria
ITSOFC	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
OCF	Open Circuit Potential
SEM	Scanning Electron Microscopy
SOFC	Solid Oxide Fuel Cell
TEC	Thermal Expansion Coefficient
TPB	Three-Phase Boundary
TZ3Y	3 mol% Y_2O_3 - ZrO_2
TZ8Y	8 mol% Y_2O_3 - ZrO_2
XRD	X-ray Diffraction
YSZ	Yttria-stabilized Zirconia

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CHAPTER 1.

INTRODUCTION

1.1 Fuel Cells

Recently, fuel cells have attracted extensive attention since they are one of the most efficient and effective solutions to energy and environmental problems that we face today. In the last century the fossil fuel, coal, oil and nature gas have been responsible for the unbelievable development of technology in the industry and the increase of mobility of mankind. Meanwhile, there are increasingly concerns about the environmental consequences of fossil fuel use in the production of electricity and for the propulsion of vehicles. The dependence of the industrialized countries on oil became apparent in the oil crises. Fuel cells offer a clean, environmental-friendly technology to generate electricity at high efficiency. Fuel cells will help to reduce our dependence on fossil fuel and diminish greenhouse gas emissions into the atmosphere.

A fuel cell is an energy conversion device that converts the chemical energy directly to electrical energy. The operating principles of fuel cells are similar to those of batteries, i.e., electrochemical combination of reactants to generate electricity. However, unlike a battery, a fuel cell does not run down or require recharging. A fuel cell operates as long as both fuel and oxidant are supplied to the electrodes. The main advantage of fuel cell over all other traditional power generation technologies is its

high conversion efficiency, not limited by Carnot cycle of a heat engine. In addition to the high conversion efficiency, fuel cells have the characteristics of environmental compatibility, modularity, sitting flexibility, and multi-fuel capability [[Minh, 1995](#)]. Fuel cells plants can be modular in design, and the energy production can be adjusted to meet the actual demand, which is a convenient feature for a power source in a technological society.

The first discovery of fuel cell is often ascribed to Sir William Grove in 1839 and the study of solid oxide fuel cells (SOFC) began with the discovery of electrical conducting oxide by Nernst in 1899. In the middle of the 20th century the developments of fuel cells accelerated. Several types of fuel cells were developed in the race for conquering the space. In the last twenty years, focus on pollution and demand for higher efficiency in the exploitation of fossil resources stimulated the research and development of fuel cell technology. Nowadays, a variety of fuel cell systems are under commercial development, and they are usually identified by the electrolyte materials within the cell: the Alkaline Fuel Cell (AFC), the Polymer Electrolyte Fuel Cell (PEFC), the Phosphoric Acid Fuel Cell (PAFC), the Molten Carbonate Fuel Cell (MCFC) and the Solid Oxide Fuel Cell (SOFC). Some of the characteristics of each of these fuel cell types are listed in Table 1.1.

Low temperature fuel cells (AFC, PEFC and PAFC) have a potential for automobile propulsion, where the time of heat-up must be short 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/heat production, where the

cell temperature can be maintained. In general high temperature fuel cells exhibit higher efficiency and are less sensitive to fuel purity than low temperature fuel cells. At high temperatures natural gas can be applied directly as fuels.

Table 1.1 Some characteristics of different types of fuel cells.

Name	AFC	FEFC	PAFC	MCFC	SOFC
Operating Temperature	80 °C	60-120 °C	160-220 °C	600-800 °C	500-1000 °C
Electrolyte	KOH	Polymer	H ₃ PO ₄	Molten Li ₂ CO ₃ +K ₂ CO ₃	Solid oxide
Conducting Species	OH ⁻	H ⁺	H ⁺	CO ₃ ²⁻	O ²⁻
Fuel	Highly Pure H ₂	Pure H ₂	CO-free H ₂	H ₂ , CH ₄ , CO	H ₂ , CH ₄ , CO
Electrical Efficiency	50-55%	40-50%	40-50%	50-60%	45-60%

SOFCs have several distinct advantages over other types of fuel cells, e.g., use of non-precious materials, no liquids involved in the fuel cell, and invariant electrolyte. The main characteristic of a SOFC is its ceramic component. The use of a solid electrolyte in the SOFC eliminates material corrosion and electrolyte management problems, which leads to highly reliable electricity generation system requiring low maintenance. The high operating temperature promotes rapid reaction kinetics, allows internal reforming or direct oxidation of hydrocarbon fuels within the fuel cell, and produces high-quality byproduct heat suitable for use in cogeneration or bottom cycles. Thus, power systems based on SOFC can be simple and are more efficient than many other technologies. Furthermore, because all the components are solid, SOFC can be

fabricated in very thin layers, and cell components can be configured into unique shapes [Minh, 1995].

1.2 Solid oxide fuel cell (SOFC)

1.2.1 Operation Principle

The operation principle of the solid oxide fuel cell is illustrated in Fig.1.1. A SOFC essentially consists of two porous electrodes separated by a dense oxygen ion conducting ceramic electrolyte. Fuel is fed to the anode where it is oxidized and electrons are released to the external circuit. Oxidant is fed to the cathode where it is reduced and electrons are accepted from the external circuit. The electrochemical reaction takes place at the electrode/electrolyte interface producing ions across the electrolyte. The electron flow (from the anode to the cathode) through the external circuit produces direct-current electricity. If the fuel fed is pure hydrogen, the only byproduct of this process is pure water and heat.

Fig.1.1 Schematic diagram of solid oxide fuel cell operated on hydrogen and air.

1.2.2 Stack design

Under operating conditions, the cell produces current as long as the reactants are provided to the electrodes. Defined by the Nernst potential of the different activity of oxygen on the electrodes, an open circuit voltage of about 1 volt is attained when a single cell is not loaded:

$$E = \frac{RT}{4F} \ln \left(\frac{P_{O_2}(\text{cathode})}{P_{O_2}(\text{anode})} \right) \quad (1.1)$$

Therefore, it is necessary to connect the single cells in series in a stack to obtain a higher voltage output for most practical application. A stack can in principle comprise any number of cells depending on the desired power, and a fuel cell can be designed in modules of stacks in series and parallel connects. SOFC power systems that have been considered range from portable devices (e.g., 500 W battery chargers) and small generators (5 kW residential power or automobile auxiliary power units) to distributed generation power plants (e.g., 100-500kW power plants). SOFC can also be integrated with a gas turbine to form large (several hundred kW to multi-MW) pressurized hybrid systems [[Minh, 2005](#)].

Four common SOFC stack configurations developed are shown in Fig.1.2, including: sealless tubular design, segmented-cell-in-series design, monolithic design and flat-plate design [[Minh, 1995](#)]. Among these stack designs, the most common configuration is the flat-plate (or planar) design, with its relative ease of manufacture and higher power density. Major problems with this design include sealing the stacks and the thermal mismatch between the ceramic components.

Fig.1.2 Schematic of different SOFC stack designs [Minh, 1995].

1.2.3 Components of a solid oxide fuel cell

A SOFC is a multiplayer structure consisting of ceramic and metallic materials. The basic components are the electrolyte, the anode, the cathode and the interconnect. Each component of the SOFC serves several different functions and therefore has to meet certain requirements. The selected materials mainly determine the stability and

compatibility as well as the performance of SOFC. Generally, all materials and components of the SOFC stack have to show chemical stability in the prevailing atmospheres whereupon changes in the gas compositions due to the fuel and oxygen utilization. The compatibility between the different materials, i.e. a well-adjusted thermal expansion behaviour, chemical compatibility and good adhesion at the interfaces has to be fulfilled.

(1) Electrolyte

The main function of the SOFC electrolyte is to conduct oxygen ions from the cathode to the anode. The electrolyte also serves as a separator to prohibit mixing of fuel from the oxidant in the fuel cell. Thus, the electrolyte material must be stable in both reducing and oxidizing environments, impermeable to the reacting gases and possess sufficient ionic conductivity at the operating conditions.

The first and only practical material used as electrolyte in high-temperature SOFC stack is the yttria stabilized zirconia (YSZ). Not only does YSZ fulfill the electrical requirement for a SOFC, but it also has good high-temperature mechanical properties for a ceramic. The commonly used YSZ material is either TZ3Y (ZrO_2 doped with 3 mol% Y_2O_3) or TZ8Y (ZrO_2 doped with 8 mol% Y_2O_3). However, the ionic conductivity of YSZ is insufficient to use in the intermediate-temperature SOFC (600-800°C). One way to decrease the electrolyte resistance is to use electrode-supported thin film electrolyte. Another is to develop new electrolyte materials with higher oxygen ionic conductivity than YSZ. The alternative electrolyte

materials under development include bismuth oxide [Ralph, 2001], doped ceria [Steele, 2001] and doped lanthanum gallate [Ishihara, 1994]. Scandium doped ZrO_2 (ScSZ) also exhibits significantly high ionic conductivity at the intermediate operating temperatures [Yamamoto, 1995].

(2) Anode

In the SOFC, anode is the electrode to provide reaction sites for the electrochemical oxidation of fuel such as hydrogen and natural gases. Thus, the anode materials must meet some basic requirements of high electronic conductivity, sufficient electrocatalytic activity for fuel oxidation reactions, chemically stable in the fuel reducing environments and have sufficient porosity for efficient gas transportation inside the bulk materials.

Ni-YSZ cermets are widely believed to be the most promising materials for anode in SOFC [Minh, 1995]. The addition of YSZ phase into Ni is to make the thermal compatibility of the composite material with the YSZ electrolyte and to improve the electrocatalytic activity for the anode reaction due to the significant extension of reaction zone. Recently, gadolinium-doped ceria (GDC) has been tested in place of YSZ in the cermet since doped ceria materials exhibit mixed ionic and electronic conductivity in a reducing environment [Xia, 2002]. This would improve the electrical property of the anode. High performance ceria-Ni-based anodes have been developed by doping with noble metals (such as Ru, Pt and Pd) [Hibino, 2002; McIntosh, 2003]. However, the Ni-based cermets are unsuitable for the direct oxidation of hydrocarbon

fuels owing to the carbon deposition and sulfur poisoning. For the direct oxidation of hydrocarbon fuels such as natural gas, some new anode materials are proposed, such as $(\text{La,Sr})(\text{Cr,Ru})\text{O}_3$ [Sauvet, 2001], $(\text{La,Ca})\text{CrO}_3$ [Steele, 1999], Cu-cermet [Gorte, 2002], $(\text{La,Sr})(\text{Cr,Mn})\text{O}_3$ [Tao, 2003] and so on.

(3) Cathode

The SOFC cathode is to provide reaction sites for the electrochemical reduction of the oxygen. Thus, the cathode materials must be stable in the oxidizing environment, have sufficient electronic conductivity and electrocatalytic activity for the oxygen reaction at the operating temperature and sufficient porosity to allow the oxygen to diffuse from the bulk to the reaction sites inside the cathode.

Because of the high operating temperature of SOFC, only noble metals and a few oxides can be considered as cathode materials. Noble metals are unsuitable for practical applications because of their prohibitive cost and insufficient long-term stability. Among the materials reported, Lanthanum strontium manganite $(\text{La,Sr})\text{MnO}_3$ (LSM) based perovskite is one of the most common cathode materials due to its excellent electrocatalytic activity for oxygen reduction, thermal and chemical stability, and relatively good compatibility with YSZ electrolyte [Minh, 1995]. Another widely used cathode material is $(\text{La,Sr})(\text{Co,Fe})\text{O}_3$ (LSCF) doped perovskite based on LaCoO_3 , a mixing ionic and electronic conductor. Its high activity for oxygen reduction enables the application within the operating temperature range of 600-800°C. Alternative new cathode materials for the intermediate temperature SOFC include $(\text{La,Sr})\text{FeO}_3$ [Ralph,

2001], (La,Sr)(Fe,Ni)O₃ [Chiba, 2002], (Sm,Sr)CoO₃ [Xia, 2002a], YBa₂Cu₃O₇ [Ralph, 2001], (Ba,Sr)(Co,Fe)O₃ [Shao, 2004], etc. To improve the electrochemical performance for oxygen reduction, composite electrode materials have also been developed, such as LSM/YSZ [Murray, 1998; Jørgensen, 2001], LSM/GDC [Murray, 2001], LSCF/GDC [Murray, 2002] and so on.

(4) Interconnect

As the voltage output of an individual cell is too low for practical application, it is necessary to connect the single cells in series as a stack. The interconnect is to connect the anode of one cell to the cathode of the next cell, as well as to separate the fuel from the oxidant in adjoining cells of a stack. Thus, the interconnect material must be stable in both the reducing and oxidizing environments, impermeable to gases, and sufficiently conductive to support electron flow at the operating conditions. Since the SOFC operates at high temperatures (500-1000°C), the interconnect must be chemically and thermally compatible with other cell components from room temperature to operating temperatures.

Ceramic interconnects like doped lanthanum chromite (LaCrO₃) have been widely used at high temperature SOFC [Minh, 1995]. The disadvantages of ceramic interconnect are poor tolerance of the sudden temperature changes, difficulties to fabricate and high material cost. In recent years, there has been significant progress in decreasing the operating temperature of SOFC to 600-800°C, which make it possible to use oxidation-resistance alloys as interconnect materials. Compared to the ceramic

interconnect, the metallic interconnect has higher electronic conductivity, higher thermal conductivity, lower cost and easier fabrication. The metallic materials studied as interconnect candidates are mostly chromia-forming alloys, such as Cr₅Fe₁Y₂O₃, Crofer22 APU alloy and ferritic stainless steels, etc [Yang, 2003]. The most serious problem arising from metallic interconnect is that an oxide scale forms at high temperatures. Volatile Cr species such as high valent vapor species (CrO₃ and Cr(OH)₂O₂) will be generated over the oxide scale in oxidizing atmospheres [Hilpert, 1996]. Without effective protective coating, the gaseous Cr species generated can seriously degrade the cathode performance such as LSM for the oxygen reduction.

The interaction between the metallic interconnect and SOFC cathode is the subject of this project. Thus more detailed introduction of the metallic interconnect and its interaction with the SOFC components will be given in the following chapter.

1.2.4 Challenges

Current activities in the areas of materials development for SOFC are increasingly focused on the decrease of operating temperature of the SOFC from traditional 1000°C to intermediate temperature of 600-800°C. The lower operating temperature would solve various problems associated with the high temperature operation, such as thermal degradation of electrodes, interfacial reaction between various ceramic components and crack formation from stress caused by the large difference in the thermal expansion coefficients of the cell components. Besides, low operating temperature will widen the range of material selection for cell components. In particular, this opens the

opportunity to use the less costly metal alloys for interconnect, which can significantly reduce the SOFC system cost. Thus, it is scientifically important and necessary to understand the interaction and compatibility between the metallic materials and the other components of SOFC before the successful use of metallic interconnect in the SOFC system.

1.3 Objective and scope of the research project

This project concentrates on the interaction between chromia-forming alloy interconnect and cathodes under SOFC operating conditions. The cathode materials are the currently promising candidates LSM, LSCF and LSM/YSZ composites.

The scope of this research project is outlined as below:

(1). Investigation of the interaction between chromia-forming alloy and LSM cathode, in particular

- Early stage deposition of Cr species at LSM cathode/YSZ electrolyte cell at high temperatures,
- Chemical interaction between chromia-forming alloy and constituent oxides of LSM, including La_2O_3 , SrO , Mn_2O_3
- Cr species deposition mechanism at the LSM cathode,
- Oxygen reduction reaction on the LSM cathodes in the absence and presence of chromia-forming alloy,

(2). Investigation of the interaction between chromia-forming alloy and mixed ionic

and electronic conducting LSCF cathode, in particular

- Characterization of Cr species deposition at LSCF cathode in the presence of cathodic current passage,
- Characterization of Cr species deposition at LSCF cathode in the absence of cathodic current passage,
- Cr species deposition mechanism at the LSCF cathode,

(3) Investigation of the interaction between LSM-based composite cathodes and metallic interconnect, in particular

- Fabrication of LSM/YSZ composite cathodes by conventional powder mixing and GDC-impregnated LSM cathode by novel ion impregnation method,
- Electrochemical characterization of LSM/YSZ composite and GDC-impregnated LSM cathodes in the presence of chromia-forming alloy interconnect,
- Microstructural characterization of LSM-based composite cathodes,

(4). Development of simple and fast evaluation technique of commercial Fe-Cr alloys as interconnect candidates for SOFC, in particular

- Oxidation behaviour of three types of chromia-forming alloys in air,
- Electrochemical and microstructural characterization of LSM cathodes with different chromia-forming alloys.

1.4 Thesis Layout

Chapter 2 is the literature review that summarizes properties of the ceramic interconnect and the metallic interconnect and the recent research activities on the metallic interconnect. Chapter 3 describes the experimental procedures and measurement techniques used in this project. From Chapter 4 to Chapter 6 documents the interaction between the chromia-forming alloy interconnect and the LSM cathode. Chapter 4 investigates the deposition of Cr species at the LSM cathode/YSZ electrolyte system and the deposition mechanism of Cr species. Chapter 5 presents the chemical interaction between the alloy and the constituent oxides of LSM material such as La_2O_3 , SrO and Mn_2O_3 under open circuit conditions. The effect of Cr species on the O_2 reduction reaction at the LSM cathode is investigated in Chapter 6. Chapter 7 and Chapter 8 investigate the interaction between the chromia-forming alloy and different cathode materials, including LSCF (Chapter 7), LSM/YSZ and GDC-impregnated LSM composite cathodes (Chapter 8). In Chapter 9 a new method is introduced to evaluate the Fe-Cr alloys for application as interconnect candidates. Finally, the conclusions and recommendations for further investigation are presented in Chapter 10.

CHAPTER 2.

LITERATURE REVIEW

In this chapter, the current status and progress in the development of interconnect materials for SOFC are reviewed with emphasis on the metallic interconnect materials and their interaction with cathodes of SOFC.

2.1 Requirements for interconnect

In flat-plate design of a SOFC stack, an interconnect acts not only as electrical connection between the individual cells but also as the mechanical support of the thin electroactive ceramic components and as gas-proof separation of fuel gas and oxidant. Furthermore, the interconnect distributes the gas in co-, cross- and/or counter flow and acts as constructional connection to the external gas inlets and outlets. In order to perform the intended functions, the interconnect materials need to fulfill the requirements listed below [[Minh, 1995](#); [Badwal, 1997](#); [Zhu, 2003](#)]:

- High density (no open porosity). The material must be impermeable to gases to avoid mixing fuel and air.
- High electrical conductivity and negligible ionic conductivity. The ohmic loss caused by the interconnect should be noticeably small so that the power density of a stack does not show profound drop as compared to that of an individual cell. A value of 1 S cm^{-1} is a well-accepted minimum electrical

conductivity for the usefulness of interconnect in the SOFC stack.

- Chemical and physical stabilities in both oxidizing and reducing environments and also chemical compatibility with other cell components with which the interconnect will make contact (anode and cathode, seal, manifold, etc).
- Match in thermal expansion coefficient (TEC) with other cell components at the operating temperatures and during thermal cycling. Since the TEC of most other components varies about 10 to $13 \times 10^{-6} \text{ K}^{-1}$, the TEC of an interconnect is preferably close to this value.
- High thermal conductivity ($> 20 \text{ W m}^{-1} \text{ K}^{-1}$) for uniform heat distribution in the stack. The interconnect material provides the major thermal conduction path for heat distribution in the fuel cell stack.
- Excellent oxidation, sulfidation and carburization resistance. This issue mainly arises as metallic interconnects are used because the formation of oxide scales in SOFC gases is a thermodynamically favored inevitable process. Presence of sulfur and carbon-bearing gas species might exacerbate the issue.
- Good high-temperature strength and creep resistant. The material should not creep under the load during operation or thermal cycling of the stack.

The stringent requirements discussed above eliminate all but a few oxide systems from consideration for the interconnect. High-temperature oxidation-resistant alloys have also been chosen as interconnect materials, especially for flat-plate SOFC.

2.2 Ceramic interconnect

Perovskite-structure ceramic doped Lanthanum chromite (LaCrO_3) is currently the most widely used interconnect material in high-temperature SOFC stack since it exhibits relatively high electronic conductivity in both fuel and oxidant atmospheres, moderate stability in the fuel cell environment as well as fairly good compatibility with other cell components in terms of phase, microstructure and thermal expansion [[Minh, 1995](#)].

Lanthanum chromite is a p-type electronic conductor due to the holes in the $3d$ band of the chromium ions [[Akashi, 2003](#)]. The conductivity of pure lanthanum chromite can be improved through doping. The most common dopants for LaCrO_3 are alkaline-earth elements, which act as electron acceptors on the trivalent lanthanum or chromium or both sites, and thus increase p-type conduction by a small polaron mechanism [[Zhu, 2003](#); [Minh, 1995](#)]. The large alkaline-earth ions, most commonly strontium and calcium occupy the lanthanum site. Magnesium, however, is much smaller and thus takes over the chromium site. Acceptor dopants (e.g. nickel, copper, cobalt) are more commonly used, although donor doped (e.g. niobium, titanium, vanadium) lanthanum chromite have been reported [[Yu, 1989](#); [Zuve, 2002](#)]. In general, the conductivity of LaCrO_3 at elevated temperatures is proportional to the dopant concentration [[Minh, 1995](#)]. However, the extent to which dopant improves the conductivity of LaCrO_3 is revealed to differ remarkably. This is probably associated with the various degrees of lattice distortion arising from ionic size different between

dopant and the host cations. It is likely that smaller lattice distortion can result in higher charge carrier mobility, and thus higher conductivity [Zhu, 2003].

Acceptor doping not only alters the electrical conductivity, but also modifies the thermal expansion coefficient (TEC) of LaCrO_3 ceramic. Table 2.1 summarizes the TECs and electrical conductivities of some undoped and doped LaCrO_3 materials developed currently [Zhu, 2003]. The substitution of Sr, Ca [Armstrong, 1995; Paulik, 1997], Co [Mori, 2002], Ni [Höfer, 1993] and Cu [Armstrong, 1999] increases the TEC, while the substitution of Mg does not affect the TEC of LaCrO_3 [Flandermeyer, 1985]. On the other hand, Fe doping reduces the TEC [Zhu, 2003]. Donor dopant such as vanadium at the chromium site reduces overall acceptor concentration and decreases

Table 2.1 TECs and electrical conductivities of LaCrO_3 -based ceramics [Zhu, 2003].

Composition	Electrical conductivity (S cm^{-1})	Composition	Average TEC $\times 10^{-6}$ (K^{-1})
LaCrO_3	0.34 at 700°C, 1 at 1000°C	LaCrO_3	9.5
$\text{LaCr}_{0.9}\text{Mg}_{0.1}\text{O}_3$	3 at 1000°C	$\text{LaCr}_{0.9}\text{Ni}_{0.1}\text{O}_3$	10.1
$\text{La}_{0.9}\text{Cr}_{0.1}\text{O}_3$	14 at 1000°C	$\text{LaCr}_{0.8}\text{Ni}_{0.2}\text{O}_3$	11.2
$\text{La}_{0.95}\text{Ca}_{0.05}\text{CrO}_3$	2.3 at 700°C	$\text{LaCo}_{0.7}\text{Ni}_{0.3}\text{O}_3$	11.8
$\text{La}_{0.95}\text{Ca}_{0.05}\text{Cr}_{0.5}\text{Co}_{0.5}\text{O}_3$	63 at 700°C	$\text{LaCr}_{0.9}\text{Mg}_{0.1}\text{O}_3$	9.5
$\text{La}_{0.8}\text{Ca}_{0.2}\text{CrO}_3$	7.1 at 700°C, 35 at 1000°C	$\text{La}_{0.9}\text{Sr}_{0.1}\text{CrO}_3$	10.7
$\text{La}_{0.8}\text{Ca}_{0.2}\text{Cr}_{0.8}\text{Fe}_{0.2}\text{O}_3$	9.2 at 700°C	$\text{La}_{0.65}\text{Ca}_{0.35}\text{CrO}_3$	10.8
$\text{La}_{0.8}\text{Ca}_{0.2}\text{Cr}_{0.8}\text{Ni}_{0.2}\text{O}_3$	18 at 700°C	$\text{La}_{0.8}\text{Ca}_{0.2}\text{Cr}_{0.9}\text{Co}_{0.1}\text{O}_3$	11.1
$\text{La}_{0.7}\text{Ca}_{0.3}\text{CrO}_3$	18 at 700°C	$\text{LaCr}_{0.9}\text{Co}_{0.1}\text{O}_3$	13.1
$\text{La}_{0.7}\text{Ca}_{0.3}\text{Cr}_{0.8}\text{Ca}_{0.2}\text{O}_3$	45 at 700°C	$\text{LaCr}_{0.8}\text{Co}_{0.2}\text{O}_3$	14.6
$\text{La}_{0.7}\text{Ca}_{0.3}\text{Cr}_{0.5}\text{Ca}_{0.5}\text{O}_3$	85 at 700°C	$\text{LaCr}_{0.6}\text{Co}_{0.4}\text{O}_3$	18.7
$\text{La}_{0.7}\text{Sr}_{0.3}\text{CrO}_3$	15 at 700°C	$\text{LaCr}_{0.2}\text{Co}_{0.8}\text{O}_3$	20.9
$\text{La}_{0.7}\text{Sr}_{0.3}\text{Cr}_{0.5}\text{Co}_{0.5}\text{O}_3$	58 at 700°C	$\text{La}_{0.7}\text{Sr}_{0.3}\text{Cr}_{0.2}\text{Co}_{0.8}\text{O}_3$	19
$\text{LaCr}_{0.6}\text{Ni}_{0.4}\text{O}_3$	26 at 700°C	$\text{La}_{0.7}\text{Sr}_{0.3}\text{Cr}_{0.5}\text{Co}_{0.5}\text{O}_3$	19
$\text{La}_{0.85}\text{Sr}_{0.15}\text{CrO}_3$	21.8 at 1000°C	$\text{La}_{0.7}\text{Sr}_{0.3}\text{Cr}_{0.8}\text{Co}_{0.2}\text{O}_3$	14.5
$\text{La}_{0.87}\text{Sr}_{0.1}\text{Cr}_{0.95}\text{Cu}_{0.05}\text{O}_3$	23.9 at 1000°C	$\text{La}_{0.87}\text{Sr}_{0.1}\text{Cr}_{0.95}\text{Cu}_{0.05}\text{O}_3$	9.81
$\text{La}_{0.85}\text{Sr}_{0.15}\text{Cr}_{0.98}\text{Cu}_{0.02}\text{O}_3$	32.5 at 1000°C	$\text{La}_{0.85}\text{Sr}_{0.15}\text{Cr}_{0.98}\text{Cu}_{0.02}\text{O}_3$	9.91
$\text{La}_{0.9}\text{Sr}_{0.1}\text{Cr}_{0.95}\text{V}_{0.05}\text{O}_3$	9.7 at 1000°C	$\text{La}_{0.9}\text{Sr}_{0.1}\text{Cr}_{0.93}\text{Mg}_{0.05}\text{Cu}_{0.02}\text{O}_3$	9.61
$\text{La}_{0.85}\text{Sr}_{0.15}\text{Cr}_{0.95}\text{V}_{0.05}\text{O}_3$	19.9 at 1000°C	$\text{La}_{0.9}\text{Sr}_{0.1}\text{Cr}_{0.95}\text{V}_{0.05}\text{O}_3$	9.87
$\text{La}_{0.9}\text{Sr}_{0.1}\text{Cr}_{0.9}\text{Mg}_{0.05}\text{V}_{0.05}\text{O}_3$	15.2 at 1000°C	$\text{La}_{0.9}\text{Sr}_{0.1}\text{Cr}_{0.92}\text{V}_{0.05}\text{Co}_{0.03}\text{O}_3$	10.4
$\text{La}_{0.95}\text{Sr}_{0.05}\text{Cr}_{0.85}\text{Mg}_{0.1}\text{V}_{0.05}\text{O}_3$	12.9 at 1000°C	$\text{La}_{0.85}\text{Sr}_{0.15}\text{Cr}_{0.95}\text{V}_{0.05}\text{O}_3$	10
$\text{La}_{0.87}\text{Sr}_{0.1}\text{Cr}_{0.935}\text{Cu}_{0.05}\text{Co}_{0.015}\text{O}_3$	25.6 at 1000°C	$\text{La}_{0.9}\text{Sr}_{0.1}\text{Cr}_{0.9}\text{Mg}_{0.05}\text{V}_{0.05}\text{O}_3$	9.64
$\text{La}_{0.85}\text{Sr}_{0.15}\text{Cr}_{0.935}\text{V}_{0.05}\text{Co}_{0.015}\text{O}_3$	22.9 at 1000°C	$\text{La}_{0.95}\text{Sr}_{0.05}\text{Cr}_{0.85}\text{Mg}_{0.1}\text{V}_{0.05}\text{O}_3$	9.22
$\text{La}_{0.9}\text{Sr}_{0.1}\text{Cr}_{0.92}\text{V}_{0.05}\text{Co}_{0.03}\text{O}_3$	12.8 at 1000°C	$\text{La}_{0.87}\text{Sr}_{0.1}\text{Cr}_{0.935}\text{Cu}_{0.05}\text{Co}_{0.015}\text{O}_3$	10.4
		$\text{La}_{0.85}\text{Sr}_{0.15}\text{Cr}_{0.935}\text{V}_{0.05}\text{Co}_{0.015}\text{O}_3$	10.5

both electrical conductivity and TEC [[Armstrong, 1999](#)]. Generally, double acceptor doping at both La and Cr sites brings about significant enhancement in electrical conductivity, but the concomitant increase in TEC is unfavorably large.

One distinct characteristic of doped LaCrO_3 ceramic is that the electrical conductivity strongly depends on the oxygen partial pressure and temperature. The electrical conductivity of doped LaCrO_3 has been interpreted by the nature of defect chemistry. Under oxidizing conditions, typically larger than 10^{-8} atm, the substitution of divalent metal ions on either La or Cr sites is electronically compensated by a transition of Cr^{3+} to Cr^{4+} ions, thereby promoting the occurrence of electron holes and enhancing the electrical conductivity of the material. Under reducing conditions, the compound loses oxygen and becomes oxygen deficient, $\text{LaCrO}_{3-\delta}$. The charge neutrality is maintained by the formation of oxygen vacancies. Electron holes are consumed due to the formation of oxygen vacancies and thus the electrical conductivity decreases with decreasing oxygen partial pressure. Due to the strong dependence of electrical conductivity on the oxygen partial pressure, the electrical conductivity of the doped LaCrO_3 in anode atmosphere like hydrogen is significantly lower than that in oxidizing atmosphere like air. Therefore, a conductivity gradient across the doped LaCrO_3 is established when it is used as interconnect in SOFC. However, the overall conductivity of doped LaCrO_3 is still sufficient for its use when the operating temperature is above 800°C . As the temperature drops below 800°C , the electrical conductivity of doped LaCrO_3 is reported to experience a substantial degradation [[Steele, 1994](#)]. This thus limits its application for the intermediate

temperature SOFC operating in the temperature range of 600-800°C.

The defect chemistry of the doped LaCrO_3 also affects the thermal expansion, especially in reducing atmospheres. The TEC increases with the decrease of oxygen partial pressure. It is generally recognized that the expansion of doped LaCrO_3 in reducing atmospheres is directly related to the loss of lattice oxygen (increase of the cation-cation repulsion) and the increased Cr ion size as Cr^{4+} transfers to Cr^{3+} to maintain charge neutrality [[Armstrong, 1996](#)]. Recently, a strong linear correlation between isothermal expansion and oxygen nonstoichiometry has been found [[Hilpert, 2003](#)]. Such isothermal expansion of doped LaCrO_3 ceramic would cause structural failure arising from the internal stresses developed during operation in SOFC environment. Besides, the acceptor-doped LaCrO_3 is more likely to have high oxygen permeability in reducing atmospheres as a result of significantly enhanced oxygen vacancy concentration. This gives rise to the promoted oxygen migration from the cathode to the anode via the interconnect, which is responsible for the deteriorated fuel cell performance [[Sakai, 2000](#)]. It has also been recognized that the mechanical properties of doped LaCrO_3 ceramics depend on the level of oxygen partial pressure, which constitutes another serious concern for their utilization as interconnects [[Paulik, 1997](#)].

One major obstacle to mass production of ceramic interconnects like LaCrO_3 or doped LaCrO_3 is their extremely inferior sintering behaviour in air due to the easy volatilization of Cr species. The poor sinterability of LaCrO_3 -based ceramics has been attributed primarily to the formation of a thin layer of Cr_2O_3 from CrO_3 gases at the

interparticle neck at the initial stage of sintering [[Yokokawa, 1991](#)]. To achieve full densification, several approaches can be considered, including (1) developing new techniques to prepare highly reactive raw powders [[Krogh, 1997](#)], (2) conducting sintering in reducing atmosphere followed by oxidation treatment to recover its high electrical conductivity [[Zhu, 2003](#)], (3) adjusting the composition deliberately to facilitate the formation of nonstoichiometric perovskite structure [[Mori, 1999](#); [Paulik, 2000](#)], (4) conventional liquid-phase sintering process can be tried to promote densification [[Chick, 1997](#)], (5) firing LaCrO_3 between Cr_2O_3 plates (sandwich configuration) in conjunction with fast heating and cooling schedule to improve the densification process [[Tai, 1991](#)]. However, this inevitably increases manufacturing complexity and cost.

2.3 Metallic interconnect

Comparing with the doped LaCrO_3 ceramic, there are many advantages to prepare the interconnect from a metallic material, such as gas-tightness, higher electronic and thermal conductivity, lower cost, easier fabrication and better workability. The ohmic losses in the metallic interconnect are small. Furthermore, unlike the ceramic interconnect, the electrical conductivity of metallic interconnect is independent of oxygen partial pressure. The excellent heat conduction of metallic materials allows the heat generated at the air electrode to be easily transported to the fuel electrode where the internal reforming reaction occurs and also eliminates the use of cooling fluid that is usually excess air at cathode. Another good feature of the metallic interconnect is

that it offers the possibility of flexible design.

Therefore the use of metallic interconnect materials has been gaining popularity. However, metals cannot tolerate high temperature as the ceramics do. Recently significant progress has been made toward intermediate-temperature SOFC (600~800°C) that keeps the cell power density and durability at the same level as those operating at higher temperature (~1000°C). This progress is achieved by reducing the thickness of electrolyte and/or by the identification of new electrolytes with improved oxygen ionic conductivity as well as by developing new electrode materials. The lower operating temperature makes it feasible for the doped LaCrO_3 ceramic to be supplanted by metals or alloys as the interconnects, especially in the flat-plate SOFC stack.

For the metallic interconnects to be used as bipolar plate in the flat-plate design SOFC, they must exhibit sufficient mechanical strength at the operating temperatures, good oxidation and corrosion resistance in service environments, good thermal and chemical compatibility with the electrode materials. Since an oxide layer is inevitably formed on the surface of metals in oxidizing atmospheres such as those at the cathode side of SOFC, the ideal situation is that the metallic interconnects possess sufficient oxidation resistance over the projected service lifetime (40,000h) of the SOFC. The oxide scale formed should exhibit sufficiently high electronic conductivity. The oxide scales should also be chemically stable, free of porosity and strongly adherent to the metallic substrate.

High-temperature oxidation-resistant alloys are generally considered to be the

promising interconnect candidates. Such alloys generally contain different amount of Al, Si, or Cr as alloying additives since they form a protective layer of alumina, silica, or chromia when exposure to oxidizing environment at high temperatures. Although alumina and silica scale can provide superior oxidation resistance, they also have much lower electrical conductivities, which lead to unacceptable high resistance when formed at the alloy/electrode interface. Therefore, only the chromia-forming alloys offer some possibility of use as interconnect since Cr_2O_3 has comparatively low electrical resistivity at elevated temperatures [[Huang, 2000](#); [Zhu, 2003](#)]. However, at high temperatures, chromia is oxidized to high valent vapor species (e.g. CrO_3 and $\text{CrO}_2(\text{OH})_2$), which leads to higher oxidation rates as a steady state between scale growth and volatilization is established.

So far, numerous studies have focused on the development of chromia-forming alloys as interconnect for SOFC, which can be divided into chromium-, nickel- and ion-based alloys. A recent review by Yang et al [[2003](#)] discusses in details the chemical composition criteria for the metallic interconnect, which is derived mainly from the requirements in oxidation resistance. Table 2.2-2.4 presents the chemical compositions of some chromia-forming alloys studied in the past few years. To define the applicability as a SOFC interconnect, it is generally to evaluate these metallic alloys in terms of relevant properties that correlate directly with the functional requirements of the interconnect. These properties include oxidation resistance, electrical resistance, thermal expansion and compatibility with other components of SOFC.

Table 2.2 Chemical compositions of chromium-based alloys.

Alloy	Composition (wt%)						Reference
	Cr	Fe	Co	Ti	Y ₂ O ₃	La ₂ O ₃	
Ducrolloy Cr5Fe1Y ₂ O ₃	Bal	5			1.0		[Qudakkers, 1994; Batawi, 1999; Glatz, 1999; Badwal, 1997]
Cr3Co	Bal		3				[Qudakkers, 1994]
Cr-5Fe-0.5CeO ₂	Bal	5				0.5	[Batawi, 1999]
Cr-5Fe-1La ₂ O ₃	Bal	5				1	[Glatz, 1999]
Cr-5Fe-0.3Ti-0.5Y ₂ O ₃	Bal	5		0.3	0.5		[Batawi, 1999]
Cr-5Fe-0.3Ti-0.5CeO ₂	Bal	5		0.3		0.5	[Batawi, 1999]
Cr-5Fe-0.3Ti-1La ₂ O ₃	Bal	5		0.3		1	[Glatz, 1999]

Table 2.3 Chemical compositions of nickel-based alloys.

Alloy	Composition (wt%)								Reference
	Ni	Cr	Fe	Mo	Mn	Co	Al	Others	
Inconel 600	Bal	14-16	6-9		0.4-1		0.2	0.2 Si; 0.2 Ti	[Taniguchi, 1995; Oishi, 1999; Uehara, 2002; Zeng, 2004]
Inclonel 601	Bal.	21.9	14.5	0.1	0.2		1.4	0.2 Si; 0.3 Ti, 0.1 Nb	[Linderoth, 1996; Zeng, 2004]
Inconel 625	Bal	25	5.4	5.7	0.55	1.03			[England, 1999 and 2001]
Inconel 718	Bal	22	18	1.9	0.38	1.0		0.9 W	[England, 1999 and 2001]
Haynes 230	Bal	22-26	3	1-2	0.5-0.7	5		5 W	[England, 1999 and 2001; Vazquez-Navarro, 1999]
Hastelloy X	Bal	24	19	5.3	1.03	1.45		0.19 W	[England, 1999 and 2001]

Table 2.4 Chemical compositions of iron-based alloys.

Alloy	Composition (wt%)							Reference
	Fe	Cr	Mn	Mo	Si	Al	Ti	
SUS 430	Bal	16-17	0.2-1.0		0.4-1.0	0.11		[Brylewski, 2001; Horita, 2003a and 2004a; Uehara, 2002; Kurokawa, 2004]
ZMG232	Bal	21.97	0.50		0.40	0.21		[Abellán, 2002; Horita, 2003a, 20003b, 2004a and 2004b; Uehara, 2002]
E-Brite	Bal	26-27	0.1	1.0	0.03-0.2	0.05	0.05	[Huang, 2000 and 2001; Hou, 1999; Yang, 2004]
446	Bal	24-26	0.7-1.5	<0.05	0.4-1		<0.05	[Abellán, 2002; Huang, 2001; Meulenberg, 2003; Honegger, 2001]
1.4742	Bal	17.3	0.31		0.93	1.04		[Abellán, 2002; Gindorf, 2001; Meulenberg, 2003]
Fe-18Cr-7W	Bal	18					7 W	[Ueda, 2000]
Fe-28Cr-9W-0.5Zr	Bal	18					9 W, 0.54 Zr	[Ueda, 2000]
Fe-25Cr-0.1Y-2.5Ti	Bal	25					0.1 Y, 2/5 Ti	[Quadakkers, 2000]
Fe-25Cr-0.2Y-1Mn	Bal	25	1.0				0.2 Y	[Quadakkers, 2000]
Fe-25Cr-0.4Y	Bal	25					0.4 Y	[Quadakkers, 2000]
Fe-17Cr-0.3Ce	Bal	17					0.3 Ce	[Quadakkers, 2000]
Fe-25Cr-0.4La	Bal	25					0.4 La	[Quadakkers, 2000]
FeCrMn(Ti,La)	Bal	16-25	?				? La	[Abellán, 2001; Teller, 2001]
Fe26CrTiY ₂ O ₃	Bal	26	0.06	<0.02			0.34	[Honegger, 2001]
Fe-18Cr-Ti-Nb	Bal	17.6	0.47				0.27	[Honegger, 2001]
Fe-26Cr-0.5Mn-Ti-Y ₂ O ₃	Bal	26.1	0.53	<0.02			0.3	[Honegger, 2001]
Crofer22 APU	Bal	22.8	0.45				0.08	[Yang, 2004]

2.3.1 Oxidation and corrosion resistance

Generally, to promote the oxidation resistance as well as the adherence of the scale to the metallic substrate, the commercially available high-temperature oxidation-resistant chromia-forming alloys invariable contain trace amount of oxygen active elements such as Y, Ce, La, in terms of either metals or their oxides [[Huang, 2001](#)]. The presence of oxygen active element in the chromia-forming alloys can (1) enhance the selective oxidation of chromium by either lowering the amount of Cr required to form a continuous protective chromia layer or by reducing the amount of oxides containing base metals in the external scale, (2) reduce the growth rate of the scale from predominantly outward cation transport to inward oxygen transport, and (3) increase the adherence of the scale to the substrate alloy. The effect of the active element is mainly due to the segregation of the active element to the grain boundaries and the metal/scale interface. The active elements at the grain boundaries change the defect structure of the grain boundary regions and make these oxygen diffusion regions. Due to the inward oxygen diffusion, new oxide is formed at or near the scale/metal interface and thereby reduces the tendency for formation of cavities and porosity near the scale/metal interface and improves the scale adherence [[Kofstad, 1996](#)]. Volatilization of chromia can also be decreased with the addition of alloying elements (e.g. Mn and Ti) that form oxides (e.g. spinel and rutile) in the outer portion of the scale and reduce the chromium volatilization. In addition, elements such as Mo and W are added to better match the thermal expansion of the alloys to those of other cell components.

According to Wagner' theory, the oxidation behaviour of metal is a diffusion-controlled process that can be approximated by the parabolic law:

$$X^2 = K_p t \quad (2.1)$$

where X can be expressed in terms of either the thickness of the oxide scale or the weight gain, K_p is the parabolic rate constant, and t is the duration time for oxidation. The parabolic rate is dependent on alloying composition, thermal history and surface conditions. Although for the chromia-forming alloys, some deviations from the parabolic law have been observed due to the volatilization and spalling of chromia scale at high temperature. In most cases the oxidation behaviour at high temperature still obeys the parabolic law.

Therefore the parabolic rate constant K_p is normally used to measure the oxidation resistance of alloys. For example, the parabolic rate constant of $\text{Cr5Fe1Y}_2\text{O}_3$, a commercial Cr-based alloy developed specifically for SOFC by Plansee and Siemens, is about $8 \times 10^{-14} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$ for oxidation in oxygen at 900°C [Kofstad, 1996]. For a dense Cr_2O_3 scale, which theoretical density is 5.21 g cm^{-3} , this corresponds to a parabolic rate constant of $K_p = 3 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1}$. It is surprised that the thickness of oxide scale will be about $10 \text{ }\mu\text{m}$ after 1 year and $23 \text{ }\mu\text{m}$ after 5 years operation at 900°C . Such thick scale layer is considered to be too thick for reliable operation [Kofstad, 1996]. However, there is a lack of data about the oxidation resistance of $\text{Cr5Fe1Y}_2\text{O}_3$ alloy at lower temperatures. England et al [1999 and 2001] examined oxidation behaviour of four types of commercially Ni-based alloys, i.e., Inconel 625, Inconel 718, Hastelloy X and Haynes 230 in both air and wet hydrogen atmospheres.

Among these alloys, Haynes 230 alloy shows the best oxidation resistance at 1×10^{-13} and $1.3 \times 10^{-15} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$ at 900 and 800°C in air, respectively. Similar oxidation rate was also measured by Yang et al [2003] and Vazquez-Navarro et al [1999]. The slower oxidation rate of Haynes 230 alloy may be due to the formation of Cr_2O_3 and $(\text{Cr,Mn})_3\text{O}_4$ in the scale.

Iron-based alloys especially ferrite stainless steels recently have attracted many attentions due to their high ductility, easy machinability and low cost. Fig.2.1 shows the oxidation behaviour of various Fe-Cr-based alloys exposed to air at 800°C [Quadakkers, 2000; Abellán, 2001]. A near parabolic oxidation behaviour is clearly observed. Recently Yang et al [2003] and Fergus [2005] summarized the parabolic rate constants of iron-based and nickel- alloys at different temperatures. The scale growth rates of Fe-Cr based alloys are in the range of 10^{-14} and $10^{-12} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$ at 800°C in air. The oxidation rates of iron-based alloys tend to be higher than those of nickel-based alloys. The addition of oxygen active elements can effectively increase the oxidation

Fig.2.1 Oxidation behaviour of various Fe-Cr-based alloys at 800°C in air [Quadakkers, 2000; Abellán, 2001].

resistance and the scale adherence of iron-based chromia-forming alloys. Taking E-Brite alloy (Fe26Cr1Mo) as an example, the incorporation of alloying element Mo moderately suppresses the oxidation rate. A parabolic rate constant of $3.5\text{--}8.8 \times 10^{-14} \text{ g}^2 \text{ cm}^{-4} \text{ s}^{-1}$ is measured at 800°C in air [Huang, 2001; Yang, 2004]. However, the weight gain is still too large for the alloy to qualify as SOFC interconnect [Yang, 2003]. As shown in Fig.2.1, the addition of oxygen active elements such as Y can significantly retard the oxidation kinetics of iron-based alloys.

While many studies have focused on the oxidation resistance in air (or at the cathode side), the oxidation and corrosion resistance of alloys at the fuel or anode side are also of great importance. The composition, microstructure, and properties of the scale growth in a fuel environment can be significantly different from those in air. Recent work by Yang et al [2004a] found that the spinel phase in the scale formed on 430 alloy in wet hydrogen grew in a fiber-like shape instead of being equi-axed in air, but the thickness of the scale was comparable to that grown on 430 alloy in air. Similar observations were reported by other researchers [Brylewski, 2001, Horita, 2003b; Kurokawa, 2004]. For example, the parabolic rate constants K_p are 3.8×10^{-6} and $3.0 \times 10^{-6} \text{ } \mu\text{m}^2 \text{ s}^{-1}$, respectively, for the scale grown in the wet hydrogen and air at 800°C [Brylewski, 2001]. The oxygen partial pressure independence of the parabolic rate constant has been interpreted with a kinetic model using diffusion coefficients for the diffusion of chromium in Cr_2O_3 [Kurokawa, 2004]. However, differences have been observed for some alloys. For example, for alloy 446 and Fe25CrMn, the weight gain after oxidation at 800°C in $\text{H}_2\text{--H}_2\text{O}$ for 250 h is about half of that in air for the same

time and temperature [Quadackers, 2000; Abbellán, 2001]. Conversely, the oxidation rates of nickel-based alloys at 800°C in H₂–H₂O are faster than those in air at the same temperature [England, 2001]. The difference of oxidation behaviour in air and wet hydrogen atmospheres is often attributed to the effect of the reduced oxygen partial pressure and the water vapor in the wet hydrogen atmosphere [England, 2001; Fergus, 2005].

One of the advantages of SOFC is that the hydrocarbon fuels can be directly used, so the stability of potential interconnect materials in carbon-containing atmospheres is important. Horita et al [2003a, 2003c, 2004a and 2004b] studied the oxidation of different ferritic stainless steels in CH₄–H₂O atmospheres. The oxidation rate at 800°C in CH₄–H₂O is only slightly higher than that in H₂–H₂O [Horita, 2003a] and does not depend on the CH₄ content (3.5-12 kPa) [Horita, 2003c]. The parabolic rate constants for ZMG232 and SUS430 are similar (ZMG232 is slightly lower) [Horita, 2003b and 2004a], but both are significantly lower than that of Fe20Cr7W [Horita, 2004a]. The higher oxidation rate for Fe20Cr7W is attributed to the absence of a Fe-Mn-rich spinel phase, which is present in the other two alloys. Another important issue for the alloys in carbon-containing atmospheres is carburization. The metallic materials could carburize at the working temperature of 600-800°C. One catastrophic carburization phenomenon is so-called metal dusting, formation of carbides or carbon on the alloy surfaces when exposure in an atmosphere with a high carbon activity. Pits can form on alloy surfaces during metal dusting and lead to deterioration of the alloy. Metal dusting corrosion is likely to occur in high carbon content and low oxygen partial pressure, and

can be essentially prevented by the formation of a dense adherent oxide layer [Zeng, 2004].

Additionally, the oxidation and corrosion behaviour of oxidation-resistant alloys may be different when exposed simultaneously to air at one side and fuel at the other (as with the condition the interconnect experiences during SOFC operation) than when exposed to air and fuel only. Yang et al [2003a and 2004a] observed that the oxidation behaviour of an alloy exposed to wet hydrogen on one side and air on the other (dual atmosphere) was different from that exposed to air on both sides. The scales formed in air on the alloys exposed to a dual atmosphere contained iron-rich spinel or Fe_2O_3 nodules, which were not present in the alloys exposed to air on both sides. The anomalous oxidation on the air side is related to the transport of hydrogen through the alloy and its subsequent presence in the air side scale. The effect of a dual hydrogen-containing atmosphere decreases with the increasing chromium content in the alloy [Yang, 2004a]. However, Kurokawa et al [2004] exposed SUS430 alloy to a dual atmosphere, but did not observe any significant difference in the oxidation behaviour as compared to a sample exposed to air on both sides. Thus, the oxidation and corrosion behaviour of chromia-forming alloys still needs to be studied further, especially under the environments, which simulate closely SOFC operating conditions.

2.3.2 Electrical resistance

One important attribute of metallic interconnect is the electrical conductivity. To function properly as a bipolar plate, the interconnect must offer a low resistance

electrical path in order to minimize electrical losses within the SOFC stack. For oxidation-resistant alloys, the electrical resistance increases with temperature and is the sum of two parts: bulk resistance and scale resistance. The bulk electrical resistance is typically quite low (e.g., $60\text{-}130 \times 10^{-6} \Omega \text{ cm}$ at room temperature) with only slight increase with increasing temperature. Therefore, in the long term, the electrical resistance of the scale dominates the electrical behaviour of oxidation-resistant alloys during SOFC operation.

For a chromia scale, the temperature dependence of the scale conductivity can be expressed by

$$\sigma = \frac{\sigma_0}{T} \exp\left(\frac{-E_{el}}{kT}\right) \quad (2.2)$$

where σ is conductivity ($= 1/\rho$, where ρ is resistivity), E_{el} is the activation energy of electrical conductivity, R is the gas constant, and T is absolute temperature. Holt et al [1994 and 1994a] found that the electrical conductivity of chromia scale is different with the temperature. In high temperature region ($>1000^\circ\text{C}$) chromia is an intrinsic electronic conductor and the activation energy is approximately about 180 kJ/mol. In the low temperature range ($<1000^\circ\text{C}$), the conductivity of chromia scale exhibits extrinsic behaviour and is therefore dependent primarily on impurities, as well as to some extent on oxygen and hydrogen activities. The activation energy of the conductivity is much smaller than that in the high temperature. For a dense specimen, the activation energy for conductivity at near atmosphere oxygen pressure is about 20 KJ/mol [Holt, 1994a; Kofstad, 1996]. The electrical conductivity of chromia scale is

1×10^{-3} - 5×10^{-2} S cm⁻¹ at 800-1000°C [Kofstad, 1996]. The difference of electrical conductivity is probably due to the various impurity levels in the chromia scale, difference in ambient oxygen activities and the lack of equilibration. Thus, the conductivity of Cr₂O₃ can be improved through substitution of various oxides into Cr₂O₃ scale [Huang, 2001].

The electrical resistance of an oxidized metallic interconnect is usually characterized by the area specific resistance (ASR), which normalizes to contact area, but changes as the interlayer thickness changes and thus increases with growth of the oxide scale. The target ASR value for the interconnect material is considered to be below 50 mΩ cm² over tens of thousands of hours of operation [Yang, 2003]. In many studies, the electrical resistance of the oxidized metal is measured through a two-point, four-wire probe approach as shown in Fig.2.2 [Hou, 1999]. A contact current in the order of ten to several hundred mA is introduced and the voltage across the specimen is measured with a multimeter.

Fig.2.2 Schematic configuration for the measurement of area special resistance [Hou, 1999].

Assuming negligible resistance through the bulk alloy, the ASR of an oxidized alloy can be expressed as

$$ASR = 2 \cdot \frac{1}{\sigma} x \quad (2.3)$$

where σ and x are the conductivity and thickness of oxide scale, respectively. The thickness of the oxide scale is determined by equation (2.1), where the parabolic rate constant, K_p , is dependent on the absolute temperature (T) and the activation energy (E_{ox}) for the diffusion of the rate-limiting species, and can be represented by the following expression:

$$K_p = K_0 \exp\left(\frac{-E_{ox}}{kT}\right) \quad (2.4)$$

where k is Boltzman constant. Therefore, equation (2.3) can be expressed as

$$ASR = 2 \frac{\sqrt{K_p t}}{\sigma} = \frac{2\sqrt{K_0 t}}{\sigma_0} T \exp\left(\frac{-1/2E_{ox} + E_{el}}{kT}\right) \quad (2.5)$$

By plotting ASR/T versus $1/T$ on a logarithmic scale, the activation energy term including the contributions of both oxidation and conductivity of the oxide scale can be obtained. Theoretically, if the appropriate material parameters are known, the ASR can be estimated according to the above equation. However, in most cases the scale contains not only chromia but also other oxides and impurities that greatly affect the scale conductivity. Thus the ASR of a given oxidized alloy is normally determined by the experimental measurements.

Liebert et al [1999] measured the electrical resistance of the Ducrolloy

$\text{Cr}_5\text{Fe}_1\text{Y}_2\text{O}_3$ after exposure to air at 1000°C for 75 h. The ASR is several $\Omega\text{ cm}^2$ at 1000°C , much larger than the target value of $50\text{ m}\Omega\text{ cm}^2$. It is also found that the thickness of chromia scale and the increase in scale resistivity with decreasing temperature lead to the prediction that the ASR would be excessively high even at low operating temperatures. The ASR is about $200\text{ }\Omega\text{ cm}^2$ at 500°C , which is unacceptably large for an interconnect material.

The effect of oxidation on the ASR of the nickel-based alloys is shown in Fig.2.3. The change in ASR with oxidation time follows a near parabolic rate law, indicating that the increase in resistance is mainly due to an increase in the scale thickness. Among these alloys, Haynes 230 exhibits the slowest oxidation kinetics, forming an oxide scale that consists predominantly of Cr_2O_3 and $(\text{Cr,Mn})_3\text{O}_4$ spinel. It is, therefore, not surprising that Haynes 230 displays the lowest ASR at 800°C in air [England, 1999]. The significant difference between the resistance of Haynes 230 alloy in air and

Fig.2.3 Area specific resistance (ASR) of nickel-based alloys during oxidation in air and fuel conditions [England, 1999 and 2001; Yang, 2003].

H₂-H₂O atmospheres is also primarily due to difference in the scale thickness [England, 2001]. There are two effects of temperature on the ASR. Because of the higher oxidation rate, the scale is thicker, and thus has a higher electrical resistance after higher temperature exposure. However, the conductivity of the scale increases with temperature, resulting in a decrease in electrical resistance. Thus, the difference between the increase of ASR at 700 and 800°C is smaller than that would be expected simply considering the oxidation reaction rate [Yang, 2003].

The electrical resistances of some ferrite stainless steels during oxidation at 800°C in air are shown in Fig.2.4. It is found that the electrical resistance of iron-based alloy is slightly higher than that of nickel-based alloys, which is due to the higher oxidation resistance of nickel-based alloys. As an example, the ASR of E-Brite (A ferrite stainless steel) is higher than that of Haynes 230 under the same conditions [Yang, 2003]. Meanwhile, the electrical conductivity of Cr₂O₃ formed on the iron-based alloys

Fig.2.4 Area specific resistance (ASR) of iron-based alloys during oxidation in air at 800°C [Abellán, 2001 and 2002; Yang, 2003 and 2004; Quadakkers, 2000].

is usually lower than that of pure chromia. This is explained by the fact that the electrical conductivity of the chromia scale is dominated by impurities, in this case Fe, and essentially exhibits extrinsic behaviour. The addition of oxygen active elements, such as La, Y, Zr, etc, into the iron-based alloys can significantly reduce the oxidation rate and improve the adherence of scale and substrate, leading to much lower ASR. The results in Fig.2.4 also show that increasing the chromium content can reduce the electrical resistance and iron-based alloys with 25-26% chromium are in the target ASR range of below $50 \text{ m}\Omega \text{ cm}^2$. Among the iron-based alloys developed for SOFC interconnect, Crofer22 APU alloy commercialized by ThyssenKrupp VDM, containing ~23% Cr and small amount of Mn, Ti and La, is one of the most promising candidates. The ASR of Crofer22 APU alloy is $9.3 \text{ m}\Omega \text{ cm}^2$ after oxidation in air at 800°C for 500 h and increases slowly to $13 \text{ m}\Omega \text{ cm}^2$ after about 1800 h [Yang, 2004]. However, extrapolation of the measured data indicates that sooner or later the scale growth will lead to an unacceptable high ASR.

So far, many recent conductivity studies on various superalloys and stainless steels indicate that the oxide scale growth, and thus the electrical resistance, of these alloys will reach an unacceptable level in the long term under the SOFC operation conditions. Thus to improve performance in terms of oxide scale electrical conductivity is still a challenge in the development of metallic interconnect materials.

2.3.3 Thermal expansion

The high operating temperature of SOFC requires that the thermal expansion of

the interconnect is matched to that of the ceramic components to avoid thermal stress and thus to improve the stack's thermomechanical stability. As the thermal expansion coefficients (TECs) of the other SOFC components (i.e., anode, electrolyte and cathode) are typically in the range of $10.5\text{-}12.5 \times 10^{-6} \text{ K}^{-1}$ [Minh, 1995], the TEC of the metallic candidates should be close to this value.

Chromium-based alloys have attracted many attentions as interconnect materials. One of the promising properties is that chromium-based alloy have a good TEC matching to the ceramic components. $\text{Cr}_5\text{Fe}_1\text{Y}_2\text{O}_3$ alloy exhibits a TEC at $11.8 \times 10^{-6} \text{ K}^{-1}$ over $20\text{-}1000^\circ\text{C}$ [Quadackers, 1994], which is similar to that of YSZ electrolyte material. In contrast, Nickel-based alloys tend to possess a relatively high TEC, in the range of $14.0\text{-}19.0 \times 10^{-6} \text{ K}^{-1}$ from room temperature to 800°C [Linderoth, 1996; Uehara, 2002]. Thus, nickel-based alloys are not favored as interconnects from a TEC point of view, although nickel-based alloys exhibit high oxidation resistance at high temperatures. Fig.2.5 shows the TECs of some potential iron-based alloys compared with those of typical SOFC components, i.e., cathode (LSM), anode (Ni/YSZ) and electrolyte (YSZ) [Abellán, 2001]. All alloys show slightly larger thermal expansion than YSZ electrolyte. $\text{Fe}_{25}\text{CrMn}$ alloy and 446 alloy have TEC close to that of the anode material, whereas $\text{Fe}_{25}\text{CrMn}(\text{Ti},\text{La})$ alloy has a TEC comparable with that of the cathode and anode ceramics. The commercial ferrite stainless steels exhibit a TEC typically in the range of $12.0\text{-}13.0 \times 10^{-6} \text{ K}^{-1}$ from room temperature to 800°C [Yang, 2003]. Therefore ferrite stainless steels have a better thermal expansion to other components, which is one of the primary advantages of the ferrite stainless steels for

application as interconnects in SOFC stack.

Fig.2.5 Thermal expansion coefficients of some iron-based alloys in comparison with other SOFC components [Abellán, 2001].

2.3.4 Compatibility between metallic interconnect and other components

In addition to the properties discussed above, compatibility with adjacent components is another key property that can dictate the applicability of a heat-resistant alloy as the interconnect in a SOFC stack. To maintain the structural integrity of the stack and minimize its degradation over time, the interconnect must be chemically compatible with other components, which may include electrode and electrolyte materials, sealing glass and contact materials.

Chemical compatibility between the chromia-forming alloys and electrode materials has been studied previously. The main feature of the high-temperature interaction between the chromia-forming alloys and different electrode materials is a

transport of chromium from the alloys into the contact electrodes. However, at the anode side of SOFC, the compatibility problem may be negligible. Previous studies on the compatibility between $\text{Cr}_5\text{Fe}_1\text{Y}_2\text{O}_3$ alloy and NiO/YSZ cermet anode material and subsequent conductivity measurement show no significant reduction in electrical conductivity after exposure at 950°C in H_2 - H_2O atmosphere up to 3000 h [Quadakkers, 1994]. The chromia oxide formed at the interface between alloy and cermet has sufficient electrical conductivity at the service temperatures. No diffusion of Cr from the iron-based alloy to the Ni contact layer material was also found at 800°C in $\text{Ar}/\text{H}_2/\text{H}_2\text{O}$ atmosphere [Teller, 2001], showing the good compatibility between the interconnect and contact material under the fuel conditions.

In contrast, the interaction between the chromia-forming alloys and cathode materials is different in air at high operating temperatures. A significant transport of chromium from the alloys into the cathode material occurs through solid-solid and solid-gas reaction, leading to the formation of new phase such as spinel at the interface. Quadakkers et al [1996] found that when $\text{Cr}_5\text{Fe}_1\text{Y}_2\text{O}_3$ alloy was placed with $(\text{La},\text{Sr})\text{MnO}_3$, LaCoO_3 or $(\text{La},\text{Sr})\text{CoO}_3$ cathode or contact layer, MnCr_2O_4 , CoCr_2O_4 or SrCrO_4 spinel was formed both at the interface and in the ceramic. Similar results were also reported by Huang et al [2000] in their study of electrical conductivity of $\text{Fe}_{26}\text{Cr}_1\text{Mo}$ alloy with different contact materials, including $(\text{La},\text{Sr})\text{CoO}_3$, $(\text{La},\text{Sr})\text{MnO}_3/(\text{La},\text{Sr})(\text{Ga},\text{Mg})\text{O}_3$ composite. After long-term oxidation at 850°C in air, Co/Cr/Fe-rich and Mn/Cr-rich regions containing spinel like CoCr_2O_4 , CoFe_2O_4 or MnCr_2O_4 were found at the interfaces. Across the $(\text{La},\text{Sr})\text{CoO}_3/\text{scale}$ interface, Co, Fe

and Cr interdiffusion distance was as long as 6 μm , while at the (La,Sr)MnO₃/(La,Sr)(Ga,Mg)O₃ composite/scale interface, the interdiffusion distance of Mn and Cr was about 3 μm . The formation of spinel layer may lead to a higher interface contact resistance.

In addition to the electrode materials, the interconnect is also in contact with the sealant. Yang et al [2003] studied the chemical compatibility of a 446 alloy with the seal glass. It was found that the interaction of the glass with the alloy led to the formation of porosity along the alloy/glass interface. The chromia scale dissolved into the sealing glass and formed a new compound, BaCrO₄ at the edge of the interface. Further study showed that the formation of such new compound initiated bond failure between the sealing glass and the scale.

Another major challenge for the chromia-forming alloy interconnect is the evaporation of Cr species from the chromia scale and the poisoning effects of those species on the electrochemical performance of SOFC [Taniguchi, 1995; Badwal, 1997; Matsuzaki, 2001; Jiang, 1999; Fujita, 2004]. At high temperatures, chromia scales are thermodynamically unstable and form vapor species through the following reactions

The volatile Cr species from the chromia scale is strongly dependent on the partial pressures of oxygen and water in the atmospheres. The detailed calculation of the equilibrium gas pressures of the volatile Cr species over Cr_2O_3 can be found in Appendix. The results show that the vapor pressures are much higher in air than in the fuel (the oxygen partial pressure in the SOFC anode gas is in the range between 10^{-11} and 10^{-7} Pa [Hilpert, 1996]). Thus the effect of Cr vapor species on the SOFC anode can be neglected. It is found that the Cr vapor species is dominated by chromium oxyhydroxides in the humid air and the partial pressures increase significantly with the increasing water partial pressures. Assuming a water vapor pressure of 3 kPa (i.e. saturation at room temperature) in air, the most abundant vapor species over Cr_2O_3 are $\text{CrO}_2(\text{OH})_2$, CrO_3 and CrO_2OH . The temperature dependence of the partial pressure of these Cr species is shown in Fig.2.6. Even though the calculation results show that the partial pressures of CrO_3 and CrO_2OH decrease rapidly with decrease of temperature,

Fig.2.6 Partial pressure of most abundant gaseous Cr species over Cr_2O_3 in humid air at different temperatures ($P_{\text{O}_2} = 2.13 \times 10^4$ Pa, $P_{\text{H}_2\text{O}} = 3 \times 10^3$ Pa).

the change in partial pressure of $\text{CrO}_2(\text{OH})_2$ with temperature is relatively small. For instant, the partial pressure of CrO_3 and $\text{CrO}_2(\text{OH})_2$ at 900°C are 1.4×10^{-3} and 9.2×10^{-2} Pa, respectively. The values decrease to 3.4×10^{-7} and 1.0×10^{-2} Pa at 600°C , respectively. Thus a substantial decrease in the Cr vapor species generated from a chromia-forming alloy interconnect is not possible due to a decrease in the operating temperature of SOFC.

Evaporation of Cr species from the chromia-forming alloy is not only dependent on the environmental conditions but also related to the scale compositions. According to the transition results [*Gindorf, 1999 and 2001*], the transportation rate of Cr species from iron-based alloy is much lower than that from the chromium-based alloy, which is due to the formation of Fe-rich oxides on the surface of iron-based alloy. It is found that the formation of $(\text{Cr,Mn})_3\text{O}_4$ spinel top layer in the scale would significantly reduce the vaporization of volatile Cr species. For instance, alloy 446 ($\text{Fe}_{25}\text{CrMn}$) has a twenty times lower chromium transport rate as compared to $\text{Cr}_{50}\text{Fe}_{10}\text{Y}_{20}\text{O}_3$ alloy at 850°C [*Gindorf, 2001*].

Chromium-containing vapor species formed over the metallic interconnect can be electrochemically or chemically reduced at the electrode surface or electrode/electrolyte interface. The resulting deposition can block the electrode active sites and rapidly degrade the cell performance. As mentioned above, the vapor pressures are much higher in air so such poisoning is most likely to take place at the cathode. This degradation can be represented by a decrease in cell voltage or an increase in the cathode overpotential. Taniguchi et al [*1995*] performed a systematic

series of experiments to demonstrate that the degradation was due to the chromium species. In these experiments, platinum wire was used for the current collectors, but materials with different chromia activities were placed in contact with the electrode. The results (see Fig.2.7) show that there is no degradation when no chromium source is present. The magnitude of the decrease in cell voltage increases from LaCrO_3 to Inconel 600 alloy to Cr_2O_3 , which follows the increase in Cr_2O_3 activity. The results also showed that, in accordance with the trend in vapor pressures, the amount of degradation decreases with decreasing oxygen partial pressure. Rapid performance degradation of a cell was also observed by Badwal et al [1997] when using a chromium-based alloy as the interconnect material, which is attributed to the significant deposition of Cr_2O_3 and $(\text{Cr,Mn})_3\text{O}_4$ spinel at the $(\text{La,Sr})\text{MnO}_3$ cathode/YSZ electrode interface. The proposed mechanisms for chromium deposition are reviewed in the next section.

Fig.2.7 Degradation in cell performance in the presence of chromium-containing material [Taniguchi, 1995] or with a Ducrolloy $\text{Cr}_5\text{Fe}_1\text{Y}_2\text{O}_8$ [Badwal, 1997].

2.3.5 Protective coatings for metallic interconnect

In order to reduce the rate of scale growth on the surfaces of chromia-forming alloys, as well as prevent the chromium vaporization from the chromia scale at the cathode side, an effective protective coating on the alloy has been suggested and currently is being extensively investigated. To qualify as a viable coating material, it should possess some essential attributes:

- Chemical compatibility and stability with substrate, contact layer and electrodes,
- Thermodynamic stability in both oxidizing and reducing atmosphere over the applied temperature range,
- Resistance to solid-state transport of Cr,
- High electrical conductivity,
- Thermal expansion coefficient matched to the substrate.

Several protective coatings have been developed to improve the oxidation resistance and electrical conductivity of chromia-forming alloy in the past few years. Examples of protective coating developed include rare earth oxides such as Y_2O_3 , CeO_2 [Huang, 2001; Qu, 2004], perovskite materials $(\text{La}(\text{Ni},\text{Fe})\text{O}_3$ [Basu, 2003], $(\text{La},\text{Sr}/\text{Ca})\text{CrO}_3$ [Gindorf, 2000; Yoo, 2001, Johnson, 2004; Zhu, 2004], $(\text{La},\text{Sr})\text{MnO}_3$ [Batawi, 1996; Honegger, 2001], $(\text{La},\text{Sr})\text{CoO}_3$ [Brylewski, 2001; Yoo, 2001], $(\text{Y},\text{Ca})\text{MnO}_3$ [Batawi, 1999]), spinel oxides such as $(\text{Mn},\text{Co})_3\text{O}_4$ [Larring, 2000; Chen, 2004], $(\text{Mn},\text{Cr})_3\text{O}_4$ [Chen, 2004], and conductive oxides (NiO [Huang, 2001], Co_3O_4 [Burriel, 2005], CrN/AlN [Gannon, 2004]). The protective coatings are prepared

through different approaches, such as vacuum plasma spraying [Urbanek, 1996], spray-pyrolysis [Brylewski, 2001], thermal spraying [Batawi, 1996], slurry dipping [Huang, 2001], electron-beam physical vapor deposition [Oishi, 1999], screen-printing [Brylewski, 2003], electrophoretic deposition [Yoo, 2001] or magnetron sputtering [Johnson, 2004]. Nevertheless, the fabrication of protective coating increases the cost of metallic interconnect.

It is well known that the addition of active elements, such as Y, Zr, Ce and La, into the chromia-forming alloys can greatly reduce the oxidation rate and increase the scale adhesion at high temperature. Thus a few attempts have been made to add the active elements or their oxides to the alloys as protective coatings. The coatings typically reduce the oxide scale growth rate, and thus the scale thickness [Oishi, 1999; Huang, 2001; Qu, 2004], but can also reduce the ASR by decreasing the resistivity of the scale. For example, the activation energy for conduction of the scale formed on a La-coated alloy is different from that formed on the uncoated alloy, indicating that the conduction mechanism has been changes, presumably due to doping of the scale [Oishi, 1999]. The electrical conductivity of the scale on the chromia-forming alloy can be improved by doping with NiO [Huang, 2001], but NiO coating has little effect on the oxidation resistance of the alloy and an appreciable scale spallation. However, Huang et al [2001] suggested that double coating of $\text{Y}_2\text{O}_3/\text{NiO}$ with low NiO level can achieve a dense, strong scale with an improved conductivity.

Currently, the most favored protective coating materials for metallic interconnect are the perovskite oxides, especially $(\text{La,Sr})\text{MnO}_3$ and $(\text{La,Sr})\text{CrO}_3$ ceramic, which are

traditionally used as cathode and interconnect compositions in SOFC. This is mainly due to their proved good high-temperature electrical conductivity, comparative thermal expansion and chemical compatibility with the chromia-forming alloys. Perovskite oxide coatings have demonstrated promising results in not only improving the surface stability of chromia-forming alloys [Quadakkers, 1996; Batawi, 1999], but also helping to decrease or even prevent the evaporation of chromium species from the scale [Gindorf, 2001]. For example, Cr₅Fe₁Y₂O₃ alloy which are thermally spray coated with HEXIS La_{0.8}Sr_{0.2}MnO₃ can maintain the cell performance for more than 1,000h [Batawi, 1996]. The dense coating hinders transport of chromium species, both in the solid and gaseous phases, eliminating any performance degradation that is caused by the deposition of chromium species at the cathode. Results by Quadakkers et al [1996] also indicate that La_{0.84}Sr_{0.16}MnO₃ coating on MA-956 (a FeCrAlY alloy) by plasma spraying can reduce the contact resistance by roughly three orders of magnitude, implying that the LSM coating is very effective in slowing down the oxidation rate of the alloy. Yoo et al [2001] studied the effect of different perovskite material coatings on the oxidation behaviour of an iron-based alloy. The coatings were prepared by electrophoretic deposition. As shown in Fig.2.8, La_{0.8}Sr_{0.2}MnO₃ and La_{0.8}Sr_{0.2}CrO₃ coatings definitely decrease the oxidation rate, leading to a low area specific resistance. In contrast, the coatings of La_{0.5}Sr_{0.5}CoO₃ and La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O₃ obtain a higher weight gain during exposure in air, which is most likely due to the formation of thicker interfacial oxide scales. However, it is also found that the (La,Sr)CoO₃ perovskite coating can lead to a low electrical resistance [Yoo,

Fig.2.8 Oxidation behaviour of a Fe-based alloy uncoated or coated with various perovskite oxides at 850°C in air [Yoo, 2001].

2001; Breyleski, 2001].

(La,Sr)CrO₃ is another favored perovskite oxide as coating material for chromia-forming alloy interconnect. (La,Sr)CrO₃ has been widely used as ceramic interconnect in high-temperature SOFC stack due to its high electrical conductivity and stability in both fuel and oxidant atmospheres [Minh, 1995]. Coating of (La,Sr)CrO₃ material significantly decreases the oxidation rate of chromia-forming alloys and reduces the chromium evaporation from the scale. Gindorf et al [2000] compared the chromium vaporization rates from uncoated and La_{0.9}Sr_{0.1}CrO₃-coated Cr₅Fe₁Y₂O₃ alloys by transpiration experiments. The 25-30 μm thick coatings were prepared by vacuum plasma spraying (VPS) technique. The transpiration results indicate a 95% reduction of the chromium evaporation from the coated Cr₅Fe₁Y₂O₃ alloy as compared to the uncoated sample.

Another alternative coating materials are the spinel oxides. Larring et al [2000] reported that a $(\text{Mn},\text{Co})_3\text{O}_4$ spinel can reduce the Cr interdiffusion significantly between a $\text{Cr}_5\text{Fe}_1\text{Y}_2\text{O}_3$ alloy and a contacting $(\text{La},\text{Sr})\text{MnO}_3/(\text{La},\text{Sr})\text{CoO}_3$ mixing perovskite coating when it was introduced as an interlayer, also leading to an ASR of the alloy/ceramic interface of only $24 \text{ m}\Omega \text{ cm}^2$ after 10,000 h at 950°C in air. This is mainly attributed to the high electrical conductivity of $(\text{Mn},\text{Co})_3\text{O}_4$ spinel. Recent studies by Chen et al [2004] and Yang et al [2005] also show that the $(\text{Mn},\text{Co})_3\text{O}_4$ coating are well bonded to the alloy substrates and can significantly reduce the oxidation rate of the alloys. The thermal expansion coefficient of $(\text{Mn},\text{Co})_3\text{O}_4$ spinel is in the range of $11.4\text{-}12.6 \times 10^{-6} \text{ K}^{-1}$, which leads to good thermal stability between the spinel protective layer and the ferrite stainless steels. A low ASR of $11 \text{ m}\Omega \text{ cm}^2$ was also detected by Yang et al [2005] on the $(\text{Mn},\text{Co})_3\text{O}_4$ -coated Crofer22 APU alloy after exposure at 800°C for 1000 h in air.

The protective coatings may help to lower the oxidation rate and to improve the contact resistance of the chromia-forming alloy interconnects, but it should be noted that the cell performance may still be deteriorated by the chromium species migrating from either the chromium-containing perovskite (e.g., $(\text{La},\text{Sr})\text{CrO}_3$) or non-chromium-containing compositions via potential chromium cation diffusion through the coatings [Hilpert, 1996; Larring, 2000]. Other challenges associated with coatings include cost and reliability, especially during the long-term operation.

2.4 Deposition mechanism of chromium species

As mentioned earlier, without effective protective coatings, the volatile Cr species from the chromia-forming alloy interconnect can cause rapid degradation of the cell performance. As the vapor pressure of volatile Cr species at the anode side of SOFC is too small to cause any problem, the deterioration mainly occurs at the cathode. The performance degradation leads to a higher overpotential for the O_2 reduction reaction at the cathode. Previous works have focused on the cathode material of $(La,Sr)MnO_3$ (LSM). It is found that the gaseous Cr species cause a rapid degradation of LSM cathode performance with significant deposition of solid Cr species (e.g., Cr_2O_3 and $(Cr,Mn)_3O_4$) at the LSM cathode/YSZ electrolyte interface regions [Taniguchi, 1995; Badwal, 1997]. The increase in cathodic polarization is found to relate to the amount of Cr at the cathode/electrolyte interface [Taniguchi, 1995]. It is, therefore, of great scientific importance to understand the transportation and deposition process of Cr species at the cathode. However, despite the potential application of chromia-forming alloys as interconnect materials in SOFC, the mechanism and kinetics of deposition process of Cr species are far from clear.

One of the proposed mechanisms for chromium deposition is the electrochemical reduction of high valent vapor species in competition with the O_2 reduction reaction, followed by the chemical reaction with LSM material to form $(Cr,Mn)_3O_4$ phases at the three phase boundary (TPB) regions [Hilpert, 1996; Taniguchi, 1995; Badwal, 1997; Matsuzaki, 2001; Fujita, 2004; Paulson, 2004]. The electrochemical deposition

mechanism is largely based on the thermodynamics compatibility of the negative Gibbs energy changes for electrochemical reduction reactions of O₂ and of high valent Cr species, according to the following cathodic reactions [Hilpert, 1996]

The result of such reactions is the precipitation of Cr₂O₃(s) phase at the cathode/electrolyte interface regions. Furthermore, the formation of Cr₂O₃(s) can react with LSM to form the spinel phase by the following chemical reaction

According to the electrochemical deposition mechanism, the formation of chromium oxide and/or spinel phase takes place at the three phase boundary areas, where is the active sites for the normal O₂ reduction reaction. Thus, the solid Cr deposits would block the active sites as well as pores in the electrode, substantially reducing the three phase boundary areas for the O₂ reduction reaction and leading to the increase of cathodic polarization. In addition, the modification of the electrode phase near the cathode/electrolyte interface, by the presence of solid Cr species or changes in the chemical composition at the surface of LSM particles could also modify the oxygen adsorption/surface diffusion kinetics at the cathode for O₂ reduction reaction, resulting in electrochemical performance degradation [Badwal, 1997]. By electrochemical impedance spectroscopy (EIS), Matsuzaki et al [2000] found that the

Cr_2O_3 deposition at the LSM cathode/YSZ electrolyte interface caused an increase in both diffusion and charge-transfer resistance for O_2 reduction reaction. The electrochemical deposition mechanism appears to explain the observed correlation between the intensity of Cr species deposited at the electrode/electrolyte interface regions and the performance degradation for the O_2 reduction reaction on the LSM electrode [Taniguchi, 1995].

However, thermodynamically deposition of Cr species can take place either by electrochemical reduction and/or chemical dissociation [Hilpert, 1996]. Jiang et al [1999, 2000 and 2001] recently provided evidences that the deposition reaction of Cr species is not electrochemical reduction of high valent Cr vapor species to Cr_2O_3 in competition with O_2 reduction reaction. They observed that the deposition of Cr species on the TZ3Y electrolyte surface took place under both anodic and cathodic polarization potentials. Fig.2.9 shows the scanning electron micrographs of the exposed TZ3Y electrolyte surface after the LSM electrode was cathodic polarized at 200 mA cm^{-2} and 900°C for 50 h and anodic polarized for 6 h in contact with chromia-forming alloy, respectively [Jiang, 2000]. Under cathodic polarization, on the electrolyte surface between the LSM particles, there were fine grains and relative large crystals of Cr species deposition. While after anodic polarization for 6 h, the TZ3Y electrolyte surface was completely covered by the fine Cr species deposits. This indicates that the deposition of Cr species is not dominated by the electrochemical reduction of high valent Cr species. Most importantly, their experimental results show that under cathodic polarization potential, the deposition of Cr species occurs not only

Fig.2.9 SEM micrographs of exposed TZ3Y electrolyte surface in contact with LSM electrode after (a) cathodic polarization of 200 mA cm^{-2} and 900°C for 50 h and (b) anodic polarization for 6 h in the presence of chromia-forming alloy [Jiang, 2000].

on the areas close to the LSM/electrolyte interface, but also on the whole electrolyte surface between the LSM particles. The deposition of Cr species beyond the electrode/electrolyte interface region is also indicated by the formation of Cr deposit rings on the TZ3Y electrolyte surface around the edge of the LSM electrode. The ring was ca. $60 \mu\text{m}$ for the electrode polarized at 200 mA cm^{-2} and 900°C for 50 h. The deposition ring is substantially wider than the width of the LSM-YSZ-air TPB region for the O_2 reduction on the LSM electrode, which is estimated to be less than $1 \mu\text{m}$ [Horita, 2002; van Heuven, 1997]. The deposition occurs preferentially on the zirconia electrolyte surface, where electrons would not be available for an electrochemical reaction. The characteristics of the Cr deposition are also affected by the air flow [Jiang, 2001]. Without air flow, deposition of Cr species on the electrolyte surface under the rib of the chromia-forming alloy interconnect was substantially higher than that under the channel of the interconnect. In addition, the deposition of Cr species

took place on the electrolyte surface in the absence of polarization potential when the LSM electrode was heated at 1100°C but not at 900°C.

Based on the experimental results, Jiang et al [1999 and 2000] proposed that the deposition of Cr species at the LSM electrode is essentially a chemical dissociation process on re-deposition. The reaction is controlled by the nucleation reaction between the nucleation agent and the gaseous Cr species. In the LSM/YSZ system, the nucleation agent is the Mn species particularly Mn^{2+} ions generated under cathodic polarization potential or high temperature. Mn^{2+} ions generated from the LSM electrode are driven to the TZ3Y electrolyte surface. The nucleation reaction between the gases Cr species and Mn species takes place when Mn^{2+} ions are in the transition state from the electrode surface into the electrolyte bulk, forming Cr-Mn-O nuclei and creating nucleation sites for the crystallization and growth of Cr_2O_3 and $(\text{Cr,Mn})_3\text{O}_4$ phases. The deposition processes of Cr species under cathodic polarization potential are proposed as followings [Jiang, 2000]:

This mechanism shows that the deposition of Cr species is strongly driven by the nucleation reaction between nucleation agent and gaseous Cr species, indicating that the deposition process is dependent on the electrode and electrolyte materials. This is

also supported by the observation that no Cr deposition occurred at the Pt electrode with a chromia-forming alloy under the same cathodic polarization conditions [Jiang, 2002] and the effect of changing of the electrolyte and electrode materials on the Cr deposition [Mazusaki, 2001].

2.5 Summary

Interconnect materials play a crucial role in the fabrication of SOFC stack and enable it to be a viable high temperature fuel cell technology. The use of metallic interconnects instead of ceramic one offers many advantages in terms of stability, electrical conductivity, thermal conductivity, easy manufacture and low cost.

The most promising interconnect candidates are the chromia-forming alloys. However, the high growth rate and easy volatilization are the two drawbacks of chromia scale. Using dense protective coatings can substantially reduce the Cr evaporation. Without effective protective coatings, the volatile Cr species can cause rapid performance degradation of cathode for the O₂ reduction reaction. The performance degradation of the electrode is considered to relate to the deposition of Cr species at the electrode and electrolyte interface regions. Two different deposition mechanisms exist in the literature. The deposition of Cr species at the LSM cathode/YSZ electrolyte cell is caused by an electrochemical reaction of gaseous Cr species in competition with O₂ reduction reaction or by a chemical reaction between nucleation agent and gaseous Cr species.

Although many efforts have been made to use the chromia-forming alloy

interconnects in SOFC, the interaction and compatibility between the chromia-forming alloy and different SOFC electrodes are still far from clear. Thus, it is critical to systematically investigate the interaction between the metallic interconnect and the electrodes under different conditions and the effect on the electrochemical performance of SOFC.

CHAPTER 3.

EXPERIMENTAL PROCEDURES

In this chapter, general descriptions of the sample preparation, the electrochemical testing set-ups, the electrochemical measurement techniques and the materials characterization techniques are given.

3.1 Sample preparation

3.1.1 Raw materials

(1) Metallic interconnect materials

The metallic interconnect materials used in this study are three types of commercial chromium-containing alloys, ferrite stainless steel, RA446 alloy and Ni-based superalloy, RA600 (Rolled Alloy Co., Canada) and Crofer22 APU (ThyssenKrupp VDM, Germany). The chemical composition of the materials is listed in Table 3.1.

Table 3.1 Chemical compositions of commercial alloys.

wt%	Fe	Cr	Ni	Mn	Si	C	Ti	La	Cu
RA446	Bal.	23-27	-	0.7	0.5	0.05	-	-	-
RA600	8	15.5	76	0.1	0.2	0.08	-	-	-
Crofer22 APU	Bal.	23	-	0.8	0.5	0.03	0.08	0.06	0.5

The alloys for the oxidation experiments were cut to rectangular shape with dimension of 20×10×7 mm (width×length×height) and were ground with sand paper of 1000-grit. After being polished with 3 μm diamond paste, the samples were ultrasonically cleaned with de-ionized water and acetone. The oxidation behaviour of the alloys was studied at 900°C in static air for 100 h or 500 h.

For the electrochemical study, the alloys were machined into coupons (12×12×4mm) with channels (1.2×1.2mm) cut on one side and holes in the center of each channel. Air was directed to the electrode coating surface through the channels by an alumina tube, simulating the air flow situation in the flat-plate SOFC. The samples were also ground with 1000-grit sand paper and cleaned in acetone. Fig.3.1 shows the interconnect design used in the electrochemical testing.

Fig.3.1 Metallic interconnect design.

(2) Electrode materials

The electrode materials used are $(\text{La}_{0.8}\text{Sr}_{0.2})_{0.9}\text{MnO}_3$ (LSM) powder with A-site nonstoichiometry and $(\text{La}_{0.6}\text{Sr}_{0.4})(\text{Co}_{0.2}\text{Fe}_{0.8})\text{O}_3$ (LSCF) powder. The LSCF powder (99.9% purity) was commercial product from Nextech Materials, USA.

There were two sources of A-site nonstoichiometric LSM material in this project. The A-site deficient LSM composition was chosen in order to avoid the formation of resistive phase formation at the LSM electrode/YSZ electrolyte interface [Mitterdorfer, 1998]. Without specification, the LSM ink was obtained from Ceramic Fuel Cell Limited, Australia, which was prepared by co-precipitation, followed by calcination at 1000°C in air [Jiang, 2000b].

In this project, LSM powder was also synthesized using a high-temperature solid-state reaction method. The raw materials were La_2O_3 (99%, Merck, USA), SrCO_3 (99%, Merck, USA) and MnCO_3 (99%, Merck, USA). The La_2O_3 powder was precalcined at 1000°C for 10 h to prevent the formation of $\text{La}(\text{OH})_3$ phase. Then required amount of La_2O_3 , SrCO_3 and MnCO_3 powders were thoroughly mixed in isopropanol and a plastic rolling bottle. Obtained powders were calcined for 30 h at different temperatures of 800°C, 900°C and 1000°C. After calcination, the powders were ground in a mortar with a pestle, then wet milled in a zirconia jar with isopropanol for 10 h. X-ray diffraction (XRD) patterns of the powders calcined at 900°C and 1000°C confirmed the single phase structure of perovskite, as shown in Fig.3.2. Thus the LSM powder calcined at 900°C was used in the later studies (Chapter 5 and Chapter 8).

Fig.3.2 XRD patterns of LSM powders calcined at 800°C, 900°C and 1000°C, respectively.

(3) Electrolyte materials

The electrolyte material for the LSM-based cathodes was 8 mol% Y₂O₃ stabilized ZrO₂ (YSZ) powder which was commercial product supplied by Tosoh Corporation, Japan.

To avoid the chemical reaction between LSCF cathode and zirconia electrolyte [Chen, 1993], gadolinium-doped ceria (Ce_{0.8}Gd_{0.2}O₂, GDC) electrolyte was used for the LSCF cathode. The GDC electrolyte disks were prepared by solid-state reaction synthesis from high purity CeO₂ (99.9%, Praxair Specialty Ceramics, USA) and Gd₂O₃ (99.9%, Praxair Specialty Ceramics, USA). The mixed oxides were ball milled in ethanol with YSZ medium for 20 h. After drying the mixture was pressed into disks at a pressure of 50 MPa and sintered at 1600°C for 6 h in air. The sintered electrolyte thickness and diameter were about 1 mm and 21 mm, respectively. The relative density of GDC disks after sintering was 94.7±0.9%.

3.1.2 Preparation of testing cells

(1) LSM electrode/YSZ electrolyte cell

For the electrochemical investigation, three-electrode cells were prepared in this project. The three electrodes are working electrode, which is the electrode under investigation, counter electrode and reference electrode. A standard preparation procedure of the LSM electrode/YSZ electrolyte testing cell in this project is shown in Fig 3.3a. Similar process was carried out to prepare other types of cells. The electrolyte disks were prepared from YSZ powder with ~1.5 wt% polyvinyl-butyril (PVB) binder

Fig.3.3 (a) Preparation procedure of a LSM/YSZ testing cell and (b) an example of sintered testing cell.

by dry die pressing at a pressure of 50 MPa, following by sintering at 1550°C in air for 4 h. The electrolyte thickness and diameter after sintering were about 1 mm and 19 mm, respectively. The relative density of YSZ disks after sintering was $96.5 \pm 1.2\%$. Pt paste (Ferro Corporation, USA) was painted on one side of the YSZ electrolyte disk to serve 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 Pt counter and reference electrodes were sintered at 1100°C for 1 h. The distance between the counter electrode and the ring reference electrode was ~ 4 mm.

LSM electrode ink was prepared by thoroughly mixing the LSM powder with polyethylene glycol (99%, Merck, USA) in a mortar in a ratio of 70 wt% LSM and 30 wt% polyethylene glycol. The LSM ink was then applied to the other side of the YSZ electrolyte disk by screen-printing, following by sintering at 1150°C for 2 h in air. The electrode thickness was ~ 20 μm and the electrode area was 0.5 cm^2 . Fig 3.3b shows an example of LSM electrode/YSZ electrolyte testing cell prepared.

(2) LSCF electrode/GDC electrolyte cell

LSCF electrode ink was prepared by mixing the $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ powder and polyethylene glycol and then applied to the GDC electrolyte substrate by screen-printing. The LSCF coating was sintered at 1000°C in air for 2 h. After sintering, the electrode thickness was ~ 20 μm and the electrode area was 0.5 cm^2 .

(3) LSM/YSZ composite electrode/YSZ electrolyte cell

LSM/YSZ composite electrodes with compositions of LSM (90 wt%)/YSZ (10 wt%) (LSM-10YSZ), LSM (70 wt%)/YSZ (30 wt%) (LSM-30YSZ) and LSM (50 wt%)/YSZ (50 wt%) (LSM-50YSZ) were studied in this project. The composites were prepared by mixing the required amount of LSM and YSZ powders in a rolling bottle and isopropanol for 20 h. The electrode ink was then prepared by mixing the powders with polyethylene glycol and applied to YSZ electrolyte by screen-printing, followed by sintering at 1150°C for 2 h in air. The electrode thickness was ~30 μm and the electrode area was 0.5 cm^2 .

(4) GDC-impregnated LSM electrode/YSZ electrolyte cell

To prepare the GDC-impregnated LSM electrode, $\text{Gd}_{0.2}\text{Ce}_{0.8}(\text{NO}_3)_x$ nitrate solution was made from $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.9%, Aldrich Chemical) and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.9%, Aldrich Chemical) and the metal ion concentration was 3 M. A dropper was used to deposit the solution on the top surface of the sintered LSM electrode and the solution was allowed to penetrate into the porous electrode. The surface of the electrode coating was wiped with a soft tissue and dried in open air. The electrode after impregnation was fired at 850°C for 1 h to decompose $\text{Gd}_{0.2}\text{Ce}_{0.8}(\text{NO}_3)_x$ nitrate solution, forming $(\text{Gd,Ce})\text{O}_2$ oxide phase. The loading of the impregnated oxide was estimated from the weight difference of the electrode before and after the impregnation treatment. A LSM electrode impregnated with GDC of 1.6 mg cm^{-2} was used in this project.

3.1.3 Preparation of oxide coatings on RA446 alloy

The chemical reactions between the chromia-forming alloy, RA446, and the constituent oxide coatings of LSM material were investigated in this project. The oxides investigated were LSM, La_2O_3 , SrO and Mn_2O_3 . La_2O_3 (99%, Merck) was precalcined at 1000°C for 10 h to prevent the formation of $\text{La}(\text{OH})_3$ phase. SrO and Mn_2O_3 powders were prepared by the decomposition of SrCO_3 (99%, Merck) and MnCO_3 (99%, Merck) at 1150°C and 950°C, respectively. The phases of the oxides were confirmed by the XRD analysis.

The oxide paste was prepared by mixing the oxide powder and 10 wt% polyethylene glycol in a mortar with a pestle. The oxide coatings were deposited on the polished surfaces of RA446 alloy substrate by slurry coating. The thickness of the coatings was about 30-50 μm . All oxide-coated alloy samples were heated in open air at 900°C and/or 800°C for up to 500 h.

3.2 Electrochemical characterization

3.2.1 Testing cell configuration

There were two kinds of separate testing cell configurations for the electrochemical measurements, which were corresponding to the test in the absence of the metallic interconnect and that in the presence of the metallic interconnect, respectively, as shown in Fig 3.4 and Fig 3.5. A three-electrode four-wire testing set-up was used in both arrangements. The three-electrode testing cell can be measured at

Fig.3.4 Testing cell configuration in the absence of metallic interconnect.

Fig.3.5 Testing cell configuration in the presence of metallic interconnect.

open circuit potential (OCP) and under polarization potential conditions. Three electrodes are working electrode (WE), counter electrode (CE) and reference electrode (RE). The counter electrode is on the opposite side of the working electrode, and the area of CE is just the same with that of a WE, a so-called symmetrical arrangement. Current was passed through the working electrode and the counter electrode, while the potential difference between the reference electrode and the working electrode was measured using a separate Pt wire as voltage probe (four-wire set-up). The overpotential at the working electrode was determined as the measured potential difference between reference and working electrode minus the voltage drop related to ohmic resistance of the electrolyte.

The testing cell was positioned inside the furnace with the working electrode exposed in controlled flow of air while the counter and reference electrodes exposed in static air. The air flow rate was controlled at 100 ml min^{-1} . In some cases, the cell was sealed with ceramic paste and balanced O_2/N_2 was introduced to working electrode, to achieve desired oxygen partial pressures. For the measurements in the absence of metallic interconnect, Pt mesh was used as the current collector for both working and counter electrodes. While for the measurements in the presence of metallic interconnect, the metallic interconnect was directly in contact with the working electrode. Two Pt wires were spot-welded to the sides of the metallic interconnect to serve as voltage and current probes, respectively. There was no extra Pt mesh placed between the metallic interconnect and the electrode coating. In this arrangement, the metallic interconnect also acted as a current collector for the working electrode. Pt

mesh was used as current collector for the counter electrode. Two separate sample holders were used to avoid the Cr contamination.

3.2.2 Electrochemical impedance spectroscopy

(1) Principle

Electrochemical impedance spectroscopy (EIS) is a powerful technique for the electrochemical characterization of a wide range of electrochemical systems and determining the contribution of individual electrode or electrolyte processes [Jiang, 1997]. The EIS technique generally 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 angular frequency. Also for a linear system, the magnitude of the response is directly related to the electrical stimulus for any given frequency. Hence, 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 , but 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. 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 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 the imaginary unit, Z_R and Z_I are the real and imaginary of impedance. The impedance is often plotted in the complex plane with minus the imaginary part along the ordinate axis and the real part along the axis of abscissas (a so-called Nyquist plot).

For a simple impedance circuit such as a capacitor in parallel with 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 and high frequency intercepts of the semicircle on the real axis gives the value of the resistor. The value of the capacitor and the time constant of the circle can be calculated from the frequency (F_0) at the top of the semicircle ($\omega_0 = 2\pi F_0 = 1/\tau = 1/RC$). However, 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 and which gives rise to a perfect semicircle arc 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 semicircle arcs with their origin on the real axis, but instead consist of depressed arcs. These arcs can often be skewed on the low or the high frequency end of the impedance spectrum. This type of behaviour often indicates heterogeneity in the system and distribution of

time constants, and can be simulated by including constant-phase elements, Q , instead of pure capacitors in the equivalent circuit.

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 to interpret the impedance data. Fig.3.6 shows an example of impedance spectrum and its equivalent circuit of a LSM electrode/YSZ electrolyte system for O_2 reduction reaction.

Fig.3.6 Fitting of the impedance spectrum of LSM electrode for O_2 reduction reaction at 800°C in air: (a) experimental data and the fitting curves and (b) the responsible equivalent circuit. In the equivalent circuit, L is inductance, R_Ω is the ohmic resistance between cathode and reference electrode, R_H , R_L and Q_H , Q_L are the polarization resistances and constant phase elements (or CPE) for the high- and low-frequency arcs, respectively.

(2) EIS measurements

Impedance spectroscopy measurements in this project were performed using a Solartron 1260 frequency response analyzer in combination with a Solartron 1287 electrochemical interface (Solartron Analytical, England). Generally, a frequency range of 0.1 Hz to 100K Hz and the signal amplitude of 10 mV were used in this study. The measured spectra were analyzed by equivalent circuit method using commercial software, Zview, developed by Scribner Associates, Inc. The electrode interface (polarization) resistance (R_E) and the electrode ohmic resistance (R_Ω) were obtained from the fitted results.

3.2.3 Polarization

The polarization behaviour of the electrodes for the O_2 reduction reaction in this project was generally carried out under a constant current density of 200 mA cm^{-2} in air at the temperature range of $700\text{-}900^\circ\text{C}$. The polarization potential (E_{Cathode}) of the cathode was measured against the Pt air reference electrode. The cathodic current passage was interrupted from time to time to make the EIS measurements. The overpotential (η) can be obtained from E_{Cathode} and R_Ω by the following equation

$$\eta = E_{\text{Cathode}} - jR_\Omega \quad (3.4)$$

where j is the current density.

3.3 Material characterization

3.3.1 X-ray diffraction (XRD)

X-ray diffraction (XRD) was carried out on a Philips PW 1830 XRD system (Netherlands) using $\text{CuK}\alpha$ radiation to study the phase composition of the specimens before and after oxidation experiments. XRD was also carried out on the raw materials and the sintered SOFC components to determine the compositions and crystal structures, and to check the phase change of the SOFC components before and after the electrochemical testing. X-ray scans were run over a 2θ range of $10\text{-}90^\circ$ at a scan rate of $0.02^\circ/\text{sec}$, and plots of X-ray intensity against 2θ were obtained.

3.3.2 Scanning electron microscope (SEM)

A Leica S360 (Cambridge, USA) scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectroscopy (EDS, Oxford, UK) was used to study the morphology of the SOFC components before and after electrochemical measurements and the distribution of the Cr species deposits. In order to examine the electrolyte surface in contact with the electrode coating, the electrode coating was removed by 20% HCl acid treatment in an ultrasonic bath at room temperature, followed by washing with de-ionized water. It was found that acid treatment by 20% HCl solution mainly removed the LSM or LSCF coating and majority of the Cr species deposits were still intact on the electrolyte surface after the 20% HCl acid treatment. In some cases, the LSM coating was carefully removed by a doctor blade. Chemical

compositions of the samples were quantitatively determined by EDS using point microanalysis or mapping. The samples for EDS mapping examination were embedded with epoxy, ground and polished to mirror finish before the examination. The samples were coated with Pt or Au before SEM examination.

SEM and EDS were also carried out to examine the morphology and elemental distribution of the oxide scales and oxide coatings on the metallic interconnects. The samples were also embedded with epoxy prior to grinding and polishing.

CHAPTER 4.

INTERACTION BETWEEN Fe-Cr ALLOY AND (La,Sr)MnO₃ CATHODE

In this chapter, the Cr deposition processes at (La,Sr)MnO₃ LSM electrode were studied at different temperatures and special attention was paid to the early stage of the reaction. The results again proof that the Cr species is basically deposited through the chemical dissociation under SOFC operation conditions.

4.1 Experimental

The chromia-forming alloy interconnect was a commercial Fe-Cr alloy RA446. The details of fabrication of LSM electrode/YSZ electrolyte testing cell and the cell arrangement for the electrochemical measurements can be found in Chapter 3. The polarization behaviour of LSM electrode was carried out under a constant cathodic current of 200 mA cm⁻² in air at 700°C, 800°C and 900°C, respectively. The polarization potential (E_{Cathode}) was measured against the Pt air reference electrode. The current passage was interrupted from time to time to make the electrochemical impedance spectroscopy (EIS) measurements. A Solartron 1260 frequency response analyzer in combine with a 1287 electrochemical interface was used for EIS measurement, with the frequency range of 0.1 Hz to 100 kHz and the signal amplitude of 10 mV. EIS curves were measured at open circuit.

SEM and EDS were used to examine the LSM electrode morphology and the elemental distribution of the deposits. In order to examine the YSZ electrolyte surface in contact with the LSM electrode coating, the LSM coating was removed by 20% HCl acid treatment, followed by washing with de-ionized water. In some cases, the LSM electrode coating was removed carefully by a doctor blade.

4.2 Results

4.2.1 Electrode behaviour of LSM electrode in the absence of chromia-forming alloy interconnect

For comparison, the initial electrode behaviour of a freshly prepared LSM electrode for the O_2 reduction reaction was firstly examined in the absence of chromia-forming alloy. Fig.4.1 shows the initial impedance and polarization responses of a LSM electrode under a cathodic current density of 200 mA cm^{-2} at 900°C in air in the absence of chromia-forming alloy. Before the cathodic current passage, the initial impedance response was characterized by a large and depressed arc and the initial electrode resistance (R_E) was $2.11 \Omega \text{ cm}^2$. However, the impedance curves reduced significantly with the current passage. After cathodic current passage treatment for 120 min, R_E was reduced to $0.82 \Omega \text{ cm}^2$, much smaller than the initial R_E value. The electrode impedance curve was no longer able to recover to the original size before the current passage.

The time behaviour of the cathodic polarization (E_{Cathode}) can be characterized by two distinct potential regions, as shown in Fig.4.1b. E_{Cathode} decreased very quickly

Fig.4.1 Initial impedance (a) and polarization (b) curves of a freshly prepared LSM electrode as a function of a cathodic current of 200 mA cm^{-2} at 900°C in the absence of Fe-Cr alloy interconnect. EIS was measured at open circuit.

with current passage, followed by a region where the decrease in E_{Cathode} was much slower. With applying of a current of 200 mA cm^{-2} , E_{Cathode} instantly jumped to 538 mV and reduced rapidly to 349 mV in 2 min. After cathodic current passage for 180 min, E_{Cathode} was further reduced to 269 mV. As the electrode ohmic resistance (R_Ω) remained almost the same with the current passage, the decrease in E_{Cathode} was mainly due to the decrease in overpotential (η). The polarization behaviour with current

passage is in a good agreement with the impedance behaviour for the O₂ reduction. The substantial reduction in both R_E and η confirms the significant activation effect of cathodic polarization on the O₂ reduction reaction on the freshly prepared LSM electrode [Jiang, 1999a; Lee, 1995]. Such activation effect of cathodic polarization is most likely related to the generation of oxygen vacancies [Lee, 1995; Jiang, 1998], the removal of the passivation species such as SrO on the LSM surface [Jiang, 2001a], the microstructural improvement [Mizusaki, 1996; Jiang, 2003a] or the removal of the cation vacancies under the cathodic polarization [Chen, 2004a].

The SEM micrographs of surfaces and fractured cross sections of a newly prepared LSM electrode before and after cathodic current passage at 200 mA cm⁻² and 900°C for 240 min in absence of chromia-forming alloy are shown in Fig.4.2. The microstructure and morphology of the LSM electrode are affected by the current passage. The freshly prepared LSM electrode before the cathodic current passage was characterized by a plate-like structure and each plate was an agglomerate of small sphere-shaped particles. After cathodic current treatment, the microstructure of the LSM electrode was characterized by much smaller and well-defined, granular-shaped particles with clear grain boundaries. Jiang et al [2003a] have observed a similar change of the microstructure of LSM electrode under cathodic polarization. The generation and migration of oxygen vacancies and cation species, lattice expansion and crystallographic distortion under cathodic current passage could contribute to the microstructural changes [Wang, 2004]. The microstructural change from large agglomerate to sphere-like particles may increase the three-phase boundary regions for

the O₂ reduction reaction.

Fig.4.2 SEM micrographs of surfaces (a & b) and fractured cross sections (c & d) of a freshly prepared LSM electrode before and after cathodic polarization of 200 mA cm^{-2} at 900°C in air in the absence of Fe-Cr alloy interconnect. (a & c) before cathodic polarization, (b & d) after cathodic polarization.

4.2.2 Electrode behaviour of LSM electrode in the presence of chromia-forming alloy interconnect

Fig.4.3 shows the initial impedance responses of the LSM electrodes as a function of a cathodic current passage of 200 mA cm^{-2} in air in the presence of chromia-forming alloy at 900 , 800 and 700°C , respectively. EIS was measured under open circuit. In general, the electrode impedance decreases with the cathodic current passage, similar

Fig.4.3 Initial impedance responses of the LSM electrodes as a function of a cathodic current passage of 200 mA cm^{-2} in the presence of Fe-Cr alloy interconnect at (a) 900°C , (b) 800°C and (c) 700°C .

to that in the absence of chromia-forming alloy. However, the relative degree in the reduction of the electrode impedance varies with the temperature. At 900°C in the presence of chromia-forming alloy (Fig.4.3a), the size of the impedance arcs fluctuated

with cathodic current passage. For the reaction at 800°C (Fig.4.3b), R_E was reduced from an initial value of $13.2 \Omega \text{ cm}^2$ to $3.6 \Omega \text{ cm}^2$ after the cathodic current passage for 240 min, a 72% reduction in R_E . At 700°C, the initial value of R_E was $77.1 \Omega \text{ cm}^2$ and it was reduced to $47.3 \Omega \text{ cm}^2$ after 120 min cathodic current passage. R_E was reduced by 39%. The reduction in the electrode polarization resistance for the O_2 reduction in the presence of Fe-Cr alloy was also reported by Matsuzaki et al [2000] and Jiang et al [2000a]. As shown previously [Matsuzaki, 2000; Jiang, 1999a and 2001a], the significant reduction in the electrode polarization resistance measured at open circuit in the presence and absence of chromia-forming alloy is most likely due to the significant activation effect of the cathodic polarization on the initial electrode impedance behaviour of freshly prepared LSM electrodes.

Different to the electrode impedance behaviour at open circuit, the polarization potential (E_{Cathode}) for the O_2 reduction reaction on the LSM electrodes in the presence of chromia-forming alloy increases with the cathodic current passage time, as shown in Fig.4.4. In the presence of chromia-forming alloy, the polarization behaviour was also characterized by two distinct regions, similar to that in the absence of chromia-forming alloy. However, the change of E_{Cathode} with current passage is just opposite to that in the absence of chromia-forming alloy. Instead of a rapid decrease, E_{Cathode} increased quickly with the current passage in region I, reaching a potential plateau (region II), as shown in Fig.4.4a. Such change of the polarization potential, E_{Cathode} , with the cathodic current passage time was quite reproducible at the temperature ranges studied. The very different behaviour of E_{Cathode} with the cathodic current passage in the absence

Fig.4.4 Initial polarization curves of the LSM electrodes as a function of a cathodic current of 200 mA cm^{-2} in the presence of Fe-Cr alloy interconnect at (a) 900°C , (b) 800°C and (c) 700°C . The electrode polarization resistance (R_E) was taken from the impedance measured at open circuit (Fig.4.3).

and presence of chromia-forming alloy is a clear indication of the significant inhibiting effect of the Cr species on the O₂ reduction at the LSM electrodes in the presence of chromia-forming alloy.

4.2.3 Microstructural observation

Fig.4.5 shows the SEM micrographs of a LSM electrode after cathodic polarization at 200 mA cm⁻² and 900°C in the presence of chromia-forming alloy interconnect for 20 h. On the YSZ electrolyte surface, the formation of deposit band with 40-50 µm wide was clearly visible at the edge of the LSM electrode, similar to the deposition ring observed for the O₂ reduction on the LSM electrode/3mol% Y₂O₃-ZrO₂ electrolyte system [*Jiang, 2000a*]. A wave-like band was also observed on the YSZ electrolyte surface under the rib of the interconnect (Fig.4.5a). The wave-like bands were not continuous. The areas under the rib and channel were easily identified from the contact mark of the Fe-Cr alloy left on the LSM electrode coating. There was also formation of crystals with distinct facets on the LSM surface at the edge of the electrode (Fig.4.5b). But the LSM electrode surface was in general clean with no visible deposition (Fig.4.5c). However, the formation of distinct crystals occurred preferentially at the LSM electrode/YSZ electrolyte interface region (Fig.4.5d). In areas between the original LSM particles, there was deposition of fine grains and relative large crystals on the YSZ electrolyte surface. The deposits formed developed distinct crystal facets and filled the spaces between the LSM particles. On the other hand, no deposit with crystal facets was observed inside the LSM electrode bulk.

Fig.4.5 SEM micrographs of a LSM electrode after cathodic current passage at 200 mA cm^{-2} and 900°C for 20 h in the presence of Fe-Cr alloy interconnect. (a) An overview of the electrode, showing the formation of deposit band, (b) the edge of the LSM electrode, (c) LSM electrode surface and (d) fractured cross section of the LSM electrode.

Fig.4.6 shows the EDS patterns of LSM electrode shown in Fig.4.5. In comparison, the EDS pattern of a freshly prepared LSM coating is also shown in the figure (Fig.4.6.d). Fig.4.6a is the EDS analysis of the well-faceted crystals formed at the areas near the edge of LSM electrode coating, showing clearly the presence of Cr. A similar EDS pattern was also examined for the deposits formed at the LSM/YSZ interface region (Fig.4.6c). The crystals were most likely due to the formation of $(\text{Cr,Mn})_3\text{O}_4$ phases, as shown in earlier work [Badwal, 1997; Jiang, 2000]. The EDS analysis of the clean LSM electrode surface as shown in Fig.4.5c was similar to that of

the freshly prepared LSM coating, indicating there is no Cr deposition on the LSM electrode surface.

Fig.4.6 EDS patterns of the LSM electrode shown in Fig.4.5. (a) Deposits on the edge of LSM electrode (Fig.4.5b), (b) LSM electrode surface (Fig.4.5c), (c) deposits at the LSM/YSZ interface (Fig.4.5d) and (d) freshly prepared LSM coating.

In order to examine the Cr species deposition at the LSM/YSZ interface region, the LSM electrode coating was removed by the HCl acid treatment. Fig.4.7 shows the SEM micrographs of the YSZ electrolyte surface in contact with the LSM electrode coating. After the removal of the LSM electrode coating, cotton-like particles with no distinct facets were observed on the YSZ electrolyte surface at areas close to the edge of the LSM electrode (Fig.4.7b and Fig.4.7c). The Cr deposition on the YSZ

Fig.4.7 SEM micrographs of the YSZ electrolyte surface in contact with the LSM electrode coating after the cathodic current passage at 900°C for 20 h in the presence of Fe-Cr alloy. The LSM coating was removed by HCl acid treatment. (a) An overview of the YSZ electrolyte surface, (b) YSZ surface in contact with LSM, the edge of the LSM electrode, (c) YSZ surface in contact with LSM, ~20 μm from the edge of LSM electrode, (d) center of the YSZ surface in contact with LSM under the rib of the interconnect, and (e) center of the YSZ surface in contact with LSM under the channel of the interconnect.

electrolyte surface also depends on the contact surface of the interconnect. Clearly the Cr deposition on the YSZ electrolyte surface under the rib of the interconnect (Fig.4.7d) is far more significant than that under the channel of the interconnect (Fig.4.7e). This again

indicates the significant effect of the interconnect flow field on the deposition of Cr species on the LSM/YSZ system [Jiang, 2001].

Fig.4.8 is the EDS analysis of the Cr deposits of Fig.4.7. The composition of the cotton-like particles formed on the YSZ surface close to the edge of the LSM electrode coating (Fig.4.7b and 4.7c) mainly consists of Cr with very small amount of Mn (Fig.4.8a), indicating that the cotton-like particles are most likely deposits of Cr_2O_3 . On the YSZ surface areas away from the edge of the LSM electrodes, the EDS pattern clearly shows the existence of Cr and Mn for the deposits under the rib (Fig.4.8b) and

Fig.4.8 EDS patterns of (a) cotton-like deposits of Fig.4.7b & 4.7c, (b) grains and crystal-like deposits under the rib of the interconnect (Fig.4.7d), and (c) grains and crystal-like deposits under the channel of the interconnect (Fig.4.7e).

the channel (Fig.4.8c) of the interconnect. This indicates that crystals formed on the YSZ surface under the rib and the channel of the interconnect are most likely $(\text{Cr,Mn})_3\text{O}_4$ spinels.

It was also found that the Cr deposition on the YSZ electrolyte surface not in contact with LSM electrode coating was significantly related to the flow field of the interconnect. Fig.4.9 shows the SEM micrographs of the Cr deposits on the YSZ electrolyte surface not in direct contact with the LSM coating under the rib of the interconnect after cathodic current passage at 900°C for 20 h. Fig.4.10 shows the corresponding Cr deposition on the YSZ electrolyte surface under the channel of the interconnect. Clearly, the deposition of Cr species is far more substantial on the YSZ electrolyte surface under the rib of the interconnect than that under the channel of the interconnect. For the YSZ electrolyte surface under the rib of the interconnect, the Cr was deposited as far as 250 μm away from the edge of the LSM electrode (Fig.4.9f) while in the case of the YSZ surface under the channel of the interconnect, the corresponding YSZ electrolyte surface with visible Cr deposits was approximately 70 μm away from the edge of the LSM electrode (Fig.4.10e). Cr deposits were observed on the concave surface of the YSZ grains but not on the convex surface of the YSZ grains. The deposits on the YSZ electrolyte surface in both cases mainly contain Cr as shown by the EDS analysis of the deposits under the rib and the channel of the interconnect (Fig.4.11). This shows that the Cr deposits on the YSZ electrolyte surface were most likely Cr_2O_3 oxides. Similar deposition of Cr patterns on the YSZ electrolyte surface under the rib and channel of the interconnect was also observed for

the reaction with no air flow [[Jiang, 2001](#)].

Fig.4.9 SEM micrographs of the Cr deposits on the YSZ electrolyte surface not in contact with the LSM electrode after cathodic current passage at 900°C for 20 h under the rib of the interconnect. (a) An overview of the YSZ electrolyte surface, showing the formation of thick band close to the edge of the LSM electrode, (b) ~20 μm next to the edge of LSM, (c) ~50 μm away from the edge of LSM, (d) ~100 μm away from the edge of LSM, (e) ~150 μm away from the edge of LSM and (f) ~250 μm away from the edge of LSM, showing the YSZ electrolyte side of the deposit band.

Fig.4.10 SEM micrographs of the Cr deposits on the YSZ electrolyte surface not in contact with the LSM electrode after cathodic current passage at 900°C for 20 h under the channel of the interconnect. (a) An overview of the YSZ electrolyte surface, showing no clear formation of the deposit band at the edge of the LSM electrode, (b) next to the edge of LSM, (c) ~20 μm next to the edge of LSM, (d) ~50 μm away from the edge of LSM, (e) ~70 μm away from the edge of LSM, and (f) YSZ electrolyte surface without deposit.

Fig.4.11 EDS patterns of the Cr deposits on the YSZ electrolyte surface under (a) the rib (Fig.4.9c) and (b) the channel (Fig.4.10c) of the interconnect.

To study the deposition process of Cr species at the LSM electrode/YSZ electrolyte system in the early stage of the reaction, the LSM electrodes were cathodic polarized in the presence of Fe-Cr alloy at 900°C for different polarization time. Fig.4.12 shows the SEM micrographs of the YSZ electrolyte surface in contact with the LSM electrode coating in the presence of Fe-Cr alloy at 900°C after cathodic polarization for different periods. The LSM electrode coating was removed by HCl acid treatment. The SEM pictures shown were taken on the YSZ surfaces under the rib of the Fe-Cr alloy interconnect. In comparison, YSZ surface in contact with a LSM electrode after cathodic current passage at 200 mA cm⁻² and 900°C for 240 min in the absence of Fe-Cr alloy is also shown in Fig.4.12. The convex rings were contact areas between LSM particles and the YSZ electrolyte surface (Fig.4.12g), formed during the electrode sintering steps [Mitterdorfer, 1998]. After cathodic current passage in the presence of Fe-Cr alloy for 5 min, there was formation of isolated fine Cr grains at

Fig.4.12 SEM micrographs of the YSZ electrolyte surface in contact with the LSM electrode coating in the presence of Fe-Cr alloy interconnect at 900°C after cathodic polarization for (a) 5 min, (b) 15 min, (c) 30 min, (d) 4 h, (e) 20 h and (f) 50 h. The SEM micrograph of YSZ surface in contact with LSM electrode after polarization at 200 mA cm⁻² at 900°C for 4 h in the absence of Fe-Cr alloy is shown in (g). The LSM electrode coating was removed by HCl acid treatment.

areas between the LSM particles (Fig.4.12a). As the cathodic current passage time increased to 15 min, the density of the fine grains increased (Fig.4.12b). However, the fine grains had no preferential deposition at the three phase boundaries (i.e., the convex ring region). Rather deposition of fine grains was random, simply filled the space between the LSM particles with the increase in the cathodic polarization time (Fig.4.12c and 4.12d). As the cathodic current passage increased to 20 and 50 h, the fine grains grew into crystals with distinct facets (Fig.4.12e and 4.12f).

The deposition of Cr species was also studied at different temperatures. Fig.4.13 shows the SEM micrographs of the YSZ electrolyte surface in contact with LSM electrode after cathodic current passage at 200 mA cm^{-2} for 20 h at different temperatures. The YSZ surface shown in the figure were taken on the YSZ surface under the rib of the chromia-forming alloy interconnect and LSM electrode coating was carefully removed by a sharp doctor blade after the testing. Fig.4.14 shows the corresponding EDS patterns of the deposits formed at different temperatures. At 900°C , the YSZ electrolyte surface in contact with the LSM coating was almost completely covered by fine grains ($\sim 0.05 \text{ }\mu\text{m}$) and large crystals ($\sim 0.4 \text{ }\mu\text{m}$) (Fig.4.13a). The crystals formed have distinct facets and were seemed to grow from the fine grains. EDS analysis of crystals revealed the existence of Cr and Mn (Fig.4.14a), indicating the crystals were $(\text{Cr,Mn})_3\text{O}_4$ spinels [Badwal, 1997]. As the reaction temperature decreases, the intensity of the Cr deposits decreased significantly. For the O_2 reduction reaction at 700°C , isolated fine particles were formed on the YSZ electrolyte surface areas between the original LSM particles with no preferential deposition at the three

Fig.4.13 SEM micrographs of the YSZ electrolyte surface in contact with LSM electrode under the rib of the Fe-Cr alloy interconnect after cathodic current passage at 200 mA cm^{-2} for 20 h at (a) 900°C , (b) 800°C and (c) 700°C . LSM electrode coating after polarization at 800°C and 700°C was removed by a sharp doctor blade.

phase boundary regions (Fig.4.13c), similar to the initial deposition of Cr species at 900°C (Fig.4.12). The large and irregular particles were LSM particles left on the YSZ electrolyte surface. On the isolated fine particles, EDS analysis clearly showed the

presence of Cr and probably Mn (Fig.4.14c).

Fig.4.14 EDS patterns of Cr deposits on the YSZ electrolyte surface of Fig.4.13 at: (a) 900°C, (b) 800°C and (c) 700°C.

4.3 Discussion

As shown in Fig.4.12, Cr deposition on the LSM electrode and YSZ electrolyte interface regions increases with the cathodic polarization time. This is widely known as well documented in the literature [[Taniguchi, 1995](#); [Matsuzaki, 2001](#); [Jiang, 2000](#)]. However, the distribution of the Cr deposits on the YSZ system observed at the early stage of the reaction shows no preferential deposition of Cr species at the areas around

the convex rings (Fig.4.12a and 4.12b). Atomic force microscopy (AFM) studies of the formation of the convex rings at the O₂/LSM/YSZ interface and the subsequent broadening under both cathodic and anodic polarization conditions indicate that convex rings are the three phase boundary regions for the O₂ reduction reactions [Jiang, 2005a]. The same random Cr deposition on the YSZ electrolyte surface between the LSM particles was also observed for the reaction at 700°C (Fig.4.13c). Cr particles simply filled the YSZ electrolyte surface space between LSM grains as the polarization time increased. On the other hand, the relative increase in the cathodic potential (E_{Cathode}) with the cathodic current passage is quite reproducible despite the continued accumulation of the Cr deposits at the LSM electrode and YSZ electrolyte interface. For example, for the reaction at 900 °C, the relative increase in E_{Cathode} after the cathodic current passage for 240 min was 397 mV, close to 345 mV after the cathodic polarization for 5 min. The relative increase in E_{Cathode} was measured by the difference between the initial E_{Cathode} when current was applied and the E_{Cathode} value at the potential plateau. However, the Cr deposition on the LSM/YSZ interface after the cathodic current passage for 240 min was far more significant than that after the cathodic polarization for only 5 min (Fig.4.12a and 4.12d). This shows that there is no intrinsic relationship between the Cr deposition and the oxygen activity or the O₂ reduction reaction at the three phase boundaries in contrast to the proposed electrochemical deposition mechanism of Cr species [Taniguchi, 1995; Badwal, 1997; Matsuzaki, 2001]. Rather, Cr deposition is basically controlled by the chemical dissociation, initiated by the nucleation reaction between the gaseous Cr species and

manganese species in particular Mn^{2+} [Jiang, 1999, 2000, and 2002].

For the nonstoichiometric perovskite-type $(\text{La}_{1-x}\text{Sr}_x)_y\text{MnO}_{3-\delta}$ where δ stands for the oxygen nonstoichiometry, the electrically neutrality due to the substitution of La^{3+} by Sr^{2+} at the A site or the oxygen nonstoichiometry under different partial pressures is maintained by a change in the valence of B-site Mn ions and/or the formation of oxygen vacancies. According to the defect model proposed by Mizusaki et al [2000], two defect equilibria can be written as a function of oxygen partial pressure and temperature:

where $\text{Mn}_{\text{Mn}}^{\bullet}$, Mn_{Mn}^x , and Mn_{Mn}' donate Mn^{4+} , Mn^{3+} and Mn^{2+} ions, respectively, and $\text{O}_{\text{O,LSM}}^x$ and $\text{V}_{\text{O,LSM}}^{\bullet\bullet}$ stand for O^{2-} ions and oxygen vacancies in LSM lattice and interstitial sites. Under cathodic polarization conditions, Mn ions in the LSM lattice and interstitial sites can also be electrochemically reduced to Mn^{2+} ions, forming concomitantly oxygen vacancies [Lee, 1995; Jiang, 1998].

where $\text{O}_{\text{O,YSZ}}^x$ and $\text{V}_{\text{O,YSZ}}^{\bullet\bullet}$ are the O^{2-} ions and oxygen vacancies in YSZ lattice sites, respectively. The mobile oxygen vacancies generated by cathodic polarization have been considered to be responsible for the observed electrocatalytic effect on the electrode performance of LSM cathodes under high cathodic polarization. Similar to oxygen vacancies, manganese ions such as Mn^{2+} generated could also be mobile under

high temperature and cathodic polarization conditions [Zhang, 1998]. Weber et al [2004] studied the microstructural change of $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ cathodes operated at 850°C and 200 mA cm^{-2} for 4500 h and observed the interdiffusion of Mn from the cathode to the YSZ electrolyte as far as $\sim 200 \text{ nm}$. Thus, the interaction between the mobile Mn^{2+} ions and gaseous CrO_3 species would lead to the formation of Cr-Mn-O nuclei. However, nucleation reaction and subsequent grain growth of Cr deposits are kinetically controlled by the contact frequencies and contact time between Mn^{2+} ions and CrO_3 species, which would be highest on the YSZ electrolyte surface close to the edge of the LSM electrode and inside the steps on the electrolyte [Jiang, 2000]. The best example is probably the observation of the Cr deposits on the concave surface rather than on the convex surface on the YSZ grains (Fig.4.10e). The formation of stable Cr-Mn-O nuclei phases in turn accelerates the crystallization and grain growth of Cr_2O_3 and $(\text{Cr,Mn})_3\text{O}_4$ solid phases. The nucleation and grain growth steps can be simply written as follows [Jiang, 2000].

Thus the formation of $(\text{Cr,Mn})_3\text{O}_4$ -type spinel would be facile if there is sufficient supply of Mn^{2+} ions. Fig.4.15 shows schematically the deposition processes of Cr species at the LSM/YSZ system under the cathodic polarization conditions in the presence of Fe-Cr alloy metallic interconnect. As the mechanism of the Cr deposition

under the SOFC operation conditions is chemical in nature, the nucleation and grain growth of the Cr deposits can occur on the YSZ electrolyte surface with and without the direct contact with the LSM electrode (Fig.4.9, 4.10, and 4.12). It is just coincident that for the O_2 reduction reaction on the LSM cathode, the generation of Mn^{2+} is directly related to the cathodic polarization via the generation of the oxygen vacancies. This in turn leads to the increased Cr deposition with the cathodic polarization potential. This explains the observed phenomena of the relationship between the Cr deposition at the LSM/YSZ interface region and the cathodic polarization.

Fig.4.15 Schematic of Cr deposition reaction at LSM cathode and YSZ electrolyte in the presence of Fe-Cr alloy interconnect under SOFC operation conditions.

The intensity and amount of Cr deposition are significantly related to the flow field design of the interconnect (Fig.4.9 and 4.10). The significant difference in the Cr deposition on the YSZ surface under the ribs and channels of the metallic interconnect can be explained by the difference in the flux of gaseous Cr species [Jiang, 2001]. The

distance between the YSZ and the interconnect surface under the rib was $\sim 20\text{ }\mu\text{m}$, thickness of the LSM coating, while the distance between the YSZ and the interconnect surface under the channel was $\sim 1220\text{ }\mu\text{m}$ (channel depth + coating thickness). It has been shown that for oxidation and vaporization of Cr_2O_3 , a stagnant gaseous boundary layer is formed adjacent to the chromia surface and the mass transport through the gaseous boundary layer is a rate-limiting step for the oxidation and vaporization of Cr_2O_3 [Graham, 1971; Stearns, 1971]. Thus, for the areas under the channel of the interconnect, air flow would greatly reduce the thickness of the gaseous boundary layer and sweep away Cr species. This in turn reduces significantly the flux of Cr species at the YSZ/LSM interface areas under the channel of the interconnect. On the other hand, the Cr flux at the YSZ/LSM interface area under the rib of the interconnect would be much less affected by the air flow and the distance for the flux of the Cr species is also much shorter. As the migration of manganese species (e.g., Mn^{2+}) generated under cathodic polarization is mainly through surface diffusion and should not be affected significantly by the air flow, the deposition of the Cr would be far more significant on the YSZ surface under the rib of the interconnect due to the much higher Cr flux, as compared to that under the channels of the interconnect.

The deposition of Cr under cathodic polarization conditions depends strongly on the reaction temperature (Fig.4.13). The deposition of Cr species at 700°C is drastically lower than that at 900°C under the same cathodic current passage conditions. As shown by Hilpert et al [1996], CrO_3 is one of the main gaseous Cr species over chromium oxide scale under dry and humidified air and the partial pressure of CrO_3 decreases

with the decrease in temperature. The partial pressure of CrO_3 is about 1.39×10^{-3} Pa at 900°C while at 700°C it decreases to 9.73×10^{-6} Pa. At reduced temperature the supply of the Mn^{2+} ions generated under cathodic polarization potentials could also be significantly reduced. Cation diffusion in perovskite oxides is known to be very slow. The diffusion coefficient of cations such as La and Mn in $(\text{La},\text{Sr})(\text{Ga},\text{Mg})\text{O}_3$ perovskite is in the range of $10^{-13} \text{ cm}^2 \text{ s}^{-1}$ at 1400°C [Schulz, 2000]. At 900°C the cation diffusion in the $(\text{La},\text{Ca})\text{CrO}_3$ perovskite bulk phase can be calculated to be $10^{-16} \text{ cm}^2 \text{ s}^{-1}$ and at 700°C , it would decrease to $10^{-19} \text{ cm}^2 \text{ s}^{-1}$ due to the high activation energy of the cation diffusion in the perovskite [Horita, 1998]. Thus, reduction in the reaction temperature not only reduces the partial pressure of Cr species but also the diffusivities of manganese species (e.g., Mn^{2+}) in the LSM-based perovskite. This in turn would lead to the reduced nucleation reaction and subsequent grain growth reactions between the manganese and Cr species. This appears to be supported by the substantial reduction in the deposition of Cr species on the YSZ electrolyte surface at reduced reaction temperatures despite the increase in the overpotential for the reaction (Fig.4.4 and 4.13).

4.4 Conclusion

The deposition process of Cr species at the LSM electrode/YSZ electrolyte/Fe-Cr alloy metallic interconnect system has been investigated under a constant cathodic current passage of 200 mA cm^{-2} in the early stages of the reaction. Cr deposits on the YSZ electrolyte surface increase with the polarization time. However, Cr species show

no preferential deposition at the three-phase boundary of O₂, LSM electrode and YSZ electrolyte. Rather, deposition of Cr species on the YSZ electrolyte surface is random at the early stage of the reaction in the presence of chromia-forming alloy interconnect. The results demonstrate again that the deposition of Cr species at LSM electrode is not an electrochemical reduction reaction of high valent Cr species to solid Cr₂O₃ at the three-phase boundary region in competition with O₂ reduction. The deposition of Cr species is essentially a chemical reaction on re-deposition. The driving force for the deposition process is related to the nucleation reaction between the gaseous Cr species and the Mn²⁺ ions generated under cathodic polarization. The kinetics of the deposition process is strongly affected by the flux of the gaseous Cr species.

The substantial reduction in the Cr deposition at the LSM electrode and YSZ electrolyte at reduced temperature is most likely due to the significant decrease in the cation diffusivities in LSM-based perovskite oxides and the partial pressure of gaseous Cr species.

CHAPTER 5.

CHEMICAL INTERACTION BETWEEN Fe-Cr ALLOY AND CONSTITUENT OXIDE COATINGS OF LSM

In this chapter, the chemical reactions between a Fe-Cr alloy (RA446) and the constituent oxides of LSM material were investigated at 800-900°C in air under normal sintering conditions. The results indicate that the chemical interaction and transportation of Cr species in the LSM coating are most likely related to the oxide species enriched at the LSM surface.

5.1 Experimental

The constituent oxides of LSM materials were investigated in this study: La_2O_3 , SrO and Mn_2O_3 . The details of the preparation of the oxide coatings on the RA446 alloy can be found in Chapter 3. All the oxide-coated alloy samples were heated in open air at 900°C and/or 800°C for up to 500 h. The oxidation behaviour of un-coated RA446 alloy was also studied at 900°C in air. The thermal expansion coefficient of the RA446 alloy was determined from room temperature to 900°C in flowing N_2 atmosphere by a Perkin-Elmer Series 7 thermal analysis system. The thermal expansion coefficient of the alloy was $12.5 \times 10^{-6} \text{ K}^{-1}$, which is close to that of the LSM electrode and YSZ electrolyte materials used in SOFC [Minh, 1995].

To study the gas-phase transportation of Cr species, La_2O_3 and SrO oxides were pressed into small disks with a diameter of 8 mm and thickness of about 3 mm. The oxide disks were arranged about 5 mm away from the RA446 alloy and there was no direct contact between the oxide disk and the alloy. Both oxide disk and alloy samples were placed inside a crucible. Oxidation treatments were also carried out in open air at 900°C for 500 h. The deposition of Cr species was indicated by the color change of the oxide samples.

5.2 Results and discussion

5.2.1 Oxidation of Fe-Cr alloy

Fig.5.1 shows the SEM micrographs of the surface and cross section of Fe-Cr alloy (RA446 alloy) after the oxidation in air at 900°C for 100 h. A thick and dense oxide scale layer was formed on the alloy surface. The oxide scale was continuous and the average thickness was $\sim 3\ \mu\text{m}$. The oxide scale at the alloy interface was dense

Fig.5.1 SEM micrographs of the (a) surface and (b) cross section of Fe-Cr alloy after the oxidation in air at 900°C for 100 h.

without any voids and cracks, indicating the good adhesion of the oxide scale to the alloy substrate. The morphology of the oxide scale surface was characterized by dense packed well-faceted crystals (Fig.5.1a).

Fig.5.2 shows the XRD and EDS pattern of the oxide scale. From XRD analysis, the identified phases on the oxidized alloy surface were $(\text{Cr,Mn})_3\text{O}_4$ -type spinel oxide, Cr_2O_3 oxide as well as the Fe of the original alloy (Fig.5.2a). EDS analysis of the crystals shows the existence of Cr and Mn, indicating that the well-faceted crystals were most likely $(\text{Cr,Mn})_3\text{O}_4$ spinel. Similar phases were also observed on the surface of other Mn-containing Fe-Cr alloys, such as SUS430 [Brylewski, 2001] and ZMG232

Fig.5.2 (a) XRD pattern of the oxide scale surface and (b) EDS pattern of the crystals of the Fe-Cr alloy surface after oxidation at 900°C for 100 h.

[[Horita, 2003b](#)]. The precipitation of the $(\text{Cr,Mn})_3\text{O}_4$ spinel on the top of the chromia scale can be attributed to the high diffusion coefficient of manganese ions. The metal ion diffusion decreases in the order of $D_{\text{Mn}} > D_{\text{Fe}} > D_{\text{Cr}}$ by assuming that these metal ions diffuse via Cr^{3+} -lattice sites in Cr_2O_3 [[Cox, 1972](#)]. According to the Cr-Mn-O system phase diagram, the $(\text{Cr,Mn})_3\text{O}_4$ spinel is thermodynamically favorable even at low Mn concentration [[Hurokawa, 2004](#)]. The formation of the $(\text{Cr,Mn})_3\text{O}_4$ spinel layer on the oxide scale can reduce significantly the vaporization pressure of gaseous chromium species [[Gindorf, 2001](#)].

5.2.2 La_2O_3 -coated Fe-Cr alloy

The La_2O_3 coating was originally white in color before the oxidation experiment. After oxidation in air at 900°C for 100 h the color of the coating changed to brownish yellow. This obviously indicates the interaction between the Fe-Cr alloy and the La_2O_3 coating. Fig.5.3 shows the SEM micrographs of the La_2O_3 coating and Fe-Cr alloy interface after oxidation at 900°C for 100 h and Fig.5.4 is the corresponding element distribution profile and EDS patterns taken at different regions of the oxide coating. The oxide scale was $\sim 2\text{--}4\ \mu\text{m}$ thick and was not uniform as compared to that of un-coated alloy (Fig.5.3a and 5.3b). There was a significant increase in the Mn content in the oxide scale towards the interface between the alloy and the La_2O_3 oxide coating (Fig.5.4a). This indicates the formation of $(\text{Cr,Mn})_3\text{O}_4$ spinel phase on the surface of the oxide scale, consistent with that observed on the un-coated Fe-Cr alloy (Fig.5.1).

Fig.5.3 SEM micrographs of the La_2O_3 coating and Fe-Cr alloy interface after oxidation treatment at 900°C for 100 h. (a) An overview of the cross section, (b) the Fe-Cr alloy/ La_2O_3 interface, (c) the bulk region of the coating and (d) the region close to the surface of the coating. Point A and B show the analyzed areas by EDS.

The La_2O_3 coating was porous and the morphology of the La_2O_3 coating in the region close to the alloy interface was characterized by the sphere-shaped particles of about $0.5\ \mu\text{m}$. The bonding between the La_2O_3 oxide coating and the Fe-Cr alloy appears to be good (Fig.5.3b). In the region close to the air side of the coating, there were flake-like particles in the coating (Fig.5.3d). This may be due to the formation of lanthanum hydroxide as the La_2O_3 is easily to absorb moisture when exposed in air. The elemental distribution analysis shows that Cr was present over the whole La_2O_3 , indicating that the Cr deposition occurred over the whole oxide coating (Fig.5.4a). Moreover, the profile of Cr followed closely with that of La and the atomic ratio of

Fig.5.4 (a) Element distribution profile of La₂O₃ oxide coating and EDS patterns taken at (b) 2 μm (point A in Fig.5.3b) from the interface and (c) 10 μm (point B in Fig.5.3d) from the interface. The EDS pattern of pure La₂O₃ oxide is shown in (d).

Cr/La was almost equal to one, probably indicating the formation of the LaCrO₃ phase. The close profile of La and Cr in the oxide coating also indicates that La₂O₃ can readily react with Cr species, inducing the deposition of Cr species in the coating. In the areas close to the alloy interface, there was a significant deposition of Cr. This is indicated by the much smaller La_{Lα}/La_{Lβ} ratio of 0.62 taken at La₂O₃ coating region of ~2 μm from the alloy surface (Fig.5.4b), as compared to the ratio of 4.81 for the pure La₂O₃ oxide (Fig.5.4d). The reduction in the La_{Lα}/La_{Lβ} ratio is due to the fact that the Kα X-ray peak of Cr is overlapped with the Lβ peak for La. As the coating distance increased to 10 μm from the oxide coating/alloy interface, the La_{Lα}/La_{Lβ} ratio increased

to 1.24 (Fig.5.4c). The higher $\text{La}_{\text{L}\alpha}/\text{La}_{\text{L}\beta}$ ratio as compared to that measured at the area close to the interface (Fig.5.4b) indicated the decrease in the Cr deposition.

It is noted the presence of the Mn from the EDS analysis of the La_2O_3 oxide coating and the strength of the Mn appeared more or less the same cross the whole La_2O_3 coating (Fig.5.4b and 5.4c). This indicates that Mn could diffuse from the oxide scale of the alloy into the oxide coating. This seems to indicate that manganese species are rather mobile, consistent with that observed for the LSM cathodes under cathodic polarization conditions. On the other hand, Fe peak at 7.2 keV was barely visible, indicating that the Fe signal in the element distribution profile could be the background noise (Fig.5.4a). The Au signal in the EDS pattern was due to the sputtered Au coating in order to improve the conductivity on the SEM sample.

5.2.3 SrO-coated Fe-Cr alloy

SrO coating deposited on the Fe-Cr alloy had poor adhesion and SrO coating was completely peeled off from the surface of alloy after the oxidation experiments at 900°C. However, the SrO coating deposited on the Fe-Cr alloy oxidized in air at 800°C for 100 h was survived. After the oxidation treatment, the SrO coating changed from the original white color to the green color, indicating that Cr species deposition occurred in the SrO coating. Fig.5.5 shows the SEM micrographs of the cross section of the SrO coating/Fe-Cr alloy after oxidation treatment in air at 800°C for 100 h and Fig.5.6 is the corresponding element distribution profile and EDS analysis of selected regions. There was a gap formed between the SrO coating and the alloy, showing the

Fig.5.5 SEM micrographs of the SrO coating/Fe-Cr alloy after oxidation treatment in air at 800°C for 100 h. (a) An overview of the cross section, (b) the Fe-Cr alloy/SrO interface, (c) the bulk region of the coating and (d) the region close to the air side of the coating. Point A and B show the analyzed areas by EDS.

poor adhesion. The thickness of SrO coating was $\sim 60\ \mu\text{m}$. The SrO coating was characterized by the significant formation of plate-like particles. EDS analysis of the plate-like particles shows the significant presence of Cr (Fig.5.6b) while in the areas with no plate-like particles, the Cr content was very small (Fig.5.6c). The plate-like particles are most likely Cr_2O_3 phases and this is supported by the formation of the green color of the coating after the oxidation at 800°C. Cr_2O_3 is a well-known green pigment. On the other hand, the formation of SrCrO_4 would give distinguish strontium yellow. This shows that Cr deposition in the SrO coating may not be uniform. This is just the case as shown by the element distribution profile of the SrO coating (Fig.5.6a).

Fig.5.6 (a) Element distribution profile of the SrO oxide coating and EDS analysis of (b) the plate-like particles (point A in Fig.5.5d) and (c) the areas with no plate-like particles (point B in Fig.5.5d).

Very different from that in the case of the La_2O_3 coating (Fig.5.4a), the distribution of Cr did not follow that of Sr and the atomic ratio of Cr/Sr was far below one. The mismatch of the Cr and Sr element distribution profile and the formation of plate-like particles indicate that the interaction between the SrO and Fe-Cr alloy primarily lead to the deposition of Cr_2O_3 rather than the formation of SrCrO_4 in this study. The diffusion of Mn from the oxide scale into SrO coating was also evident (Fig.5.6b and 5.6c), consistent with that observed for the La_2O_3 oxide coating.

5.2.4 Mn_2O_3 -coated Fe-Cr alloy

Fig.5.7 shows the SEM micrographs of the cross section of the Mn_2O_3

coating/Fe-Cr alloy interface after the oxidation treatment in air at 900°C for 500 h and Fig.5.8 is the corresponding element distribution profile and the EDS analysis of selected regions. The thickness of oxide scale and Mn_2O_3 coating was about 5 μm and 50 μm , respectively. The morphology of the coating was characterized by fine grains and some large particles (Fig.5.7b). Particles as large as 5 to 10 μm in diameter were observed. EDS analysis showed that the fine particles contained significant amount of Mn as compared to Cr (Fig.5.8b) and on the other hand the large particles contained much higher Cr (Fig.5.8c). This indicates that the large particles in the Mn_2O_3 coating may be the $(\text{Cr,Mn})_3\text{O}_4$ spinel phase with high Cr content. The distribution profile of Cr in the Mn_2O_3 coating generally followed with that of Mn, similar to that of La_2O_3 oxide coating. However, the atomic ratio of Cr/Mn was less than one and varied somehow within the Mn_2O_3 coating. This indicates that the product of the Cr deposition in the Mn_2O_3 oxide coating would be primarily $(\text{Cr,Mn})_3\text{O}_4$ phase with Cr/Mn ratio less than one. Thus Mn_2O_3 would facilitate the deposition of Cr species, leading to the preferential formation of $(\text{Cr,Mn})_3\text{O}_4$ spinel.

Fig.5.7 SEM micrographs of the Mn_2O_3 coating/Fe-Cr alloy interface after oxidation treatment in air at 900°C for 500 h. (a) An overview of the cross section and (b) the bulk region of the coating. Point A and B show the analyzed areas by EDS.

Fig.5.8 (a) Element distribution profile of the Mn₂O₃ oxide coating and EDS analysis of (b) region with small grains (point A in Fig.5.7b) and (c) region with particle (point B in Fig.5.7b). The EDS pattern of pure Mn₂O₃ is shown in (d).

5.2.5 LSM-coated Fe-Cr alloy

Fig.5.9 shows the SEM micrographs of the cross section of the interface between the LSM coating and Fe-Cr alloy after oxidation in air at 900°C for 100 h. Fig.5.10 is the EDS patterns of the selected regions of the LSM coating. The formation of an oxide scale layer at the alloy/LSM coating interface can be clearly seen. The oxide scale contained the Cr, Mn and Fe, similar to that on the uncoated alloy (Fig.5.10a). However, the oxide scale formed was much thinner and not uniform on the LSM-coated Fe-Cr alloy compared with the uncoated alloy, indicating that LSM coating affects the oxidation behaviour of Fe-Cr alloy. The slurry-coated LSM coating

Fig.5.9 SEM micrographs of the cross section of the interface between the LSM coating and Fe-Cr alloy after oxidation at 900°C for 100 h. (a) An overview of the cross section, (b) the Fe-Cr alloy/LSM interface, (c) the coating bulk region and (d) the top surface of the LSM coating. Point A, B and C show the analyzed areas by EDS.

was porous, forming good contact between the LSM coating and Fe-Cr alloy (Fig.5.9b). Throughout the whole coating region ($\sim 45 \mu\text{m}$ thick), the morphology of the LSM coating was quite uniform and the LSM grain size was $\sim 1 \mu\text{m}$ (Fig.5.9). However, the deposition and distribution of Cr species varied with the thickness of LSM coating. It is known that on the EDS patterns the $K\alpha$ X-ray peak of Cr is overlapped with the $L\beta$ peak for La meanwhile the $K\alpha$ peak of Mn overlaps with the $K\beta$ peak for Cr. Nevertheless, the presence of Cr can be verified from the variation in the intensity ratio of $L\alpha/L\beta$ for La in LSM/alloy couple as compared to that of pure LSM. For pure LSM, the $La_{L\alpha}/La_{L\beta}$ ratio was 4.38 (Fig.5.10d). The $La_{L\alpha}/La_{L\beta}$ ratio of the LSM coating/Fe-Cr alloy was 2.21 and 2.98 in the LSM coating region at a

distance of 5 and 10 μm away from the LSM/alloy interface (Fig.5.10b and 5.10c), respectively. The low $\text{La}_{\text{L}\alpha}/\text{La}_{\text{L}\beta}$ ratio indicates the presence of Cr. Thus the higher $\text{La}_{\text{L}\alpha}/\text{La}_{\text{L}\beta}$ ratio indicates the lower content of Cr presented in the coating. This indicates that Cr deposition in the LSM coating decreases with the distance away from the alloy surface.

Fig.5.10 EDS patterns of the selected regions of the LSM coating and Fe-Cr alloy after oxidation at 900°C for 100 h. (a) The oxide scale (point A in Fig.5.9b), (b) the bulk region of the coating (point B in Fig.5.9c) and (c) the top surface of the coating (point C in Fig.5.9d). The EDS pattern of pure LSM is shown in (d).

Fig.5.11 shows the SEM micrograph and the element distribution profile of the LSM coating/Fe-Cr alloy interface after oxidation at 900°C for 500 h. A gap between the LSM coating and Fe-Cr alloy substrate was observed, which could be formed

Fig.5.11 SEM micrographs showing (a) the cross section and (b) the plate-like deposits of LSM coated specimen after oxidation at 900°C for 500 h. The element distribution profile is shown in (c) and EDS pattern of the plate-like deposit is shown in (d).

during the cooling of the sample or during the SEM specimen preparation. LSM generally showed good adhesion to the alloy. In areas close to the alloy/LSM interface, the microstructure of the LSM coating was characterized by fine grains, similar to that oxidized for 100 h under the same temperature (Fig.5.9). In the areas 20 μm away from the LSM coating/Fe-Cr alloy interface there were formation of plate-like particles (Fig.5.11a). The size of the plate-like particles varied and the morphology of the plate-like particles was similar to that observed for the SrO/Fe-Cr alloy couple (Fig.5.5). EDS analysis revealed that these particles contain chromium as the intensity ratio of $La_{L\alpha}/La_{L\beta}$ was 2.69, which is significantly lower than 4.38 of the pure LSM particle.

Form the distribution profile of the elements (Fig.5.11c), there was a high concentration of Mn in the oxide scale, which is consistent with the observed formation of the $(\text{Cr,Mn})_3\text{O}_4$ spinel at the outer surface of the oxide scale (Fig.5.2a). In the LSM coating, the element distribution of La, Mn and Sr was quite homogeneous and did not show visible enrichment of the constituent elements of the LSM in the coating as reported by Quadakkers et al [1996]. The distribution of chromium did not follow with particular elements over the whole width of the LSM coating. However, the distribution of the Cr indicates the almost uniform deposition of Cr across the whole LSM coating.

5.2.6 Reaction between Fe-Cr alloy and constituent oxides of LSM

Additional experiments were carried out to study the interaction between the constituent oxides (La_2O_3 and SrO) of LSM and the Fe-Cr alloy by separating the oxide disks and the alloy samples under the oxidation condition at 900°C for 500 h. The color of La_2O_3 oxide disk changed partially from the original white to yellow and in the case of the SrO oxide disk, it became green after the oxidation experiment. This is similar to that observed for the oxide coating experiments. The color change indicates again the significant deposition of Cr in the oxide disks and the transport of chromium species is most likely through the gas phase diffusion of high valent Cr species such as CrO_3 and/or $\text{CrO}_2(\text{OH})_2$ [Quadakkers, 1996].

The gaseous Cr species (e.g., CrO_3) formed from the oxide scale of the

chromia-forming alloy can directly deposit to form Cr_2O_3 by dissociation according to the following reaction:

However, depending on the nature of the oxides, the formation of Cr_2O_3 by dissociation may not always be kinetically preferable. The results in current study indicate that the deposition and formation of Cr compounds depend strongly on the constituent oxides. In the cases of La_2O_3 coatings with the Fe-Cr alloy, the distribution profile of Cr closely matches that of La and the atomic ratio of Cr/La was close to unity. This shows that La has high affinities for the deposition or dissociation of Cr species. The unit atomic ratio of La/Cr probably indicates the formation of LaCrO_3 . The formation of LaCrO_3 by the reaction between Cr_2O_3 and La_2O_3 is also thermodynamically favorable [Peck, 2001]. Zhu et al [2004] deposited the La_2O_3 thin film onto a pre-oxidized stainless steel by sputtering method and observed the formation of LaCrO_3 phase after annealing at 800°C for 1 h.

In the case of Mn_2O_3 oxide coating, Cr distribution also in general followed that of Mn (Fig.5.8a) though the atomic ratio of Cr/Mn was less than unity. This indicates that Mn_2O_3 also has high affinities for the Cr deposition, similar to that of La_2O_3 . From the Mn_2O_3 - Cr_2O_3 phase diagram [Speidel, 1963], at high temperature (above 900°C) Mn_2O_3 oxide would be partially reduced to Mn_3O_4 oxide, a mixture of Mn^{2+} and Mn^{3+} . Significant amount of Cr species deposited in the Mn_2O_3 coatings indicates the nucleation reaction and the grain growth between the gaseous Cr species and Mn species, leading to the formation of $(\text{Cr,Mn})_3\text{O}_4$ spinel phase with Cr/Mn ration less

than one under conditions of the present study.

The formation of Cr_2O_3 is most likely dominant for the chemical interaction between the SrO coating and Fe-Cr alloy in this study. This is indicated by the appearance of green color of the original white SrO coating after the heat treatment, the very different Sr and Cr distribution profiles and the formation of the plate-like particles with high Cr content. However, the deposition of Cr species is most likely induced by the SrO. The deposition of Cr species is substantial on the LSCF electrode surface in the absence of polarization and this has been attributed to the originally enriched SrO species on the LSCF electrode surface [Jiang, 2002]. Thus, the presence of SrO will lead to the preferential deposition of Cr_2O_3 phase under the experimental conditions in this study. However, the formation of SrCrO_4 may also be possible under long-term sintering conditions [Quadackers, 1996; Fujita, 2004a]. In conclusion, the main reaction between the Cr species and the constituent oxides of LSM materials at the early stage of the reaction can be written as follows.

In the case of A-site nonstoichiometric LSM electrode materials, the surface composition may not be same as that of the bulk. As shown by the acid etch analysis of the LSM electrodes prepared by chemical co-precipitation, there are Mn and Sr enrichments on the freshly-prepared LSM electrode surface but not La [Jiang, 2001a]. Decorse et al [1999] investigated the surface composition of LSM powders and pellets

and found that Sr and oxygen contents of the surface were higher than that in the bulk. This indicates the segregation of SrO on the LSM surface. The segregation and enrichment of the oxides on the LSM coating surface could have significant effect on the interaction between the LSM coating and the Fe-Cr alloy. In the case of the LSM coating/Fe-Cr alloy, the formation of the $(\text{Cr,Mn})_3\text{O}_4$ phase would most likely be significant due to the significant segregation of the Mn species on the LSM surface in the case of A-site nonstoichiometric LSM in the present study. This appears to be supported by the uniform distribution of the Cr over the whole LSM coating and is in general consistent with that reported in the literature [[Quadakker, 1996](#)]. The significant deposition of Cr species and the formation of $(\text{Cr,Mn})_3\text{O}_4$ spinels for the O_2 reduction reaction on the LSM electrode in the presence of Fe-Cr alloy have been considered to be related with the Mn^{2+} species generated under cathodic polarization, as shown in Chapter 4. This is consistent with high affinities of the manganese oxides for the Cr deposition as shown in the $\text{Mn}_2\text{O}_3/\text{Fe-Cr}$ couple (Fig.5.7 and 5.8). The SrO species enriched on the freshly prepared LSM coating surface can lead to the preferential deposition of Cr_2O_3 . This appears to be supported by the formation of plate-like particles in both LSM/Fe-Cr alloy and SrO/Fe-Cr alloy couples. The reasons for the appearance of the plate-like particles in the LSM/Fe-Cr alloy couple after the oxidation at 900°C for 500 h are not clear. One reason could be the increase of the Sr segregation on the LSM surface with the increase in the oxidation treatment. However, the formation of LaCrO_3 phase in the LSM coating/Fe-Cr alloy would be less likely under the conditions studied because there is little La segregation or enrichment on the

surface of the A-site nonstoichiometric LSM [[Jiang, 2001a](#)]. Nevertheless, in the case of stoichiometric LSM where the La enrichment occurs, the formation of LaCrO_3 in the LSM coating/Fe-Cr alloy couple would be kinetically favorable, as shown by Quadakkers et al [[1996](#)].

5.3 Conclusion

The interaction between the constituent oxides of LSM materials such as La_2O_3 , SrO and Mn_2O_3 and a Fe-Cr alloy has been investigated. The reaction processes of the deposition of Cr species and the reaction products between Fe-Cr alloy and the constituent oxides of LSM are significantly different. In the case of La_2O_3 and Mn_2O_3 coatings, the dominant products of the reaction between the Fe-Cr alloy and the coatings were probably LaCrO_3 and $(\text{Cr,Mn})_3\text{O}_4$ while in the case of SrO , the main deposits were Cr_2O_3 through the chemical dissociation of Cr species. The observations of the interaction between the LSM coating and Fe-Cr alloy are in general consistent with that observed between the constituent oxides and the Fe-Cr alloy, taking into consideration of the fact that surface oxides such as SrO and MnO_x are segregated originally on the LSM surface. The results indicate that the chemical interaction between the LSM electrodes and Fe-Cr alloys would be essentially related to the nature of the oxide species segregated/enriched on the freshly prepared LSM towards deposition and reaction of gaseous Cr species.

CHAPTER 6.

EFFECT OF Cr SPECIES ON OXYGEN REDUCTION REACTION AT LSM CATHODE

In this chapter, the O_2 reduction reactions on the LSM cathodes in the absence and presence of a chromia-forming alloy interconnect were studied. Major attention was paid to the investigation of the effect of Cr species including gaseous Cr species and solid Cr species deposition on the O_2 reduction reaction in comparison with the O_2 reduction reaction in the absence of chromia-forming alloy.

6.1 Experimental

The details of the LSM cathode/YSZ electrolyte sample preparation and the set-up of the electrochemical testing can be found in Chapter 3. The initial impedance and polarization behaviour of the freshly prepared LSM electrode in the absence and presence of a chromia-forming alloy with the current passage time were studied under a constant current density of 200 mA cm^{-2} in air at 900°C . The polarization potential (E_{Cathode}) was measured against the Pt air reference electrode. The current passage was interrupted from time to time to make EIS measurements using a Solartron 1260 frequency response analyzer in combination with a 1287 electrochemical interface. The frequency range was from 0.1 Hz to 100 kHz and the signal amplitude was 10 mV.

EIS measurements were performed at open circuit potential (OCP) and under cathodic dc bias. For EIS measurements under dc bias, a continuous cathodic current of 200 mA cm^{-2} without interruption was passed to the LSM electrode using an external galvanostatic/potentiostatic generator (Hokuto Denko HAB-151). The impedance responses were analyzed by the equivalent circuit, using a non-linear least square (NLLS) fitting program.

The dependence of temperature and partial pressure of oxygen on the O_2 reduction in the absence and presence of a chromia-forming alloy were studied in the temperature of $900\text{--}750^\circ\text{C}$ with the increments of 50°C and at the oxygen partial pressure between 0.01 atm to 1 atm. For the cases in the absence of chromia-forming alloy LSM electrodes were polarized at 900°C with a constant current of 200 mA cm^{-2} for 4 h prior to the impedance measurements. In the presence of chromia-forming alloy, the EIS measurements were conducted for LSM electrode after polarization at 900°C and 200 mA cm^{-2} for 45 h in air.

6.2 Results

Fig.6.1 shows the initial impedance responses of a freshly prepared LSM electrode for the O_2 reduction under a cathodic current passage of 200 mA cm^{-2} at 900°C in air in the absence of chromia-forming alloy. The impedance was measured under open circuit. The impedance responses for the LSM electrode were characterized by two overlapped and depressed arcs in the high-frequency range and low-frequency range, respectively. The equivalent circuit for the fitting is shown in Fig.6.1d, which is

Fig.6.1 Initial impedance responses of a LSM electrode for the O_2 reduction under cathodic current passage of 200 mA cm^{-2} at 900°C in the absence of chromia-forming alloy. (a) Nyquist plots, (b) Bode plots and (c) fitted electrode polarization resistances for individual impedance arcs. EIS was measured at OCP. Symbols are experimental data and lines are fitted results. The equivalent circuit used to evaluate the impedance curves is shown in (d).

composed of two (RQ) circuits in series (e.g., $LR_{\Omega}(R_HQ_H)(R_LQ_L)$). In the equivalent circuit, L, Q and R denote inductance, constant phase element (CPE) and electrode resistance, respectively. R_{Ω} is the ohmic resistance between cathode and reference electrode and subscript H and L correspond to the high and low frequency arcs. Generally, in a solid electrode/electrolyte system studied here, a constant phase element used represents a nonideal capacitance, given as $Z_{CPE}=A(j\omega)^{-n}$ [Jiang, 1997]. ω is the angular frequency and j is imaginary unit and n is the frequency power. For $n=0.5$, the CPE is a Warburg-type diffusion impedance and for $n=1$, the CPE is a pure capacitance. For the O₂ reduction at the LSM cathodes, the n values for the high-frequency arc (R_HQ_H) and low-frequency arc (R_LQ_L) are in the range of 0.55 to 0.95, indicating that Q_H and Q_L are not pure capacitance. In the figure, the symbols represent the experimental data and the solid lines are fitted results. Good agreement was found between the fitted and experimental data, indicating the reasonability of the equivalent circuit used. The time behaviour of the total electrode polarization resistance (R_E) and the resistances for individual impedance arcs is shown in Fig.6.1c. R_E is the sum of R_H and R_L .

For the O₂ reduction on the freshly prepared LSM electrode in the absence of chromia-forming alloy, the initial electrode interface (or polarization) resistance (R_E) was $2.15 \Omega \text{ cm}^2$, and reduced significantly with cathodic current passage. After cathodic current passage for 5 min, R_E was reduced to $1.28 \Omega \text{ cm}^2$ and further to $0.78 \Omega \text{ cm}^2$ after 240 min, about 3 times smaller than the initial R_E of LSM electrode before the current passage. The rapid reduction in the electrode polarization resistance

indicates the significant activation effect of the cathodic polarization on the electrochemical performance of freshly prepared LSM electrode. The characteristic frequency (indicated by the arrow in Fig.6.1b) initially at ~ 250 Hz for the reaction on the freshly prepared LSM electrode was increased to ~ 400 Hz after a cathodic current treatment for 5 min. The frequency peak was further shifted slightly to ~ 500 Hz after treatment for 60 min and stabilized. This indicates that different processes may dominate the O_2 reduction reaction before and after the cathodic polarization treatment on the LSM electrode. This appears to be supported by the time behaviour of R_H and R_L for the reaction on the freshly prepared LSM electrode, as shown in Fig.6.1c. Before the current passage, R_H and R_L were $0.65 \Omega \text{ cm}^2$ and $1.50 \Omega \text{ cm}^2$, respectively, showing that the electrode process associated with low-frequency arc dominates the O_2 reduction reaction. Both R_H and R_L decreased with the passage of cathodic current but the reduction in R_L was much more significant than that in R_H . This indicates that the enhancing effect of the cathodic polarization is primarily on the electrode process associated with the low-frequency arc, consistent with previous studies [[Wang, 1998](#); [Jiang, 2002a](#), [Chen, 2004b](#)].

The activation effect of cathodic polarization on the initial electrode behaviour of freshly prepared LSM electrode was also observed in the presence of chromia-forming alloy, as shown in Fig.6.2. However, in the presence of chromia-forming alloy, the reduction of impedance was much smaller compared to that in the absence of chromia-forming alloy. R_E was reduced from an initial value of $1.42 \Omega \text{ cm}^2$ to $0.97 \Omega \text{ cm}^2$ at the end of 240 min cathodic current treatment, a reduction of about 31%.

Fig.6.2 Initial impedance responses of a LSM electrode for the O_2 reduction under cathodic current passage of 200 mA cm^{-2} at 900°C in the presence of chromia-forming alloy. (a) Nyquist plots, (b) Bode plots and (c) fitted electrode polarization resistances for individual impedance arcs. EIS was measured at OCP.

Similarly, the effect of cathodic current treatment is mainly on the R_L at the early polarization stage, as shown in Fig.6.2c. However, different to that in the absence of

chromia-forming alloy, the characteristic frequency initially at ~250 Hz was slightly shifted to ~200 Hz after the passage of cathodic current in the presence of chromia-forming alloy (Fig.6.2b). This indicates that the O_2 reaction at the LSM electrode in the presence of chromia-forming alloy is increasingly dominated by the low-frequency electrode process.

The initial polarization curves of the freshly prepared LSM electrodes with cathodic current passage in the absence and the presence of chromia-forming alloy are shown in Fig.6.3. For the reaction in the absence of chromia-forming alloy, the time behaviour of polarization potential (E_{Cathode}) with cathodic current passage was consistent with that of impedance behaviour. The characteristic of E_{Cathode} with current passage can be divided into two distinct regions, as shown in Fig.6.3a. E_{Cathode} decreased rapidly with cathodic current passage (region I), followed by a region where the decrease in E_{Cathode} was much slower (region II). With applying of a current of 200 mA cm², E_{Cathode} instantly jumped to 538 mV and decreased rapidly to 349 mV in 2min. With the application of cathodic current passage, the starting value of E_{Cathode} decreases with the current passage. For example, after cathodic current passage for 60min, the starting E_{Cathode} was reduced to 343 mV. The reduction of E_{Cathode} in region II was smaller. After current passage for 60min and 240 min, E_{Cathode} was reduced to 282 mV and 266 mV, respectively. As the electrode ohmic resistance (R_{Ω}) remained almost the same with current passage, the decrease in polarization potential was mainly due to the decrease in overpotential (η). The significant decrease of E_{Cathode} under cathodic current passage confirms the enhancing effect of the cathodic polarization on the

Fig.6.3 Initial polarization curves of LSM electrodes as a function of a cathodic current density of 200 mA cm^{-2} at 900°C (a) in the absence and (b) the presence of chromia-forming alloy interconnect.

electrochemical activity of LSM electrode.

However, the polarization behaviour of LSM electrode in the presence of chromia-forming alloy was very different to that in the absence of chromia-forming alloy, as shown in Fig.6.3b, indicating clearly the effect of the presence of chromia-forming alloy on the O_2 reduction reaction. Instead of a rapid decrease, E_{Cathode} increased very quickly with the cathodic current passage in region I, followed

by a region II where the increase in E_{Cathode} was much slower. Different from that in the absence of chromia-forming alloy, the polarization behaviour was almost fully recoverable for the reaction in the presence of chromia-forming alloy at the early stage of the polarization. After cathodic current passage for only 2 min, E_{Cathode} increased rapidly from an initial value of 352 mV to 649 mV. After current passage for 180 min, E_{Cathode} started at 343 mV, almost the same as the initial value. In contrast, the change of E_{Cathode} in region II was much smaller and slower. After current passage for 60 min and 120 min, E_{Cathode} was 771 mV and 815 mV, respectively. It was found that the increase of E_{Cathode} in region II was mainly affected by the overall polarization time and not by the times of the current interruption, as indicated by the continuity of E_{Cathode} in region II. The significant difference in the trend and change of E_{Cathode} with current passage is a clear indication of the inhibiting effect of Cr species on the O_2 reduction reaction on LSM electrode. Such polarization behaviour with cathodic current passage was also reported by Jiang et al [2000a, 2002] and Matsuzaki et al [2000] for the reaction on LSM cathodes in the presence of chromia-forming alloy. The instantaneous and fully recoverable behaviour of E_{Cathode} with current passage time indicates that the inhibiting effect at the initial stage of polarization is most likely due to the gaseous Cr species rather than the Cr deposits on the cathode/electrolyte interface [Jiang, 2000a, 2002].

Fig.6.4 shows the electrode performance of LSM electrode for O_2 reduction reaction under a current density of 200 mA cm^{-2} at 900°C in the presence of chromia-forming alloy for 20 h. The cathodic current was interrupted from time to

Fig.6.4 Electrode performance of a LSM electrode for the O_2 reduction in the presence of chromia-forming alloy at 200 mA cm^{-2} and 900°C for 20 h.

time to carry out the impedance measurements. The value of electrode polarization resistance was directly obtained from the impedance curve, which was measured under open circuit. The change in R_Ω with current passage was negligible. Thus, the initial and steady state increase in polarization potential was mainly due to the increase in η . Similar to that in Fig.6.3b, there was a rapid increase in η , followed by a gradual increase with the current passage. After cathodic current passage for 20 h, η increased significantly from an initial value of 170 mV before current passage to 920 mV. However, the change of R_E with the current passage time was not in agreement with that of η during the long polarization period. R_E fluctuated with the cathodic current passage at the early stage.

Clearly, the impedance measured under the open circuit condition in the presence of chromia-forming alloy is not fully consistent with the change of η , which is most likely due to the partial recovery of LSM electrode performance after interruption of

the current in the presence of chromia-forming alloy [Matsuzaki, 2000]. Thus, The electrode performance of LSM electrode in the presence of chromia-forming alloy was tested under continuous cathodic current of 200 mA cm^{-2} without interruption at 900°C , and the impedance was measured under DC polarization potential (DC bias). In comparison, the electrode behaviour of LSM electrode for the O_2 reduction reaction was also analyzed in the absence of chromia-forming alloy under the same conditions, as shown in Fig.6.5. For the O_2 reduction reaction on the LSM electrode in the absence of chromia-forming alloy, the impedance reduced significantly with the cathodic current passage (Fig.6.5a). Compared with the impedance measured under open circuit (Fig.6.1a), the impedance measured under polarization potential was much smaller, indicating the significant enhancing effect of the cathodic polarization on the O_2 reduction reaction. It was observed that the change of R_E was consistent with that of E_{Cathode} under the cathodic current passage, as shown in Fig.6.5c. After continuous cathodic current passage for 15 min, E_{Cathode} decreased rapidly from the initial value of 502 mV to a steady value of 230 mV and stabilized with further current passage. R_E was reduced from $2.61 \text{ } \Omega \text{ cm}^2$ to $0.52 \text{ } \Omega \text{ cm}^2$ after polarization for 15 min and $0.45 \text{ } \Omega \text{ cm}^2$ for 60 min, respectively. It was also found that the cathodic polarization could lead to the decreasing in both R_H and R_L at the initial stage. However, with the continuous cathodic current passage, the decrease in R_E was mainly due to the decreasing in R_L . The characteristic frequency was abruptly increased from $\sim 250 \text{ Hz}$ to $\sim 1000 \text{ Hz}$ after cathodic current passage for 5 min, an indication of the dominant role of the high-frequency electrode process for the O_2 reduction under cathodic

Fig.6.5 Electrochemical behaviour of a LSM electrode for the O_2 reduction at a continuous cathodic current of 200 mA cm⁻² and 900°C in the absence of chromia-forming alloy. (a) Nyquist plots, (b) Bode plots and (c) polarization curves. EIS was measured under the polarization potential.

polarization. This again shows that the cathodic polarization enhances the O_2 reduction process associated the low-frequency arc, which is in agreement with impedance responses measured under open circuit.

Fig.6.6 shows the electrode behaviour of the LSM electrode in the presence of chromia-forming alloy under continuous cathodic current of 200 mA cm^{-2} at 900°C for 20 h. The impedance was measured under polarization potential. It was found that the impedance arc observed at the additional high frequencies (above 63K Hz) was due to the impedance ($\sim 0.48 \Omega \text{ cm}^2$) of the external galvanostatic/potentiostatic generator. Thus, the following discussion will be only on the high- and low-frequency arcs. With the cathodic current passage, the impedance arcs decreased in the early 60 min of current passage and then increased gradually (Fig.6.6a). It is interesting to see that the change of R_E almost follows the change of the polarization potential (E_{Cathode}). After continuous current passage for about 600 min, E_{Cathode} and R_E were stable and the increase in E_{Cathode} and R_E with the polarization was very small. The decrease in R_E at the early stage is most likely related to the activation effect of cathodic polarization on the O_2 reduction reaction on LSM electrode. R_E was $3.27 \Omega \text{ cm}^2$ after current passage for 1200 min, which is much higher than the R_E of $0.68 \Omega \text{ cm}^2$ after current passage for 2 min measured at the same current polarization conditions. Again, the rapid and significant increase in E_{Cathode} at the initial stage is due to inhibiting effect of gaseous Cr species generated from the chromia-forming alloy on the O_2 reduction reaction, as proposed earlier. The significant increase in R_E and E_{Cathode} indicates clearly the inhibiting effect of Cr species on the O_2 reduction reaction at the LSM electrode.

Fig.6.6 Electrochemical behaviour of a LSM electrode for the O_2 reduction at a continuous cathodic current of 200 mA cm^{-2} and 900°C in the presence of chromia-forming alloy. (a) Nyquist plots, (b) Bode plots and (c) polarization curves. EIS was measured under the polarization potential.

On the other hand, the characteristic frequency fluctuated with the cathodic polarization, showing that different electrode process may dominate the reaction during the polarization period. At the early stage of current passage, the characteristic frequency was shifted gradually from ~ 200 Hz to ~ 20 Hz after current passage for 120 min, indicating the dominated role of the low-frequency electrode process on the O_2 reduction reaction. However, an additional frequency shoulder was developed at ~ 250 Hz after current passage for 480 min, an indication of the increasing role of high-frequency electrode process on the reaction. However, the characteristic frequency was reduced to low frequencies again with the continuous current passage and it was ~ 40 Hz at the end of 1200 min current passage. This is further illustrated by the time behaviour of R_H and R_L under cathodic polarization (Fig.6.6c). After an initial decrease at the early stage of polarization, both R_H and R_L increased with the cathodic current passage, indicating that the presence of Cr species would affect significantly the O_2 reduction reaction processes associated with both high-frequency and low-frequency arcs.

The evolution of impedance for the O_2 reduction on the LSM electrodes was performed in the absence and presence of chromia-forming alloy just after the interruption of the continuous cathodic current passage. Fig.6.7 compares the impedance responses under the cathodic current of 200 mA cm^{-2} and open circuit. The impedances under the polarization potential are the same as that shown in Fig.6.5 and Fig.6.6 for the reaction in the absence and presence of chromia-forming alloy, respectively. For the O_2 reduction in the absence of chromia-forming alloy, after the

Fig.6.7 Impedance responses of LSM electrodes for O_2 reduction reaction at 900°C under the cathodic polarization of 200 mA cm^{-2} (a & c) in the absence and (b & d) the presence of chromia-forming alloy interconnect. (a & b) Nyquist Plots, (c & d) Bode plots. The measurements were made before and after the cathodic current was switched off.

cathodic current was switched off, the polarization potential became zero very rapidly.

The impedance increased significantly. The characteristic frequency was shifted quickly from $\sim 1000 \text{ Hz}$ to $\sim 500 \text{ Hz}$ after interruption of the current passage (Fig.6.7c), showing the enhancing effect of the cathodic polarization on the electrode process at the low frequencies. Such behaviour was also observed for the O_2 reduction reaction on a LSM thin film electrode [Gharbage, 1994]. However, for the O_2 reduction in the

presence of chromia-forming alloy, the impedance reduced significantly after the removal of the cathodic polarization, just opposite to that in the absence of chromia-forming alloy. The characteristic frequency at ~ 40 Hz was significantly increased to ~ 250 Hz after the current was interrupted (Fig.6.7d). An additional frequency shoulder was also observed at frequencies around 2500 Hz. This indicates that the O_2 reduction reaction under cathodic polarization in the presence of chromia-forming alloy is primarily dominated by the low-frequency electrode process.

Fig.6.8 shows the steady state polarization performance (e.g., η - j curves) for the O_2 reduction reaction at 900°C in the absence and presence of chromia-forming alloy, respectively. In the case of the absence of chromia-forming alloy, the LSM electrode was polarized at 200 mA cm^{-2} for 4 h before the measurement. For the LSM in the presence of chromia-forming alloy, the measurement was conducted after current passage for 20 h. In the presence of chromia-forming alloy, η increased rapidly with the increase of current and reached the concentration limiting region at a current density of about 80 mA cm^{-2} while for the O_2 reduction in the absence of chromia-forming alloy, the polarization curve did not show the concentration-limited behaviour even at a high current density of 300 mA cm^{-2} . The concentration-limited polarization behaviour of the LSM electrode in the presence of chromia-forming alloy again confirms the inhibiting effect of Cr species on the rate of the O_2 reduction reaction.

Fig.6.8 Polarization curves of LSM electrodes in the absence and presence of chromia-forming alloy at 900°C in air. LSM electrodes were polarized at 200 mA cm⁻² for 4 h and 20 h in the absence and presence of chromia-forming alloy prior to the measurement, respectively.

Fig.6.9 shows the impedance responses of LSM electrodes measured at open circuit and 900°C in the absence and the presence of chromia-forming alloy as a function of oxygen partial pressure. In the absence and the presence of chromia-forming alloy, the LSM electrodes were polarized for 4 h and 45 h at 200 mA cm⁻² prior to the impedance measurements, respectively. The EIS was measured at open circuit and oxygen partial pressure of 0.01-1 atm. Two depressed arcs can be observed at the high- and low-frequency regions. The size of impedance curves increased with the decrease of oxygen partial pressure in both cases. The values of R_H and R_L can be obtained through fitting the impedance curves to the proposed equivalent circuit.

Fig.6.9 Impedance responses of LSM electrodes for the O_2 reduction in (a) the absence and (b) presence of chromia-forming alloy interconnect as a function of oxygen partial pressure at 900°C . The LSM electrode in the absence and presence of chromia-forming alloy was polarized at 200 mA cm^{-2} for 4 h and 45 h, respectively, before the impedance measurement.

Fig.6.10 and Fig.6.11 show the plots of P_{O_2} -dependence of the electrode conductivity (σ is the reciprocal of electrode polarization resistance) of the electrode processes at high- and low-frequency arcs ($\sigma_H=1/R_H$ and $\sigma_L=1/R_L$) for the O_2 reduction reaction on LSM electrodes in the absence or presence of chromia-forming alloy at the temperature range of $750\text{-}900^\circ\text{C}$. The reaction orders with respect to P_{O_2} determined from the slopes are listed in Table 6.1. It was found that the reaction orders for both high- and low-frequency arcs did not show particular dependence on the temperature. The average reaction order of the total electrode conductivity for the reaction in the absence of chromia-forming alloy was about 0.34 and the value for the reaction in the presence of chromia-forming was slightly increased to 0.40. However, the reaction order of the high-frequency arc (σ_H) was independent of the oxygen partial pressure regardless of the presence of chromia-forming alloy. On the other hand, for the

Fig.6.10 Dependence of the electrode conductivities (σ_E , σ_H and σ_L) on the oxygen partial pressure for the O_2 reduction on the LSM electrodes in the absence of chromia-forming alloy interconnect at different temperatures.

low-frequency electrode process (σ_L) in the absence of chromia-forming alloy, the reaction order with respect to P_{O_2} was approximately 0.50, which is close to that reported on the LSM electrodes in the literature [Wang, 1998; Jiang, 2002b]. But the reaction order for σ_L in the presence of chromia-forming alloy was increased to 0.62, which was higher than that in the absence of chromia-forming alloy. This again indicates that the presence of Cr species would affect strongly the electrode process at the low-frequency arc for the O_2 reduction reaction on the LSM electrode.

Fig.6.11 Dependence of the electrode conductivities (σ_E , σ_H and σ_L) on the oxygen partial pressure for the O_2 reduction on the LSM electrodes in the presence of chromia-forming alloy at different temperatures.

Table 6.1 Reaction orders with respect to P_{O_2} of the electrode conductivities (σ_E , σ_H and σ_L) for the O_2 reduction on the LSM electrodes in the absence and presence of chromia-forming alloy at different temperatures.

Temperature (°C)	Reaction order, x in $P_{O_2}^x$					
	LSM cathode			LSM cathode/Fe-Cr alloy		
	σ_H	σ_L	σ_E	σ_H	σ_L	σ_E
900	0.05	0.58	0.34	-0.05	0.55	0.32
850	0.09	0.51	0.36	0.15	0.55	0.41
800	0.02	0.45	0.32	0.05	0.72	0.43
750	0.10	0.46	0.35	0.11	0.68	0.44

Fig.6.12 shows the activation energy plots of the electrode conductivity of high- and low-frequency arcs of LSM electrodes in the absence and presence of chromia-forming alloy in air. The activation energy value was calculated from the slopes of the curves. For the O_2 reduction on the LSM electrode in the absence of chromia-forming alloy, the activation energy of σ_L was 142 kJ mol^{-1} while the value of σ_H was 95 kJ mol^{-1} . The activation energy of $70\text{--}90 \text{ kJ mol}^{-1}$ for the electrode process at the high-frequency arc is also found by Youngblood et al [1993] and is close to that of the conductivity of a 8 mol% yttria stabilized zirconia [Ciacchi, 1994]. While for the O_2 reduction in the presence of chromia-forming alloy, the activation energy of σ_L was 153 kJ mol^{-1} , slightly higher than that in the absence of chromia-forming alloy. However, for electrode process at high-frequency arc, the activation energy increased significantly to 167 kJ mol^{-1} . The higher activation energy for the O_2 reduction at the

Fig.6.12 Activation energy plots of electrode conductivity of high- and low-frequency arcs (σ_H and σ_L) for the O_2 reduction on LSM electrodes in the absence and presence of chromia-forming alloy in air.

high-frequency arc in the presence of chromia-forming alloy than that in the absence of chromia-forming alloy was also found in earlier study of O_2 reduction on the LSM electrode/3 mol% Y_2O_3 - ZrO_2 electrolyte system [Jiang, 2000a]. This shows that after long-term cathodic polarization in the presence of chromia-forming alloy, the O_2 reduction process at the high-frequency arc was also strongly inhibited by the presence of Cr species.

6.3 Discussion

In the presence of chromia-forming alloy interconnect, for the O_2 reduction reaction on the LSM electrode after being cathodic polarized for a long time, there is considerable deposition of Cr species of fine grains and large crystals on the YSZ electrolyte surface, especially near the LSM electrode/YSZ electrolyte interface regions, as shown in Chapter 4. This is widely known and well reported in the literature [Taniguchi, 1995; Badwal, 1997; Matsuzaki, 2001; Paulson, 2004]. The Cr deposition on the LSM/YSZ interface increased with the cathodic polarization time. At the same time, the performance degradation (increase in E_{Cathode} and η) for the O_2 reduction increased significantly with the cathodic current passage (Fig.6.3 and Fig.6.4). Previous studies attribute the performance degradation to the loss of active sites at the TPB regions for the O_2 reduction on the LSM electrode [Taniguchi, 1995; Badwal, 1997]. However, the distribution of Cr deposits on the YSZ system observed shows no preferential deposition of Cr species at the TPB regions at 700-900°C (see Chapter 4). This indicates that there is no intrinsic relationship between the Cr

deposition and the TPB regions. As proposed earlier, the Cr deposition is basically a chemical dissociation process, initiated by the nucleation reaction between the gaseous Cr species and the nucleation agent. The Cr species deposition is not controlled by the electrochemical reaction in competition with the O₂ reduction at the TPB. However, as the microstructure and morphology of the electrode/electrolyte interface are very different for the reactions in the absence and presence of chromia-forming alloy, it is argued that the O₂ reduction on the LSM cathode would be strongly affected by the presence of Cr species. This has been clearly demonstrated in the present study.

The O₂ reduction reaction on the LSM-based electrodes in the absence of chromia-forming alloy has been extensively investigated [Lee, 1995; van Heuveln, 1997; Jiang, 1998; Kim, 2001; Chen, 2003]. Due to the high electronic conductivity but negligible oxygen ion conductivity of the LSM material, the O₂ reduction on the LSM cathode is believed to occur mainly at the three phase boundary between the LSM electrode, YSZ electrolyte and oxidant gas. Although there are still considerably disagreements in the exact reaction mechanism and kinetics for the reaction on the LSM electrode [Horita, 1998; Wang, 1998; Kim, 2001; Jiang, 2000a; Chen, 2003], the reaction steps of the O₂ reduction processes could be summarized as follows:

where $V_O^{\bullet\bullet}$ stands for an oxygen vacancy, subscript denoting the oxygen vacancy in the LSM electrode or YSZ electrolyte lattice. $O_{ad,LSM}$ indicates that the intermediate oxygen species dissociative adsorption and diffusion on the LSM electrode surface. Fig.6.13 is the schematic of the reaction steps of O_2 reduction on the LSM cathodes in the absence of chromia-forming alloy. Thus, one or several of above steps could be the rate-limiting steps for the O_2 reduction reaction. Detailed investigation of the O_2 reduction on the LSM electrodes shows that the reaction is most likely determined by at least two reaction steps, corresponding to the impedance arcs at the high- and low-frequency range.

Fig.6.13 Schematic of the reaction processes of O_2 reduction reaction on the LSM electrode in the absence of chromia-forming alloy.

The electrode processes at the low-frequency arc are commonly associated with the dissociated adsorption and diffusion of oxygen intermediate at the surface of LSM

[Jiang, 2000a; Horita, 1998; Jørgensen, 2001], i.e., step (6.1) and (6.2). In this study, for the O_2 reduction in the absence of chromia-forming alloy, the reaction order with respect to the partial pressure of oxygen for σ_L is around 0.5. As shown by Takeda et al [1987], a reaction order of 0.5 on the dependence of P_{O_2} indicates a reaction limited by atomic oxygen concentration, whereas a value of 1 indicates a reaction limited by molecular oxygen concentration. This clearly suggests that the electrode process associated with the low-frequency arc is a mixed process of dissociative adsorption and diffusion limited by atomic oxygen species.

With the high cathodic current passage, the electrode polarization resistance was reduced significantly and the characteristic frequency was shifted from ~ 250 Hz to ~ 500 Hz (Fig.6.1). The enhancing effect of cathodic current treatment is primarily on the low-frequency electrode process, which has also been reported in earlier studies [Wang, 1998; Chen, 2003]. This is also supported by the clear difference in the impedances measured under the cathodic polarization potential and just after the current is interrupted, as shown in Fig.6.7. This is most likely related to the generation of oxygen vacancies under cathodic polarization. Jiang et al [1998] and Lee et al [1995] proposed that when the cathodic potential is sufficiently negative, the reduction of LSM electrode, e.g., the partial reduction of Mn^{3+} to Mn^{2+} , could take place with concomitantly generation of oxygen vacancies, according to Reaction (4.3). The formation of oxygen vacancies increases active sites on the LSM surface, enhancing the dissociate adsorption and diffusion of oxygen species from the active sites to the TPB. At the early stage of the polarization, the formation of oxygen vacancies could

also lead to the decrease and removal of passivation species such as SrO and MnO_x originally existed on the electrode surface [Jiang, 2001a]. This is probably indicated by the non-recoverable behaviour of E_{Cathode} with the cathodic current passage (Fig.6.3a). However, the exact mechanism by which the cathodic polarization enhances the electrochemical performance of LSM electrode needs to be investigated further.

The electrode process at high-frequency arc is characterized by an activation energy of about 95 kJ mol^{-1} , similar to that for oxygen conduction in YSZ electrolyte material. No dependence of the electrode conductivity (σ_H) on the oxygen partial pressure suggest that neither atomic oxygen nor molecular oxygen be involved in the reaction step. A recent investigation of O_2 reduction on porous LSM electrodes shows that R_H is basically independent of the dc bias [Jiang, 2002], which is in agreement with the results in this study (Fig.6.5). This indicates that the electrode process at the high-frequency arc cannot be associated with a charge-transfer process (step (6.3)). The high-frequency arc most likely corresponds to the migration and diffusion process of oxygen ions from the TPB regions into the YSZ lattice, e.g., step (6.4) and (6.5) [Jiang, 1998; Wang, 1998; Jiang, 2000a; Kim, 2001; Chen, 2004]. Uchida et al [1999] found that the electrode performance of LSM increased with the ionic conductivity of the zirconia electrolyte in the temperature range of 800 to 1000°C. This indicates that the transport of oxygen ions into the electrolyte would be strongly related to the ionic conductivity of the electrolyte. The importance of electrolyte is also demonstrated by the decrease in R_H with the addition of YSZ material into pure LSM electrode due to the spatial enlargement of TPB area [Wang, 1998; Kim, 2001]. Under a high current,

the YSZ electrolyte could be decomposed to form a suboxide (ZrO_{1-x}), which is electronic conductor and contains a great number of oxygen vacancies [Nguyen, 1986]. This maybe lead to the small decrease of R_H measured under the cathodic current at the initial stage of polarization, as shown in Fig.6.5.

When the LSM cathode is in contact with the chromia-forming alloy interconnect, gaseous Cr species such as CrO_3 in dry air is produced from the chromium oxide scale formed on the alloy surface. The gaseous Cr species would kinetically inhibit the dissociative adsorption and diffusion of oxygen species on the LSM electrode surface and the activation energies of σ_L of 153 kJ mol^{-1} is close to that in the absence of chromia-forming alloy of 142 kJ mol^{-1} , indicating that gaseous Cr species does not affect the mechanism of the reaction. The inhibiting effect of the gaseous Cr species can be clearly demonstrated by the initial polarization potential (E_{Cathode}) behaviour for the reaction on the LSM electrode in the presence of chromia-forming alloy. As shown in Fig.6.3, the time behaviour of E_{Cathode} with the current passage in the presence of chromia-forming alloy is just opposite to that in the absence of chromia-forming alloy at the early stages of cathodic polarization. Instead of the rapid decrease, E_{Cathode} increased rapidly with the cathodic current passage. Considering that there is very little the Cr species deposit on the TPB regions at the initial stage, the initial performance degradation is mainly affected by the gaseous Cr species rather than the solid Cr deposits. This can also be demonstrated by the much lower increase in E_{Cathode} for O_2 reduction on the LSCF electrode compared to the LSM electrode in the presence of chromia-forming alloy [Jiang, 2001b]. LSCF electrode is a mixed ionic and electronic

conducting material [Esquirol, 2004]. It is generally believed that the O_2 reduction at LSCF electrode is dominated by the electrode bulk process and to a less extent by the electrode surface process. The inhibiting effect of the gaseous Cr species on the O_2 reduction would be in principle similar to that of oxygen-containing species (OCS) such as Pt-O on the oxygen diffusion and charge-transfer for the reaction on the Pt electrode [Sridhar, 1997]. The instantaneous and substantial increase of E_{Cathode} for the reaction on LSM electrode indicates that the gaseous Cr species could quickly adsorb at the oxygen vacancies on the electrode surface generated under the cathodic polarization, effectively blocking the active sites for the dissociative adsorption and diffusion of oxygen species on the LSM surface and significantly increasing the resistance for the electrode surface process. The inhibiting effect of gaseous Cr species on the surface diffusion process would be most effective under polarization. This is supported by the relative stable R_E measured at open circuit for the reaction in the presence of chromia-forming alloy and the gradually increasing R_E under the cathodic current passage (Fig.6.2 and 6.7). As shown in Fig.6.7, the impedance under polarization was much larger than that just after the current is interrupted in the presence of chromia-forming alloy. The significant inhibiting effect of gaseous Cr specie on the dissociative adsorption and diffusion of oxygen species also appears to be supported by the shift of characteristic frequency to lower frequencies for the O_2 reduction (Fig.6.2 and 6.6). A characteristic frequency of ~ 40 Hz was developed for the reaction under continuous cathodic polarization (Fig.6.6d), an indication of the dominated role of the low-frequency electrode process. Moreover, after polarization

for 45 h, the low-frequency electrode process (σ_L) showed a 0.62 power of dependence of oxygen partial pressure, larger than 0.5 for the reaction in the absence of chromia-forming alloy. This indicates that the presence of gaseous Cr species greatly inhibits the oxygen dissociation and diffusion process on the LSM electrode surface and leads to a much slower rate.

While for the electrode process at the high-frequency arc in the presence of chromia-forming alloy, as a dense and thick Cr species layer (fine Cr_2O_3 grains and $(Cr,Mn)_3O_4$ spinels) was formed at the YSZ electrolyte surface after long-term cathodic polarization, the oxygen ions from the TPB have to diffuse through the Cr species deposits layer before entering the YSZ electrolyte body. It is well known that Cr_2O_3 is a poor oxygen ion conductor. The oxygen self-diffusion coefficient in polycrystal Cr_2O_3 is $10^{-13} \text{ cm}^2 \text{ s}^{-1}$ at 1100°C [Sabioni, 1992], significantly lower than that in doped ZrO_2 electrolyte of 10^{-8} to $10^{-7} \text{ cm}^2 \text{ s}^{-2}$ at 900°C [Simpson, 1966; Park, 1991]. Therefore, the migration of oxygen ions into electrolyte would be dominated by the diffusion of oxygen through the solid Cr_2O_3 and $(Cr,Mn)_3O_4$ deposit layer, leading to a significant increase in the electrode resistance of the migration of oxygen ions into YSZ electrolyte. This is indicated by that the increase of R_H and the shift of characteristic frequency from low to high frequencies with the cathodic current passage (Fig.6.6). The activation energy of 167 kJ mol^{-1} of R_H in the presence of chromia-forming alloy was much higher than that of 95 kJ mol^{-1} for the reaction in the absence of the alloy. This could be associated with the high activation energy of $\sim 230 \text{ kJ mol}^{-1}$ for oxygen diffusion in Cr_2O_3 [Sabioni, 1992]. Therefore, in the case of thick

deposition of Cr species on the YSZ electrolyte surface, the electrode process associated with the high-frequency arc can be written as follows

where $\text{V}_{\text{O, Cr deposits}}^{\bullet\bullet}$ is an oxygen vacancy in the $\text{Cr}_2\text{O}_3/(\text{Cr, Mn})_3\text{O}_4$ oxide lattice or interstitial site. As the diffusion of oxygen ions in Cr_2O_3 is much lower than that in the YSZ electrolyte, the inhibiting effect of the Cr species deposits on the overall O₂ reduction reaction becomes increasing dominant with the growth of thickness of Cr deposition, thus with the polarization time, resulting in much poor electrode performance. This is also supported by the rapid increase in R_H with the current passage, showing the migration of oxygen ions to be the dominant rate-limiting step for the O₂ reduction. Fig.6.14 schematically shows the reaction steps of the O₂ reduction on the LSM electrode in the presence of chromia-forming alloy.

Fig.6.14 Schematic of the reaction processes of O₂ reduction reaction on the LSM electrode in the presence of chromia-forming alloy.

Thus, Cr species, i.e., gaseous Cr species and solid $C_2O_3/(Cr,Mn)_3O_4$ deposits, not only has a significant inhibiting effect on the kinetics for the O_2 reduction reaction on the LSM electrode but also has a significant effect on the reaction mechanism. The combined inhibiting effect of gaseous Cr species on the surface diffusion of oxygen on the LSM surface and of solid Cr deposits on the migration of oxygen ions into the electrolyte is clearly indicated by the concentration-limited polarization behaviour as shown in Fig.6.8, compared to that in the absence of chromia-forming alloy. On the other hand, it is unavoidable that the Cr species deposits layer at the YSZ electrolyte surface would cover physically some of the TPB region and reduce the active sites for the O_2 reduction, leading to the performance degradation for O_2 reduction reaction on LSM electrode during the long-term operation.

One of the important observations in the present study is that the impedance responses under polarization potential for the O_2 reduction on the LSM electrode in the presence of chromia-forming alloy is significantly different from that measured under open circuit. As shown in Fig.6.7, when η was as high as 1480 mV at a current density of 200 mA cm^{-2} and 900°C in air but the electrode resistance was much larger than that under open circuit. In comparison, for the O_2 reduction in the absence of chromia-forming alloy, R_E reduced significantly under cathodic polarization potential, showing the clear sign of electrocatalytic effect of cathodic polarization on the LSM electrode performance. This indicates that the enhancing effect of oxygen vacancies generated under high cathodic polarization is no longer effective due to the presence of gaseous Cr species in the system, preventing the propagation of oxygen vacancies into

the LSM electrode bulk and thus reducing the reaction sites. This is also demonstrated by the extraordinary increase in the polarization potential with the cathodic current passage for the reaction in the presence of chromia-forming alloy.

6.4 Conclusion

The effect of chromia-forming alloy interconnect on the O_2 reduction reaction at the LSM electrodes has been investigated in comparison with the reaction without chromia-forming alloy. The O_2 reduction is strongly inhibited by the existence of Cr species, leading to a significant increase of polarization potential. Two electrode processes are identified for the O_2 reduction in the absence of chromia-forming alloy, i.e., adsorption and diffusion of oxygen on the LSM surface and incorporation of oxygen ions into the YSZ electrolyte, corresponding to the low- and high-frequency arcs in the impedance curve, respectively. In the presence of chromia-forming alloy interconnect, the surface diffusion process of oxygen species is inhibited by the gaseous Cr specie generated at high temperature while the migration process of oxygen ions into YSZ electrolyte is limited by the $Cr_2O_3/(Cr,Mn)_3O_4$ solid species deposited on the YSZ electrolyte surface. The solid Cr species deposits layer formed at the LSM electrode/YSZ electrolyte interface increased with the polarization time, which would not only significantly affect the kinetics but also change the mechanism for the O_2 reduction on the LSM electrode.

CHAPTER 7.

DEPOSITION OF Cr SPECIES AT (La,Sr)(Co,Fe)O₃ CATHODE

(La,Sr)(Co,Fe)O₃ (LSCF) perovskite material has been extensively investigated and considered as one of the most promising cathode candidates for the intermediate-temperature solid oxide fuel cell (ITSOFC) due to its high mixed electronic and ionic conductivities and high electrocatalytic activity for the O₂ reduction reaction [[Adler, 1996](#); [Liu, 1998](#); [Esquirol, 2005](#)]. However, despite the promising potentials of LSCF materials in the development of ITSOFC cathode, few studies are reported on the interaction reaction between the LSCF electrode and the chromia-forming alloy interconnect and the mechanism of the Cr deposition at the LSCF cathode is not clear. In this chapter, the results of detailed investigation on Cr species deposition process at the LSCF electrode/GDC electrolyte cell system are reported and mechanism and kinetics of the Cr species deposition at the LSCF electrode are discussed.

7.1 Experimental

The Fe-Cr alloy interconnect, the LSCF/GDC testing cell configuration and the arrangement of the metallic interconnect for the electrochemical tests were the same to that with the LSM/YSZ cell (see Chapter 3). In a different experiment, a Pt mesh was

placed between the metallic interconnect and the electrode coating to avoid the direct contact between the alloy and the coating. Polarization behaviour of LSCF electrode was carried out under a constant current density of 200 mA cm^{-2} in air at 900°C and 800°C . The current passage was interrupted from time to time to make the EIS measurements. EIS curves were measured at open circuit.

7.2 Results

Fig.7.1 shows the initial impedance and polarization behaviour of a LSCF electrode for the O_2 reduction reaction under a cathodic current of 200 mA cm^{-2} at 900°C in the absence of Fe-Cr alloy interconnect. The impedance responses measured at open circuit and 900°C were quite small, indicating high electrochemical activity of the LSCF electrode for the O_2 reduction reaction [Liu, 1998; Esquirol, 2004]. The initial electrode resistance (R_E) was $\sim 0.15 \Omega \text{ cm}^2$ and the change with the cathodic current passage time is very small (Fig.7.1a). The high activity of LSCF electrode is also indicated by the very low η ($\sim 12 \text{ mV}$ at 200 mA cm^{-2}), as shown in Fig.7.1b. The cathodic polarization potential, E_{Cathode} , changed very little with the cathodic current passage, showing that cathodic polarization has little activation effect on the electrocatalytic activity of the LSCF electrode.

Fig.7.1 Initial impedance responses and polarization curves of the LSCF electrode as a function of the cathodic current passage time at 200 mA cm^{-2} and 900°C in the absence of Fe-Cr alloy.

Fig.7.2 is the impedance and polarization behaviour of a LSCF electrode for the O_2 reduction reaction at 200 mA cm^{-2} and 900°C in the presence of Fe-Cr alloy interconnect. The impedance arcs were larger than that in the absence of Fe-Cr alloy, indicating the increased electrode resistance for the O_2 reduction on the LSCF electrode in the presence of gaseous Cr species. The initial R_E was $0.21 \text{ } \Omega \text{ cm}^2$ and

increased considerably with the current passage time. After the cathodic current passage for 1200 min, R_E increased to $0.78 \Omega \text{ cm}^2$, more than three times larger than the initial R_E . There was a small decreasing in the ohmic resistance (R_Ω) in the early stage of the cathodic current passage, which is likely due to the improved contact between the cathode coating and the alloy interconnect with the current passage. The time behaviour of E_{Cathode} for the reaction on the LSCF electrode is also remarkably different from that in the absence of Fe-Cr alloy. E_{Cathode} increases steadily with the current passage and developed two distinct potential regions. E_{Cathode} increases rapidly with the cathodic current passage, reaching a potential plateau where the increase in E_{Cathode} is much slow. This is similar to the polarization behaviour for the O_2 reduction reaction on the LSM cathode in the presence of Fe-Cr alloy interconnect. The magnitude of the polarization potential change increases with the current passage time. As the change in R_Ω is quite small, the increase of E_{Cathode} would be mainly due to the increase of overpotential (η) (Fig.7.2b). For the O_2 reduction reaction in the presence of Fe-Cr alloy, η at 200 mA cm^{-2} was 343 mV after cathodic current passage for 1200 min, much larger than the initial η of 21 mV. The remarkably different impedance and polarization behaviour for the O_2 reduction reaction in the presence of Fe-Cr alloy interconnect, compared to that in the absence of the alloy, indicate the significant poisoning effect of the gaseous Cr species on the O_2 reduction reaction at the LSCF electrode.

Fig.7.2 Initial impedance responses and polarization curves of the LSCF electrode as a function of the cathodic current passage time at 200 mA cm^{-2} and 900°C in the presence of Fe-Cr alloy.

Fig.7.3 shows the SEM micrographs of LSCF electrode and GDC electrolyte surface in the presence of Fe-Cr alloy interconnect after cathodic polarization at 200 mA cm^{-2} and 900°C for 20 h. For comparison, the SEM micrograph of a LSCF electrode after polarization at 200 mA cm^{-2} and 900°C in the absence of Fe-Cr alloy for

Fig.7.3 SEM micrographs of a LSCF electrode after polarized at 200 mA cm^{-2} and 900°C in the presence of Fe-Cr alloy for 20h. (a) Electrode surface under the rib of interconnect; (b) electrode surface under the channel of interconnect; (c) the edge of the LSCF electrode under the rib of interconnect and (d) the edge of the LSCF electrode under the channel of interconnect. The surface of a LSCF electrode after polarization at 200 mA cm^{-2} and 900°C for 2 h in the absence of Fe-Cr alloy is shown in (e).

2 h is also shown in the figure. The very different morphologies of the LSCF electrode surfaces in the absence and presence of Fe-Cr alloy interconnect show the significant deposition of Cr species on the LSCF electrode surface in the presence of Fe-Cr alloy

interconnect. In the absence of Fe-Cr alloy interconnect, the microstructure of LSCF electrode is characterized by very fine and uniformly distributed LSCF particles with grain size of less than 0.1 μm (Fig.7.3e). There is also a good distribution of large and small pores. In the presence of Fe-Cr alloy interconnect, the deposition of Cr occurs. On the LSCF electrode surface under the rib of the Fe-Cr alloy interconnect, there was significant deposition of particles with distinct crystal facets (Fig.7.3a). The LSCF electrode surface was almost covered by the deposited particles. The size of the crystals was in the range of 4-6 μm , significant larger than the grain size of the LSCF particles (less than 0.1 μm). The deposition on the LSCF electrode surface under the channel of Fe-Cr alloy was significantly lower than that under the rib of the alloy, as indicated by the significant difference in the densities and quantities of the deposited particles (Fig.7.3b). On the LSCF electrode surface under the channel of Fe-Cr alloy, the deposited particles are not continuous and the fine LSCF particles are clearly visible. The areas of the electrode surface under the rib or channel of Fe-Cr alloy interconnect were easily identified from the contact mark of the alloy left on the LSCF electrode coating. The significant difference in the Cr deposition on the LSCF electrode surface under the rib and channel of the metallic interconnect indicates the significant effect of the interconnect flow field on the deposition, which is similar to that on the LSM/YSZ system under similar experimental conditions. On the other hand, the surface of the GDC electrolyte close to the edge of the LSCF electrode was in general very clean with no significant deposits on the areas under the ribs and channels of the alloy interconnect except a few isolated particles (Fig.7.3c & 7.4d). There is no

formation of deposition bands or rings on the GDC electrolyte surface close to the edge of the LSCF electrode. This is very different from that observed for the Cr deposition in the LSM/YSZ system [Paulson, 2004; Jiang, 2000a, 2001 and 2005]. It appears that the Cr deposition preferentially occurs on the LSCF electrode surface rather than on the GDC electrolyte surface at the initial stage of the polarization.

Fig.7.4 shows the EDS patterns of the deposition particles formed on the LSCF electrode surface under the rib and channel of the Fe-Cr alloy interconnect after cathodic polarization at 200 mA cm^{-2} and 900°C for 20 h. The crystals formed on the

Fig.7.4 EDS patterns of the deposit particles on the LSCF electrode (a) under the rib of Fe-Cr alloy interconnect (shown in Fig.7.3a) and (b) under the channel of interconnect (shown in Fig.7.3b).

LSCF electrode surface under the rib of interconnect primarily contained Sr and Cr with relatively minor amounts of La, Co and Fe (Fig.7.4a). EDS results indicate the high Sr and Cr contents in the deposits formed on the LSCF electrode. A similar composition was also found for the particles on the LSCF electrode surface under the channel of interconnect, although the intensity of Cr compared to other elements of LSCF was relatively lower. Fig.7.5 is the corresponding XRD pattern taken on the LSCF surface in the presence of a Fe-Cr alloy interconnect after cathodic polarization at 200 mA cm^{-2} and 900°C for 20 h. In addition to the existence of the LSCF electrode and GDC electrolyte, the formation of the SrCrO_4 phases is identified. Some small peaks may be related to the Cr_2O_3 phase. This indicates that the large particles formed on the LSCF electrode surface (Fig.7.3a & 7.3b) are SrCrO_4 phase.

Fig.7.5 XRD pattern of the LSCF electrode/GDC electrolyte cell after cathodic current passage at 200 mA cm^{-2} and 900°C for 20h in the presence of Fe-Cr alloy.

To view the bulk of LSCF electrode, the Cr deposit layer on the surface of the LSCF electrode coating was carefully removed by a doctor blade. The electrode was

pre-polarized at 200 mA cm^{-2} and 900°C in the presence of Fe-Cr alloy interconnect for 20 h. Fig.7.6 shows the SEM micrographs of the LSCF electrode underneath the Cr deposit layer and the cross section of the electrode coating. There is no formation of large crystals inside the LSCF electrode or at the LSCF electrode and GDC electrolyte interface region. EDS analysis could not detect the presence of Cr inside the LSCF electrode or near the LSCF/GDC interface regions under the conditions of the present study. This again indicates the preferential deposition of Cr species on the LSCF electrode surface. The observation of Cr deposition on LSCF electrode/GDC electrolyte in the present study is consistent with that reported by Simner et al [2005].

Fig.7.6 SEM micrographs of (a) LSCF electrode coating underneath the deposit layer and (b) cross section of LSCF electrode. The LSCF electrode was polarized at 200 mA cm^{-2} and 900°C for 20h in the presence of Fe-Cr alloy.

Fig.7.7 shows the SEM micrographs of the LSCF electrode surface under the rib of the Fe-Cr alloy interconnect after cathodic current passage at 200 mA cm^{-2} and 900°C for different times. Fig.7.8 is the corresponding SEM micrographs of the LSCF electrode surface under the channel of the Fe-Cr alloy interconnect. Before the application of the cathodic current passage, the LSCF electrode was already partially covered by the Cr species deposits (Fig.7.7a). In this case the LSCF electrode was heated to the testing temperature of 900°C and held for 1 h under open circuit. This indicates that the deposition of Cr species on the LSCF electrode has no direct relationship with the cathodic polarization. In another words, the deposition of Cr species on the LSCF electrode is not limited by the electrochemical reaction of gaseous Cr species and could not be in direct competition with the O_2 reduction reaction, which is consistent with the proposed mechanism for the Cr deposition in the LSM/YSZ system (Chapter 4). Large Cr species deposits with distinct crystal facets were formed on the LSCF electrode in the presence of Fe-Cr alloy, despite the different cathodic polarization time. Nevertheless, the Cr deposition increased with the increase of cathodic polarization time. After the polarization for 20 h, the LSCF surface was almost completely covered by the Cr deposits (Fig.7.7e). In the case of the surface of the LSCF electrode under the channels of the alloy, the deposition of Cr species was much less (Fig.7.8). There was no visible formation of Cr particles on the LSCF electrode surface before the cathodic current passage (Fig.7.8a). However, with the increasing of the polarization time, Cr deposits with distinct facets were also formed on the LSCF electrode surface (Fig.7.8e).

Fig.7.7 SEM micrographs of a LSCF electrode under the rib of Fe-Cr alloy interconnect after cathodic current passage at 200 mA cm^{-2} and 900°C for (a) 0 min; (b) 30 min; (c) 60 min; (d) 4 h and (e) 20 h.

Fig.7.8 SEM micrographs of a LSCF electrode under the channel of Fe-Cr alloy interconnect after cathodic current passage at 200 mA cm^{-2} and 900°C for (a) 0 min; (b) 30 min; (c) 60 min; (d) 4 h and (e) 20 h.

Fig.7.9 shows the SEM micrographs of the GDC electrolyte surface in contact with the LSCF electrode coating in the presence of Fe-Cr alloy at 200 mA cm^{-2} and 900°C after cathodic polarization for different time. The LSCF electrode coating was

removed by HCl acid treatment. The electrolyte surfaces were clean and there was no deposition of large crystal even after cathodic polarization for 20 h (Fig.7.9d). The fine concave marks were the contacts between the LSCF particles and GDC electrolyte, formed during the sintering of the electrode. EDS analysis did not detect Cr species on the surface of the GDC electrolyte. This indicates that isolated small particles were the LSCF left on the GDC electrolyte surface. This again shows that in contrast to the Cr deposition on the LSM electrode and YSZ electrolyte system, Cr does not preferentially deposit on the GDC electrolyte surface.

Fig.7.9 SEM micrographs of GDC electrolyte surface in contact with LSCF electrode in the presence of Fe-Cr alloy after cathodic current passage at 200 mA cm^{-2} and 900°C for (a) 30 min; (b) 60 min; (c) 4 h and (d) 20 h. LSCF electrode was removed by HCl acid treatment.

Fig.7.10 shows the SEM micrographs of a LSCF electrode surface after cathodic polarization at 200 mA cm^{-2} and 900°C for 20 h in the presence of Fe-Cr alloy interconnect. In this experiment, a Pt mesh was placed between the LSCF electrode coating and the Fe-Cr alloy so that the Fe-Cr alloy was not in direct contact with the LSCF electrode coating. Fig.7.11 shows the corresponding EDS patterns of the deposited particles on the LSCF electrode under the rib and channel of the Fe-Cr alloy interconnect. Particles with distinct crystal facets were formed on the LSCF electrode surface under the rib of Fe-Cr alloy (Fig.7.10a). The morphology of the deposits was

Fig.7.10 SEM micrographs of a LSCF electrode after cathodic current passage at 200 mA cm^{-2} and 900°C for 20 h in the presence of Fe-Cr alloy interconnect. (a) The LSCF surface under the rib of the interconnect and (b) the LSCF surface under the channel of the interconnect. In this test, LSCF electrode was separated from the Fe-Cr alloy interconnect by Pt mesh.

somewhat similar to that formed on the LSCF electrode surface in direct contact with the Fe-Cr alloy. However, the amount of the Cr deposits was much less in comparison to that on the LSCF electrode surface in direct contact with the Fe-Cr alloy interconnect (Fig.7.3a & 7.3b). Deposition of Cr species on the LSCF electrode surface in contact with Pt mesh under the channel of Fe-Cr alloy was also lower than that under the rib of the alloy, consistent with the observation of the LSCF electrode in direct contact with Fe-Cr alloy (Fig.7.7 & 7.8). EDS identified the presence of Cr and high intensity of Sr, indicating that the deposited crystals were also SrCrO_4 spinels (Fig.7.11). EDS pattern analysis also shows that the content of Cr species on the LSCF coating under the channel was significantly lower than that under the rib of alloy (Fig.7.11b). As there was no direct contact between LSCF electrode and Fe-Cr alloy, Cr species can only transport from the alloy to the LSCF coating via vapor phase diffusion. This indicates that the Cr deposition on the LSCF electrode is dominated by the gas phase transportation and thus strongly affected by the flow field design of the metallic interconnect [[Jiang, 2001](#)].

The deposition of Cr species on the LSCF electrode was also investigated at different temperatures. Fig.7.12 shows the SEM micrographs of the LSCF electrode surface after cathodic current passage at 200 mA cm^{-2} and 900°C for 20 h and 800°C for 40 h in the presence of Fe-Cr alloy interconnect. The micrographs were taken on the LSCF electrode surface under the rib of the Fe-Cr alloy. At 900°C , the LSCF electrode surface was almost covered by the Cr deposits. However, the Cr deposits formed at 800°C was smaller in size and much lower in quantity as compared to that

Fig.7.11 EDS patterns of the deposited particles on the LSCF electrode as shown in Fig.7.10 (a) under the rib and (b) under the channel of Fe-Cr alloy interconnect.

formed at 900°C even though the electrode was polarized for longer time at 800°C. This indicates that the deposition of Cr species is significantly affected by the operation temperature of the fuel cell.

7.3 Discussion

As shown in this study, the deposition of Cr species in the system of LSCF electrode and GDC electrolyte is significant under SOFC operation conditions. The results for the Cr deposition process can be summarized as follows.

- The impedance and polarization responses for the O₂ reduction reaction in the

Fig.7.12 SEM micrographs of the LSCF electrode surface under the rib of the Fe-Cr alloy interconnect after cathodic current passage at 200 mA cm^{-2} at (a) 900°C and (b) 800°C . The LSCF electrode at 900°C was polarized for 20 h while the electrode at 800°C was polarized for 40 h.

presence of Fe-Cr alloy interconnect behaved very differently as compared to that in the absence of the alloy. There is significant increase in the electrode polarization resistance and overpotential for the reaction on the LSCF electrode in the presence of Fe-Cr alloy interconnect, indicating the poisoning effect of the gaseous Cr species on the O_2 reduction at the LSCF electrodes. Nevertheless, the magnitude of the inhibiting effect on the electrochemical activity of LSCF electrode for the O_2 reduction reaction is relatively smaller than that on the LSM electrode under similar experimental conditions (see Chapter 4).

- Deposition of Cr species occurred on the LSCF electrode surface with and without the cathodic current passage (Fig.7.7). This clearly indicates that the deposition of Cr species at the LSCF electrode has no intrinsic relationship with the electrochemical polarization.

- Under the present testing conditions, Cr species preferentially deposited on the surface of the LSCF electrode rather than within the LSCF electrode or at the LSCF electrode/GDC electrolyte interface under the present testing conditions (Fig.7.3 & 7.6). There is no formation of deposit bands or rings on the GDC electrolyte surface close to the edge of the LSCF electrode. The Cr deposits are mainly SrCrO_4 spinel phase in addition to Cr_2O_3 .

- The deposition of Cr species on the LSCF electrode surface under the rib of Fe-Cr alloy interconnect is significantly higher than that under the channels of the interconnect. This is similar to that on the LSM electrode, as show in Chapter 4.

- Separation of the LSCF electrode coating and Fe-Cr alloy interconnect by a Pt mesh does not change the nature of the Cr deposition process though the amount of the Cr deposits is reduced.

- Similar to the Cr deposition in the LSM electrode/YSZ electrolyte system, the deposition of Cr species is significant reduced with the decrease in the temperature.

Adler et al [[1996](#)] studied in detail the reaction mechanism of the O_2 reduction reaction on mixed ionic and electronic conducting oxides such as LSCF and proposed that the impedance for the reaction is limited by the processes associated with interface

charge-transfer and oxygen-exchange at the gas/mixed conductor surface. The interface charge-transfer occurs at the electrode/electrolyte for ionic transfer and at the electrode/current collector for electron-transfer. The important role of the charge transfer at the electrode/electrolyte interface for the O_2 reduction reaction on porous mixed conducting electrodes such as LSCF cathodes is also reported by others [Liu, 1998; Gödickemeier, 1997; Hu, 1998]. However, as observed in the present study, Cr deposition preferentially occurs on the surface of the LSCF electrode and there is negligible Cr deposition inside the LSCF electrode or at the LSCF/GDC interface region, consistent with that reported by Simner et al [2005]. The deposition of Cr species on the LSCF electrode surface under open circuit also indicates that Cr deposition in the LSCF/GDC system is not controlled by the electrochemical process. This shows that Cr deposition in the LSCF/GDC system cannot be an electrochemical reduction of gaseous Cr species in competition with O_2 reduction reaction. Consequently, the deposition of Cr species at the LSCF electrode is in nature a chemical process. This conclusion is consistent with the proposed mechanism of the Cr deposition process at the LSM electrode.

However, there are significant differences in the manner of the Cr deposition process between the LSCF/GDC and LSM/YSZ systems. In the case of LSM/YSZ system, the Cr deposition occurs preferentially on the YSZ electrolyte surface and characterized by the formation of distinct deposit bands and rings on the YSZ electrolyte surface close to the edge of the LSM electrode (see Chapter 4). Cr deposition on the YSZ electrolyte surface can occur as far as $\sim 250\text{ }\mu\text{m}$ away from the

edge of the LSM electrode. On the other hand, as shown in the present study, the deposition of Cr species in the LSCF electrode and GDC electrolyte system occurs preferentially on the surface of the LSCF electrode and the deposition of Cr inside the LSCF coating and on the GDC electrolyte surface in contact with the LSCF electrode is negligible under the conditions of the study (Fig.7.6 & 7.9). There are no Cr deposit bands or rings on the GDC electrolyte surface close to the edge of the LSCF electrode. As the Cr deposition processes in both systems are chemical in nature, the significant difference in the preferential deposition observed in the LSCF/GDC and LSM/YSZ system is most likely related to the nature of the nuclei for the Cr deposition.

As discussion in Chapter 4, for the Cr deposition in the LSM/YSZ system, the nucleation for the Cr deposition is induced by the manganese species particularly the Mn^{2+} formed under cathodic polarization and at high temperatures. Due to the fact that Mn^{2+} species are very mobile, the deposition would occur preferentially on the YSZ electrolyte surface where the contact frequency and duration between the mobile Mn species and gaseous Cr species would be high enough for the nucleation reaction. However, in the case of the LSCF/GDC system, the nuclei for the Cr deposition reaction are most likely Sr species enriched or segregated on the LSCF electrode surface. Miura et al [1995] studied oxygen permeability of LSCF membrane with and without acid etching and found the acid etching significantly improved the oxygen surface diffusion and permeability of the membrane. X-ray Photoelectron Spectroscopy (XPS) analysis shows that acid etching mainly reduced the SrO content on the membrane surface. The most direct evidence of the Sr surface segregation in

ABO₃-type perovskite is likely the one provided by Majkic et al on the study of the stress-induced diffusion and defect chemistry of La_{0.2}Sr_{0.8}Fe_{0.8}Cr_{0.2}O_{3-δ} (LSFCr) [Majkic, 2004]. When the specimen was quenched from 1100°C, the Sr-3d region on the XPS spectra shifted to higher binding energies for samples quenched from low oxygen partial pressure (10⁻¹⁰-10⁻¹³ Pa) in comparison to the sample quenched in air. This indicates more surface-bounded Sr on the samples quenched from low oxygen partial pressure. On a creep-quenched LSFCr specimen, the elemental map of ⁸⁸Sr by SIMS technique revealed the Sr segregation at grain boundaries and corresponding elemental maps of La, Fe and Cr revealed no grain boundary segregation. Detailed XPS study of La_{1-x}Sr_x-based perovskite-type oxides including La_{0.4}Sr_{0.6}Fe_{0.8}Co_{0.2}O₃ also revealed the strontium segregation towards the surface [van der Heide, 2002]. Viitanen et al [2002] studied the surface composition of LSCF membranes by Low-Energy Ion Spectroscopy (LEIS). Before the oxygen permeation experiments, the LEIS measurements only showed the presence of La, Sr and O in the outermost atomic layer and no Fe and Co on the contamination-free LSCF membranes. This suggests that Sr species is originally enriched or segregated at the surface of LSCF. This probably stems from the abrupt termination of the lattice structure, which decreases the stability and induces segregation and structural distortion over the outermost atomic layer region. Thus, different to the Mn²⁺ species in the LSM/YSZ, the existence of Sr on the LSCF surface is not dependent on the cathodic polarization potential. Since Sr does not exist in the free state, the Sr-enriched regions are most likely in the form of SrO. In contrast to the high mobility of the Mn species generated under cathodic

polarization or at high temperatures, SrO species on the LSCF surface may not be mobile. Thus, the nucleation between the static SrO and gaseous Cr species would occur at the first contact, i.e., on the electrode surface, leading to the formation of Sr-Cr-O nuclei and subsequent crystallization and grain growth of SrCrO₄ and/or Cr₂O₃ solid phases. This is supported by the observed Cr deposition on the LSCF electrode surface and not within the LSCF electrode at the early stage of the reaction. As the SrO is not mobile under the cathodic polarization or high temperature, the deposition of Cr species on the GDC electrolyte surface or the formation of the deposit rings close to the edge of the LSCF electrode would be difficult (see Fig.7.3c & 7.3d). Hatchwell et al [1999] showed that chemical stability between Cr₂O₃ and GDC is high. Thus, the deposition of gaseous Cr species on the GDC electrolyte surface would not take place without the existence or introduction of additional nuclei on the GDC surface. The relatively small Cr deposition inside the LSCF electrode coating indicates that the grain growth of the SrCrO₄ spinel phase is facile, stopping the migration of the Cr species into the LSCF electrode coating at the early stage of the reaction. However, for prolonged heat treatment or under cathodic polarization conditions, extensive formation of SrCrO₄ would lead to the significant depletion of Sr and the subsequent decomposition of LSCF [Quadackers, 1996]. Based on the deposition mechanism proposed for the LSM/YSZ system, the deposition process in the LSCF/GDC system can be written as follows.

A similar deposition process can also be written for other gaseous Cr species such as $\text{CrO}_2(\text{OH})_2$. Fig.7.13 shows schematically the deposition processes of Cr species at the LSCF/GDC system in the presence of Fe-Cr alloy interconnect under SOFC operation conditions. As shown in Chapter 5, the interaction between Fe-Cr alloy and SrO oxide coating shows that SrO induces the nucleation and the formation of Cr_2O_3 , which is consistent with the above mechanism (Reaction 7.1 & 7.2).

Fig.7.13 Schematic of Cr deposition reaction at LSCF cathode/GDC electrolyte cell in the presence of Fe-Cr alloy interconnect under SOFC operation conditions.

Similar to the Cr deposition in the LSM/YSZ system, the Cr deposition in the LSCF/GDC system is far more significant on the areas under the rib of the alloy interconnect as compared to that under the channels of the interconnect. This indicates that the nucleation reaction and grain growth of Cr deposits are kinetically controlled by the contact frequencies and contact time between the SrO species and gaseous Cr

species and can be explained in similar fashion. The significant difference in the Cr deposition on the LSCF electrode surface under the ribs and channels of the metallic interconnect is most likely related to the difference in the flux of Cr species (see Chapter 4). The contacts between SrO species and gaseous Cr species would be very high on the LSCF surface under the rib of the interconnect, significantly increasing the nuclei formation reaction between the SrO and gaseous Cr species and subsequently growth and crystallization of SrCrO_4 solid deposits. This also can explain the much low Cr deposits on the LSCF electrode surface when a Pt mesh was placed between the LSCF coating and Fe-Cr alloy, which significantly increased the diffusion distance for gaseous Cr species to reach the LSCF coating. The significant dependence of the deposition of Cr under cathodic polarization conditions on the reaction temperature (Fig.7.12) can also be explained by the fact that the partial pressure of gaseous Cr species such as CrO_3 decreases significantly with the decrease in temperature. As shown by the calculation results of the gas pressure of volatile Cr species over Cr_2O_3 (see Appendix), the partial pressure of CrO_3 is about 1.39×10^{-3} Pa at 900°C while at 800°C it decreases to 1.47×10^{-4} Pa. Similar dependence of the Cr deposition on the temperature is also found for the LSM/YSZ system.

Similar to the effect of the Cr deposition on the O_2 reduction reaction in the LSM/YSZ system, the deposition of SrCrO_4 species on the surface of LSCF surface would unavoidably result in the degradation of LSCF electrode performance, as indicated by the increase of the electrode polarization resistance and cathodic polarization potential of the LSCF electrode for the O_2 reduction in the presence of

Fe-Cr alloy in comparison to that in the absence of alloy (Fig.7.1 & 7.2). The performance degradation is most likely related to due to the poor electrical conductivity of SrCrO_4 deposits and the blocking of the surface pores by the dense deposit layer. The initial increase in the E_{Cathode} and the partial reversible behaviour of polarization potential indicate the strong inhibiting effect of gaseous Cr species on the electrode process associated with the surface process for the O_2 reduction on LSCF electrode. The performance degradation of LSCF cathodes in the presence of gaseous Cr species is also reported in the literature [[Benson, 1999](#); [Jiang, 2002a](#); [Simner, 2005](#)].

7.4 Conclusion

The deposition process of Cr species at the LSCF electrode/GDC electrolyte system has been investigated under a constant cathodic current passage of 200 mA cm^{-2} at the early stage of the reaction. It was found that the deposition of Cr species preferentially took place on the surface of LSCF electrode, forming SrCrO_4 spinel and Cr_2O_3 phase and very little Cr species deposition inside the bulk of the LSCF electrode and at the LSCF electrode/GDC electrolyte interface. Significant deposition of Cr species on the LSCF electrode surface also occurred under open circuit at 900°C . The results clearly demonstrate that the deposition of Cr species on the LSCF electrode surface is not controlled by the electrochemical reaction and the deposition of Cr species is basically a chemical reaction and is kinetically controlled by the nucleation reaction between the gaseous Cr species and SrO species enriched on the LSCF

electrode surface. This is consistent with the proposed mechanism of the Cr deposition process in the LSM electrode/YSZ electrolyte system. The preferential deposition of Cr species on the surface of the LSCF electrode is most likely due to fact that the nucleation agent, SrO in the LSCF electrode/GDC electrolyte system, is not mobile.

CHAPTER 8.

INTERACTION BETWEEN Fe-Cr ALLOY AND (La,Sr)MnO₃-BASED COMPOSITE CATHODES

8.1 Introduction

Sr-doped LaMnO₃ (LSM) perovskite has been extensively investigated and regarded as one of the most promising cathode materials for high temperature solid oxide fuel cell (SOFC) because of its high electrochemical activity for O₂ reduction reaction, good thermal and chemical stability as well as relatively good compatibility with yttria stabilized zirconia (YSZ) electrolyte [*Minh, 1995; Jiang, 2003*]. However, the oxygen ion conductivity of LSM materials is very low [*Yasuda, 1996*] and this limits the application of LSM cathode for intermediate temperature SOFC operating at 600-800°C. One common approach to improve the electrocatalytic activity of LSM is to add ionic conducting phases such as YSZ and Gd-doped CeO₂ (GDC) to form a composite cathode [*Murray, 1998 and 2001; Kim, 2001; Wang, 1998; Kamata, 1998; Jørgensen, 2001; McIntosh, 2004*]. Modification of the LSM electrode by a simple impregnation with Gd-doped CeO₂ (GDC) particles can also achieve excellent electrocatalytic activity for the O₂ reduction reaction [*Jiang, 2003b and 2005a*]. The addition of YSZ and GDC significantly improves the performance of LSM cathode and

the improvement in the performance is generally attributed to the extension of three phase boundary (TPB) area from the LSM electrode/YSZ electrolyte interface into the electrode bulk.

Despite the importance of the LSM-based composite cathode, few studies have been reported on the interaction between the Fe-Cr alloy metallic interconnect and the LSM-based composite cathodes. In this chapter, the results on the Cr deposition process on LSM/YSZ composite and GDC-impregnated LSM electrodes will be reported and it shows that composite electrodes have much higher tolerance to Cr deposition than that of the pure LSM electrode.

8.2 Experimental

The details of the sample preparation and the experimental set-up for the electrochemical testing can be found in Chapter 3. The initial electrochemical behaviours of LSM, LSM-YSZ and GDC-impregnated LSM composite electrodes in the presence of Fe-Cr alloy were investigated under a constant current density of 200 mA cm⁻² in air at 900°C. The current passage was interrupted from time to time to make the EIS measurements. EIS measurements were carried out at open circuit.

8.3 Results and discussion

8.3.1 Electrochemical behaviour

Fig.8.1 shows the initial impedance responses of the pure LSM, LSM/YSZ and 1.6 mg cm⁻² GDC-impregnated LSM electrodes as a function of a cathodic current

Fig.8.1 Initial impedance curves of (a) pure LSM, (b) LSM-10YSZ, (c) LSM-30YSZ, (d) LSM-50YSZ and (e) 1.60 mg cm^{-2} GDC-impregnated LSM electrodes for O_2 reduction in the presence of Fe-Cr alloy under current passage of 200 mA cm^{-2} and 900°C . EIS was measured at open circuit.

passage at 200 mA cm^{-2} and 900°C in the presence of Fe-Cr alloy. EIS was measured under open circuit. For the pure LSM electrode, the initial electrode interface (or polarization) resistance (R_E) was $4.04 \Omega \text{ cm}^2$, and reduced significantly with cathodic current passage. After cathodic current passage for 10 min, R_E was reduced to 0.87

$\Omega \text{ cm}^2$, which is much smaller than the initial value. The rapid reduction in the electrode polarization resistance is similar to that for the O_2 reduction in the absence of Fe-Cr alloy, showing the significant activation effect of cathodic polarization on the O_2 reduction reaction on the freshly prepared LSM electrode [Lee, 1995; Jiang, 1999a and 2001a]. The decrease in the electrode polarization resistance is also an indication that Cr species deposition is not dominated by the electrochemical reduction of gaseous Cr species in competition with O_2 reduction at the three phase boundaries [Jiang, 2000].

After addition of YSZ, the LSM/YSZ composite electrodes behaved very differently. First, the initial R_E for the O_2 reduction reaction on the composite electrodes before cathodic current passage was decreased significantly compared to the pure LSM electrode. For example, the initial R_E was $3.08 \Omega \text{ cm}^2$ for the LSM-10YSZ electrode. In the case of LSM-30YSZ electrode, it was $0.77 \Omega \text{ cm}^2$, much smaller than that of the pure LSM electrode. The lower electrode polarization resistance for the O_2 reduction reaction on the LSM/YSZ composite electrodes has been well documented and attributed to the enlargement of TPB areas [Murray, 1998; Wang, 1998; Kamata, 1998; Jørgensen, 2001; Kim, 2001; Leng, 2004; McIntosh, 2004]. Also, different to the reaction on the pure LSM electrode, the electrode polarization resistance decreased initially but then increased again with the current passage time for the O_2 reduction on the LSM/YSZ composite electrodes.

For the O_2 reduction reaction on the GDC-impregnated LSM electrode, the polarization resistance increases with the cathodic current passage time. The initial R_E

was $0.02 \Omega \text{ cm}^2$ and increased to $0.14 \Omega \text{ cm}^2$ after current passage for 240 min. Nevertheless, the polarization resistance is very small compared to that of pure LSM electrode, demonstrating the very high electrochemical activity of GDC-impregnated LSM electrode for O_2 reduction even in the presence of gaseous Cr species. The change in the polarization resistance with the cathodic current passage is small, indicating that the overall effect of the Cr species on the O_2 reduction would be relatively low.

Fig.8.2 shows the polarization potential (E_{Cathode}) behaviour of the pure LSM, LSM/YSZ and GDC-impregnated LSM electrodes as a function of cathodic current passage at 200 mA cm^{-2} and 900°C in the presence of Fe-Cr alloy. E_{Cathode} increased rapidly with the cathodic current passage, reaching a potential region where the increase in E_{Cathode} was much slower. The change of E_{Cathode} with the cathodic current passage time was quite reproducible at the early stages of the polarization. The polarization behaviour for the O_2 reduction on the LSM electrode in the presence of Fe-Cr alloy is very different to that in the absence of Fe-Cr alloy, as shown in Chapter 6. Such polarization behaviour at the early stage of the reaction in the presence of chromia-forming alloy has been explained by the strong inhibiting effect of gaseous Cr species on the surface process such as the dissociate adsorption and diffusion of oxygen on the LSM electrode for the O_2 reduction reaction. The increase of polarization potential is mainly due to the increase of overpotential (η) as the electrode ohmic resistance (R_Ω) remains almost the same with the current passage.

Fig.8.2 Polarization potential curves of (a) pure LSM, (b) LSM-10YSZ, (c) LSM-30YSZ and (d) LSM-50YSZ and (e) 1.60 mg cm^{-2} GDC-impregnated LSM electrodes as a function of cathodic current passage of 200 mA cm^{-2} at 900°C in the presence of Fe-Cr alloy.

Similarly, the polarization potential for O_2 reduction on the LSM/YSZ and GDC-impregnated LSM composite electrodes in the presence of Fe-Cr alloy also developed two distinct potential regions. However, the magnitude of the initial E_{Cathode} increase (i.e, $\Delta E_{\text{Cathode}}$ as shown in the figure) for the reaction on the LSM/YSZ and

GDC-impregnated LSM composite electrodes became much smaller as compared to that on the pure LSM electrode. For example, after cathodic current passage for 120 min, $\Delta E_{\text{Cathode}}$ for the O_2 reduction was ~ 656 mV and ~ 642 mV on the pure LSM and LSM-10YSZ electrode, respectively (Fig.8.2a and 8.2b). But $\Delta E_{\text{Cathode}}$ was only ~ 170 mV for the LSM-30YSZ electrode and ~ 124 mV for the LSM-50YSZ electrode under the identical experimental conditions (Fig.8.2c and 8.2d). In the case of the LSM-50YSZ electrode, the initial decrease in the E_{Cathode} with the current passage for O_2 reduction at the first 30 min might be due to the decrease of R_{Ω} . For the reaction on the 1.60 mg cm^{-2} GDC impregnated LSM electrode the $\Delta E_{\text{Cathode}}$ was only ~ 9 mV after cathodic current passage for 120 min. In all cases, the change of E_{Cathode} with the cathodic current passage time is largely reproducible. The much smaller $\Delta E_{\text{Cathode}}$ for the O_2 reduction on LSM/YSZ and GDC-impregnated LSM electrodes in the presence of Fe-Cr alloy shows the less extent of inhibiting effect of gaseous Cr species on the kinetics of the O_2 reduction reaction in comparison to that on the pure LSM electrode.

Fig.8.3 compares the change of overpotential (η) as a function of current passage time for the reactions on the pure LSM, LSM/YSZ and 1.6 mg cm^{-2} GDC-impregnated LSM composite electrodes in the presence of Fe-Cr alloy for 20 h at 900°C . At the end of 20 h cathodic current passage, the overpotential increased from 256 mV to 1490 mV for the reaction at 200 mA cm^{-2} on the pure LSM electrode at 900°C . On the other hand, the final overpotential of LSM-30YSZ and LSM-50YSZ electrode was 520 mV and 384 mV, respectively. In the case of the GDC-impregnated LSM electrode, η was 105 mV after polarization for 20 h, much smaller than that on the LSM electrode. The

Fig.8.3 Plots of overpotential (η) as a function of polarization time under a cathodic current of 200 mA cm^{-2} in the presence of Fe-Cr alloy at 900°C .

deterioration of electrode performance caused by the Cr species was substantially smaller for the composite electrodes. This clearly indicates that the composite based structure electrodes show much higher tolerance towards the gaseous Cr species as compared to the pure LSM electrode.

8.3.2 Cr deposition on LSM-based composite cathodes

Fig.8.4 shows the SEM micrographs of a pure LSM electrode after cathodic current passage at 200 mA cm^{-2} and 900°C for 20 h. The EDS patterns of selected areas in the electrode are shown in Fig.8.5. On the YSZ electrolyte surface, there was a formation of deposition ring $50\text{--}70 \mu\text{m}$ wide at the edge of the LSM electrode. It has been shown that the deposition of Cr species on the YSZ electrolyte surface is significantly dependent on the flow channel of the metallic interconnect [Jiang, 2001].

Fig.8.4 SEM micrographs of pure LSM electrode after cathodic polarization at 200 mA cm⁻² and 900°C in the presence of Fe-Cr alloy for 20 h. (a) An overview of the electrode, showing the formation of a deposition band close to the edge of the electrode, (b) deposition ring next to the electrode, (c) LSM electrode surface and (d) fractured cross section of LSM electrode.

A wavelike deposition band was observed on the YSZ electrolyte surface under the rib of the interconnect (Fig.8.4a). In the ring areas close to the LSM electrode, the deposits were mainly fine grains and small crystals (Fig.8.4b). EDS analysis showed the presence of Cr species and small amount of Mn (Fig.8.5a). In contrast, the surface of the LSM electrode was in general very clean with no visible Cr deposit (Fig.8.4c). The EDS analysis of the electrode surface as shown in Fig.8.5b was a typical pattern for LSM materials, indicating that the well-defined and granular-shaped particles were LSM particles and there is no Cr deposition on the LSM electrode surface. The size of

the LSM particles was in the range of 0.8 to 2.5 μm . However, there was formation of distinctive crystal at the LSM/YSZ electrolyte interface region (Fig.8.4d). On the electrolyte surface between the large LSM particles, there were deposition of fine grains and relative large crystals. The crystals formed developed distinct facets, very different from that of LSM particles. EDS analysis showed that the crystals contained significant amount of Cr (Fig.8.5c), indicating the crystals were most likely $(\text{Cr,Mn})_3\text{O}_4$ -type spinels [Badwal, 1997]. The results indicate that deposition of Cr species preferentially occurs on the electrolyte surface at the early stages of polarization. The details of Cr species deposition at LSM electrode/YSZ electrolyte system can be referred to Chapter 4.

Fig.8.5 EDS patterns of the LSM electrode shown in Fig.8.4. (a) Deposits on the ring area next to the edge of the LSM electrode (Fig.8.4b), (b) LSM electrode surface (Fig.8.4c) and (c) crystals at the LSM/YSZ interface (Fig.8.4d).

Fig.8.6 shows the SEM micrographs of the surface and fractured cross section of LSM/YSZ composite electrodes after cathodic polarization at 200 mA cm^{-2} and 900°C for 20 h in the presence of Fe-Cr alloy interconnect. For the LSM/YSZ composite electrodes, the LSM and YSZ particles appear to have sintered well with each other

Fig.8.6 SEM micrographs of (a) surface and (b) cross section of LSM-10YSZ; (c) surface and (d) cross section of LSM-30YSZ; (e) surface and (f) fractured cross section of LSM-50YSZ composite electrodes after cathodic polarization at 200 mA cm^{-2} and 900°C in the presence of Fe-Cr alloy for 20 h in air.

and had good contact to the electrolyte. The average size of YSZ particle ranged from 0.4 to 0.7 μm , smaller than that of LSM particles. The fine particles in the electrodes were YSZ particles. With the increase in the YSZ content in the composite cathode, there was a significant increase in the coverage of LSM particles by the fine YSZ particles, particularly for the LSM (50wt%)/YSZ (50wt%) composite cathode (Fig.8.6f). Similar to that on the pure LSM electrode, no Cr species deposit was observed on the surface of the LSM/YSZ composite electrodes (Fig.8.6a, 8.6c and 8.6e). However, there was significant deposition of Cr species at the electrode/YSZ electrolyte interface for LSM-10YSZ, similar to that at the pure LSM electrode, as shown by the formation of distinctive crystals at the interface (Fig.8.6b). In contrast to the pure LSM and LSM-10YSZ electrode, the electrode/YSZ electrolyte interface were much cleaner in the case of LSM-30YSZ and LSM-50YSZ composite electrodes (Fig.8.6d and Fig.8.6f), indicating that the deposition of Cr species would no longer preferentially take place at the electrode/electrolyte interface in comparison to that at the pure LSM and LSM-10YSZ electrodes.

Fig.8.7 shows the SEM micrographs of the 1.60 mg cm^{-2} GDC-impregnated LSM electrode in the presence of Fe-Cr alloy after cathodic polarization at 200 mA cm^{-2} and 900°C for 20 h. The fine particles formed on the surface or around the LSM particles were most likely $(\text{Ce,Gd})\text{O}_2$ oxides as identified by the EDS pattern (Fig.8.7d). Clearly, the impregnated GDC particles were much smaller than that of LSM particles. However, the distribution of nano-sized GDC particles appeared to be discrete and did not form a continuous network inside the electrode (Fig.8.7b and Fig.8.7c), which is

most likely due to the relatively low loading of GDC in this case. Similar to the LSM-30YSZ and LSM-50YSZ composite electrodes, there was no visible deposition of Cr species with clear crystal facets at the electrode/electrolyte interface, as shown in Fig.8.7c.

Fig.8.7 SEM micrographs of 1.60 mg cm^{-2} GDC-impregnated LSM after cathodic polarization at 200 mA cm^{-2} and 900°C in the presence of Fe-Cr alloy for 20 h in air. (a) Electrode surface, (b) fractured cross section of electrode bulk and (c) electrode/electrolyte interface. EDS pattern of the fine particles in (b) is shown in (d).

Fig.8.8 is the SEM micrographs of the YSZ electrolyte surface next to the LSM-YSZ and GDC-impregnated LSM electrodes after cathodic polarization for 20 h at 900°C in the presence of Fe-Cr alloy. Similar to that of the pure LSM electrode,

Fig.8.8 SEM micrographs of the YSZ electrolyte surface next to the composite electrodes. (a) LSM-10YSZ, (b) LSM-30YSZ, (c) LSM-50YSZ and (d) 1.60 mg cm⁻² GDC-impregnated LSM electrodes. The electrodes were polarized at 200 mA cm⁻² and 900°C for 20 h in the presence of Fe-Cr alloy.

there was a deposition of Cr species and formation of Cr deposition ring at the edge of the LSM/YSZ composite electrodes. The average ring width was 40-60 μm. It seems that the density of the Cr deposits at the edge of the electrode decreases with the increase of YSZ content in the LSM/YSZ composite electrode. For the LSM-10YSZ electrode, the Cr deposits formed a dense layer and relatively large crystals were observed (Fig.8.8a). But in the case of LSM-30YSZ and LSM-50YSZ electrodes, the deposits were mainly characterized by fine grains with reduced density (Fig.8.8b and 8.8c). On the other hand, for the reaction on the GDC-impregnated LSM electrode, the

Cr species was also deposited on the YSZ electrolyte surface (Fig.8.8d). However, the coverage or the deposition of the Cr species is low as shown by the individually separated Cr deposits on the YSZ electrolyte surface.

To reveal detailed the deposition of Cr species on the YSZ electrolyte surface in contact with the electrode, the electrode coating was removed by HCl acid treatment. Fig.8.9 shows the SEM micrographs of the YSZ electrolyte surface in contact with different electrodes in the presence of Fe-Cr alloy after cathodic polarization at 900°C for 20 h. Fig.8.10 shows the corresponding EDS patterns of the particles left on the electrolyte surfaces. For the pure LSM electrode, the YSZ electrolyte surface was almost completely covered by large crystals (~0.8-2 μm) (Fig.8.9a). The crystals formed have distinct facets. EDS analysis of crystals showed the existence of Cr and Mn (Fig.8.10a), indicating that the crystals are $(\text{Cr,Mn})_3\text{O}_4$ spinels. The intensity of the Cr species deposits at the YSZ electrolyte surface decreased significantly with the increase of YSZ content in the LSM/YSZ composite electrode. For the reaction between the LSM-10YSZ and Fe-Cr alloy, there still was clear deposition of Cr species on the YSZ electrolyte surface (Fig.8.9b). In the case of LSM-30YSZ electrode, the contact convex rings between the LSM particles and the YSZ electrolyte surface were observed on the YSZ electrolyte surface. Fine Cr species deposits were formed on the YSZ electrolyte surface between the original LSM particles and the intensity is much smaller than that on LSM and LSM-10YSZ electrode (Fig.8.9c and 8.10c). The irregular large particles were the YSZ particles left on the electrolyte electrode. For the YSZ-50YSZ electrode, the YSZ electrolyte surface was clean with no obvious Cr

Fig.8.9 SEM micrographs of exposed YSZ electrolyte surface in contact with (a) LSM, (b) LSM-10YSZ, (c) LSM-30YSZ, (d) LSM-50YSZ and (e) 1.60 mg cm^{-2} GDC-impregnated LSM electrode after cathodic polarization at 900°C and 200 mA cm^{-2} for 20 h. The electrode coating was removed by HCl acid treatment.

species deposits (Fig.8.9d). EDS analysis results revealed that the particles on the YSZ electrolyte surface were YSZ particles (Fig.8.10d). This clearly indicates that the deposition of Cr species is no longer preferential on the YSZ electrolyte surface in the

case of LSM-50YSZ composite electrode. For the reaction on the GDC-impregnated LSM composite electrode there was no significant deposition of Cr species on the YSZ surface. After removed the LSM coating by HCl acid treatment, there was a layer of fine grains and isolated large particles formed between the original LSM particles on the YSZ electrolyte surface (Fig.8.9e). However, the EDS analysis showed that the fine grains left on the YSZ surface mainly consist of Ce while the isolated particles were composed of Ce and small amount of Cr (Fig.8.10e). The results indicate that the distribution of nanosized impregnated-GDC particles appears to be relatively homogenous on the YSZ electrolyte surface, which filled the spaces between the LSM particles. The isolated Cr species deposition clearly shows that Cr species at the GDC-impregnated LSM electrode no longer preferentially deposited on the YSZ electrolyte surface.

Fig.8.11 shows the cross section SEM micrographs and corresponding EDS Cr element maps of the pure LSM, LSM-YSZ and 1.6 mg cm^{-2} GDC-impregnated LSM electrodes. The electrodes were cathodically polarized at 200 mA cm^{-2} and 900°C in the presence of Fe-Cr alloy for 20 h. Cr accumulation can be seen near the interface between the electrode and YSZ electrolyte for the reaction on the pure LSM and LSM-10YSZ composite electrode. The high concentration of Cr species at the LSM/YSZ interface for the pure LSM electrode has been reported in the literature [Taniguchi, 1995; Badwal, 1997; Jiang, 2000 and 2005; Paulson, 2004]. This indicates that there is a preferential deposition of Cr species on the electrolyte surface at the early stage of polarization. With the further increase of YSZ content in the LSM

Fig.8.10 EDS patterns of particles on the YSZ electrolyte surface of Fig.8.9: (a) LSM, (b) LSM-10YSZ, (c) LSM-30YSZ, (d) LSM-50YSZ and (e) GDC-impregnated LSM electrodes.

composite, e.g., for the LSM-50YSZ composite electrode, there is no concentrated distribution of Cr near the electrode/electrolyte interface and the Cr distribution in the electrode is uniform. The intensity of Cr is relative low in the LSM-50YSZ electrode, indicating reduced deposition of Cr species. Similarly, the distribution of Cr in the GDC-impregnated LSM electrode also showed that no accumulation of Cr species was formed near the electrode/electrolyte interface.

See following page

Fig.8.11 SEM micrographs of polished cross section and corresponding Cr element mapping of electrodes after cathodic polarization at 900°C and 200 mA cm⁻² in the presence of Fe-Cr alloy for 20 h. (a) and (b) LSM, (c) and (d) LSM-10YSZ, (e) and (f) LSM-30YSZ, (g) and (h) LSM-50YSZ, (i) and (j) GDC-impregnated LSM electrode.

8.3.3 Effect of YSZ and GDC phases on the Cr deposition at LSM-based composite cathodes

The results in this study demonstrate the LSM composite electrodes have higher electrochemical performance for the O₂ in the presence of Fe-Cr metallic interconnect in comparison to the pure LSM electrode. As shown in Fig.8.2, for the O₂ reduction reaction in the presence of Fe-Cr alloy, there are similarities between the polarization behaviour of pure LSM and LSM-based composite electrodes. E_{Cathode} is characterized by a rapid increase, followed by a relatively slow increase with the current passage time. As shown before, the rapid increase of E_{Cathode} for the O₂ reduction on the pure LSM electrode is attributed to the significant inhibiting effect of gaseous Cr species on the surface process of the reaction at the early polarization stage. However, for the reaction in the presence of Fe-Cr alloy interconnect on LSM/YSZ composite and

GDC-impregnated LSM cathodes, the magnitude of the initial increase of E_{Cathode} is very low and the polarization performance for the O_2 reduction reaction is much more stable in comparison to that of the pure LSM electrode (Fig.8.2 and 8.3).

Addition or impregnation of an oxygen ion conducting phase such as YSZ or GDC to the LSM electrodes have shown to improve significantly the electrochemical performance for the O_2 reduction reaction [Murray, 1998 and 2001; Wang, 1998; Kamata, 1998; Jørgensen, 2001; Kim, 2001; McIntosh, 2004]. This is generally attributed to the enlargement of the TPB area and the extension of the active reaction sites from the electrode/electrolyte interface to the electrode bulk. On the other hand, there are evidences that the addition of ionic conducting phase to LSM not only enhances the electrochemical activity of the LSM electrode but also changes the electrode behaviour [Kim, 2001; Jiang, 2005a]. Recent study by Jiang et al [2005a] shows that impregnation of oxygen ion-conducting GDC phase in the LSM electrode has significant influence on the electrode behaviour, particularly on the electrode process associated with low frequencies as compared to that at high frequencies. The activation energy of the electrode process at high frequencies for the O_2 reduction on the GDC-impregnated LSM composite electrode is $\sim 100 \text{ kJ mol}^{-1}$ and the corresponding electrode conductivity at high frequencies is essentially independent of the oxygen partial pressure, similar to that for the reaction on the pure LSM. Similar electrode behaviour for the high-frequency electrode process was also reported for the reaction on the LSM/YSZ and LSM/GDC composite electrodes [Murray, 1998 and 2001; Wang, 1998]. This indicates the dominant role of the electrolyte on the

high-frequency electrode process for the O_2 reduction reaction on LSM and LSM-based composite cathodes [Jiang, 2000a and 2002a].

However, the effect of the addition/impregnation of GDC on the low-frequency electrode process is remarkable [Jiang, 2005a]. The reaction order of the electrode conductivity at low frequencies with respect to the partial pressure of oxygen is in the range of 0.23-0.34, lower than 0.5 to 0.85 on pure LSM, but similar to that reported on a $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ (LSCF) cathode [Esquirol, 2004]. The activation energy of the low-frequency electrode process is $\sim 140 \text{ kJ mol}^{-1}$, lower than 170-200 kJ mol^{-1} reported for the reaction on pure LSM [Jiang, 2005a]. The low reaction order and reduced activation energy for the low-frequency electrode process of the O_2 reduction reaction was also observed for the reaction on LSM/GDC composite cathodes [Murray, 2001]. The excellent performance of GDC-impregnated LSM electrode is most likely related to the high ionic conductivity of GDC material [Mogensen, 2000]. This indicates impregnation of ionic conducting GDC phase greatly accelerates the oxygen dissociation and diffusion process of the O_2 reduction reaction. This is supported by the fact that LSCF is a well-known mixed ionic and electronic conductor and the O_2 reduction reaction is most likely controlled by the oxygen dissociation and ionic diffusion on the LSCF electrode [Esquirol, 2004; Jiang, 2002a].

The significant effect of the addition/impregnation of an ionic conducting phase is also demonstrated by the gradual reduction of the initial cathodic potential increase and the much stable overpotential for the reaction in the presence of Fe-Cr alloy metallic interconnect (Fig.8.2 and 8.3). Thus, with the addition/impregnation of ionic

conducting YSZ and GDC phase in the LSM, the electrode process associated with adsorption, dissociation and diffusion on the LSM surface would become less important for the O₂ reduction reaction on the LSM-based composite electrode in comparison to the pure LSM electrode. In another word, the limiting electrode process associated with the reduction of manganese species with the concomitant formation of Mn²⁺ species and oxygen vacancies for the reaction on the LSM electrode under high polarization [Lee, 1995; Jiang, 1998] would be diminished for the reaction on the LSM-based composite electrodes. This implies that the amount of Mn²⁺ species generated under cathodic polarization would be small for the O₂ reduction on the LSM-based composite electrodes.

The reduced concentration of Mn²⁺ generated for the O₂ reduction reaction on LSM/YSZ composite and GDC-impregnated LSM cathode could explain the Cr deposition process observed in this study. As discussion in Chapter 4, Mn²⁺ ions generated under cathodic polarization and high temperature conditions react with gaseous Cr species, forming Cr-Mn-O nuclei and subsequently leading to the formation of Cr₂O₃ grains and (Cr,Mn)₃O₄ spinel. The kinetics of the deposition of the Cr species is controlled by the nucleation reaction between the Mn²⁺ and gaseous Cr species. Manganese ions such as Mn²⁺ are known to be mobile under SOFC operation conditions. Due to the high mobility of the Mn²⁺ species, the deposition occurs preferentially on the YSZ electrolyte surface where the contact frequency and duration between the mobile Mn and gaseous Cr species would be much high enough for the nucleation reaction, as shown in Fig.8.4 for the Cr deposition on pure LSM. In the case

of LSM-10YSZ composite electrode, the Cr deposition process is very similar to that on the pure LSM electrode (Fig.8.6b and 8.11d). This indicates that small addition of YSZ does not affect significantly the electrode process associated with the generation of Mn^{2+} species.

On the other hand, for the O_2 reduction at the LSM/YSZ composite electrodes in the presence of Fe-Cr alloy, deposition of Cr species on the YSZ electrolyte surface in contact with the electrode became much less with the increase of YSZ content in the composite electrodes (Fig.8.6 and 8.9). The Cr species showed no preferential deposition at the electrode/electrolyte interface but distributed randomly in the electrode bulk (Fig.8.11). In the case of the LSM-50YSZ composite electrode, the YSZ electrolyte surface was clean and there was no accumulation of the Cr deposits in any particular region in the electrode. The amount of Cr deposits is also much smaller in comparison to that on the pure LSM electrode. Similar deposition behaviour of Cr was also observed for the reaction on the 1.6 mg cm^{-2} GDC-impregnated LSM. This indicates that the nucleation/grain growth reaction for the Cr deposition is significantly reduced or inhibited in the composite electrode system. Nevertheless, the mechanism of the Cr deposition at the LSM-based electrodes should not be, in principal, affected by the addition/impregnation of the ionic conducting YSZ and GDC phase. This is indicated by the some deposition of Cr species on the YSZ electrolyte surface at the edge of the LSM composite electrodes (Fig.8.8), similar to that on the pure LSM electrode. As the flux of gaseous Cr species in the electrode system would not change significantly with the addition/impregnation of ionic conducting phase in the LSM

electrodes, the significantly reduced deposition of Cr species at the LSM/YSZ composite and GDC-impregnated LSM electrodes is most likely due to the significant decrease of Mn^{2+} ions generated under cathodic polarization.

As shown in Chapter 6, the Cr deposits on the YSZ electrolyte surface strongly inhibit the electrode process of the oxygen migration and incorporation into the electrolyte for the O_2 reduction reaction on the LSM electrode, resulting in the rapid performance degradation. The much cleaner electrode/electrolyte interface for the O_2 reduction reaction on the LSM-based composite electrodes (see Fig.8.11) shows that the inhibiting effect of Cr deposits on the oxygen migration and diffusion process would be substantially smaller in comparison to that on the pure LSM electrode. This explains the stable electrochemical performance of YSZ/LSM composite and GDC-impregnated LSM electrodes in the presence of Fe-Cr alloy (Fig.8.3). The results in this study clearly demonstrate that the composite electrodes not only show high and stable activity for the O_2 reduction but also significantly reduce the deposition of Cr species. This opens a potential route to significantly reduce the poisoning effect of Cr species on the O_2 reduction reaction on the LSM-based composite electrode when the metallic interconnect is used in SOFC.

8.4 Conclusion

The interaction and performance of pure LSM, LSM-YSZ composite and GDC-impregnated LSM electrodes in the presence of Fe-Cr alloy metallic interconnect have been investigated. The LSM/YSZ composite and GDC-impregnated LSM

electrodes showed much higher electrochemical performance and stability than that of the pure LSM electrode. The magnitude of the initial increase in the cathodic polarization potential was much smaller for the O₂ reduction reaction on the composite electrodes in comparison to that on the pure LSM. The best performance and stability were observed on the 1.60 mg cm⁻² GDC-impregnated LSM electrode.

SEM and EDS element mapping analysis clearly show that the deposition of Cr species is much less on the YSZ electrolyte surface in contact with the electrode coating for the reaction on the LSM-based composite electrodes in comparison to that on the pure LSM electrode. The Cr species shows no preferential deposition at the electrode/electrolyte interface. In the case of LSM-50YSZ composite electrode, the YSZ electrolyte surface is clean and the amount of Cr deposits is also much smaller in comparison to that on the pure LSM electrode. Similar deposition behaviour of Cr was also observed for the reaction on the GDC-impregnated LSM. This indicates that the nucleation and grain growth reaction for the Cr deposition is significantly reduced or inhibited in the LSM-based composite electrodes. The reason for the significantly reduced Cr deposition in the LSM composite cathodes is most likely due to the decrease of Mn²⁺ ions generated under cathodic polarization.

CHAPTER 9.

EVALUATION OF Fe-Cr ALLOYS AS INTERCONNECT

9.1 Introduction

As shown in previous chapters, the volatile Cr species generated over the chromia-forming alloy interconnect at high temperatures can lead to a rapid degradation of SOFC performance due to the poison of cathodes such as (La,Sr)MnO₃ (LSM), (La,Sr)(Co,Fe)O₃ for the O₂ reduction reaction. This is also well documented in the literature [[Tangichi, 1995](#); [Badwal, 1997](#); [Matsuzaki, 2000](#); [Jiang, 2000a](#); [Fujita, 2003](#)]. Thus, it is important to measure, quantitatively or qualitatively, the Cr volatility of Fe-Cr alloys in order to assess their applicability as interconnect for SOFC. Gindorf et al [[2000 and 2001](#)] used the transpiration method to determine the chromium vaporization and found that the vaporization rate was related to the composition of oxide scale formed on the alloy surface. As shown in this study, the deposition of Cr species on the LSM electrode is essentially dominated by the chemical dissociation of the gaseous Cr species and the O₂ reduction is limited by the surface diffusion of oxygen species on the LSM electrode surface due to the strong inhibiting effect of the gaseous Cr species generated from the Fe-Cr alloy. The results indicate that the magnitude of the performance degradation of LSM electrode could be used to diagnose the volatility of the Cr species generated from the oxide scale and to qualitatively

evaluate the application potential of the alloy as interconnect for SOFC.

In this chapter, the electrochemical performance degradation of LSM electrode/YSZ electrolyte cell in contact with three different Fe-Cr alloys were measured under identical SOFC operating conditions. The results demonstrate that Cr volatility of Fe-Cr alloys can be qualitatively assessed by a simple and quick electrochemical performance measurement based on LSM/YSZ system.

9.2 Experimental

The Fe-Cr alloys used in the present study were Ni-based superalloy, RA600 and ferrite stainless steel, RA446 alloy (Rolled Alloy Co., Canada) and Crofer22 APU (Thyssen Krupp VDM, Germany). The chemical composition of the materials is listed in Table 3.1.

Standard LSM electrode/YSZ electrolyte cells as described in Chapter 3 were used in this study. The electrochemical tests of the LSM electrodes with different Fe-Cr alloys were carried out under a constant current density of 200 mA cm^{-2} in air at 900°C . The polarization potential (E_{Cathode}) was measured against the Pt reference electrode. The current passage was interrupted from time to time to make the EIS measurements. EIS was conducted at open circuit potential.

9.3 Results and discussion

Fig.9.1 shows the impedance response of the LSM electrodes for the O_2 reduction under a cathodic current passage of 200 mA cm^{-2} at 900°C in air in the presence of

Fig.9.1 Impedance responses of LSM electrodes for O_2 reduction under current passage of 200 mA cm^{-2} and 900°C in air in the presence of different Fe-Cr alloys: (a) RA600 alloy, (b) RA446 alloy and (c) Crofer22 APU alloy. The total electrode polarization resistance (R_E) as a function of current passage time is shown in (d). EIS was measured at OCP.

different chromia-forming alloys. Before the cathodic current passage, the initial impedance of the LSM electrode was characterized by a large and depressed arc. In all cases, the size of the impedance arcs fluctuated with the cathodic current passage. At the initial stage, the electrode polarization resistance (R_E) decreased with the cathodic current passage, showing the enhancing effect of cathodic current treatment on the electrochemical activities of the freshly prepared LSM electrode for O_2 reduction reaction. After cathodic current passage for 20 h, R_E for reactions in the presence of RA446 alloy and Crofer22 APU alloy was reduced from an initial 1.42 and 1.72 $\Omega \text{ cm}^2$

to 0.69 and 0.79 $\Omega \text{ cm}^2$, respectively. For the O_2 reduction in the presence of RA600 alloy, R_E decreased initially and increased again to 2.03 $\Omega \text{ cm}^2$ after cathodic current passage for 20 h. The change of R_E measured at OCP did not show consistent pattern with the cathodic current passage. Such behaviour of R_E with the cathodic current passage has been discussed in Chapter 4. The inconsistency in R_E behaviour may be due to the complex effect of the gaseous Cr species and solid Cr deposits on the O_2 reduction reaction on the LSM electrode.

Fig.9.2 shows the initial polarization behaviour of the LSM electrodes for the O_2 reduction at 200 mA cm^{-2} and 900°C in the presence of different chromia-forming alloys. In all cases, the time behaviour of the cathodic polarization potential (E_{Cathode}) can be characterized by two distinct potential regions. E_{Cathode} increased very quickly with the cathodic current passage, reaching a potential plateau where the increase in E_{Cathode} was much slower. The magnitude of the E_{Cathode} change with the cathodic current passage time was measured by $\Delta E_{\text{Cathode}}$, as shown in the figure.

Such polarization behaviour for the O_2 reduction on the LSM electrode in the presence of chromia-forming alloy has been studied in detail in comparison with that in the absence of chromia-forming alloy. As shown in Chapter 6, the very different behaviour of E_{Cathode} with cathodic current passage in the absence and presence of chromia-forming alloy indicates the significant inhibiting effect of the gaseous Cr species on the surface process for the O_2 reduction on the LSM electrodes. Electrode surface process such as surface dissociation and diffusion generally plays a dominant role for the O_2 reduction on the porous LSM electrodes [[Wang, 1998](#); [Kim, 2001](#);

Fig.9.2 Polarization curves of LSM electrodes under a cathodic current of 200 mA cm^{-2} at 900°C in air in the presence of different Fe-Cr alloys: (a) RA600, (b) RA446 and (c) Crofer22 APU alloy.

Chen, 2003; Jiang, 2000a and 2002a]. The existence of gaseous Cr species is considered to effectively block the diffusion path for the oxygen species on the LSM surface and significantly increase the resistance for the electrode surface process [*Jiang, 2000a and 2002a*]. As the distribution and concentration of the gaseous Cr species in the electrode system would be primarily affected by the temperature, oxygen pressure and the Cr volatility of chromia-forming alloy. This means that the generation of gaseous Cr species from the oxide scale could be qualitatively assessed by the magnitude of the initial E_{Cathode} change with the cathodic current passage (i.e., $\Delta E_{\text{Cathode}}$) under controlled testing conditions.

The initial E_{Cathode} increases with the cathodic current passage ($\Delta E_{\text{Cathode}}$) for the O_2 reduction on the LSM electrodes in the presence of three Fe-Cr alloys is shown in Fig.9.3. In the case of the RA446 alloy, the $\Delta E_{\text{Cathode}}$ value was taken as an average of the measurements of four samples. At the beginning of the experiments, the $\Delta E_{\text{Cathode}}$ values were similar for the alloys studied, 310 mV for RA600, 358 mV for Crofer22 APU, and 364 mV for RA446. However, $\Delta E_{\text{Cathode}}$ values increased with the cathodic polarization time and the magnitude of the $\Delta E_{\text{Cathode}}$ started to differentiate after the cathodic current passage for 5 h among the alloys studied. The rather similar $\Delta E_{\text{Cathode}}$ values for the reaction at the first 4-5 h indicate that there may be a transition period for the system to reach a steady-state response between the polarization and the alloy. In the presence of RA600 alloy, $\Delta E_{\text{Cathode}}$ increased rapidly to ~1400 mV after polarization for 8 h, much larger than the initial value of ~310 mV. On the other hand, $\Delta E_{\text{Cathode}}$ of LSM electrodes in the presence of RA446 and Crofer22 APU alloys were

much lower than that in the presence of RA600 alloy. For example, after cathodic polarization for 10 h, $\Delta E_{\text{Cathode}}$ of the LSM electrode with Crofer22 APU alloy was 484 mV, much smaller than 1480 mV of LSM electrode in the presence of RA600 alloy. The substantial difference in the $\Delta E_{\text{Cathode}}$ values indicates that the evaporation of gaseous Cr species from Crofer22 APU alloy may be much lower than that from RA600 alloy.

Fig.9.3 $\Delta E_{\text{Cathode}}$ of LSM electrodes as a function of current passage time for the O_2 reduction in the presence of different Fe-Cr alloys at 200 mA cm^{-2} and 900°C . Error bars were obtained from regression analysis of the results shown in Fig.6.3b, Fig.6.4, Fig.8.2a and Fig.9.2b.

The evaporation of gaseous Cr species from different alloys is deemed to relate to the microstructure and composition of oxide scale formed on the surfaces of the alloys. Fig.9.4 shows the SEM micrographs of the alloys after cathodic current passage for 20 h at 900°C in air. Rough oxide scale with irregular cracks and voids was formed on the surface of RA600 alloy, while on the surfaces of RA446 and Crofer22 APU alloy, crystals with distinctive facets were clearly observed. The oxide scale formed on the Crofer22 APU alloy was dense without any cracks or voids. The XRD patterns of the

Fig.9.4 SEM micrographs of oxide scales formed on the surface of different chromia-forming alloys after cathodic current passage at 900°C for 20 h: (a) RA600, (b) RA446 and (c) Crofer22 APU alloy.

oxide scales of the alloys are shown in Fig.9.5. The alloys were annealed in air at 900°C for 500 h. The oxide scales formed on the RA446 alloy and Crofer22 APU alloy showed similar XRD patterns, which mainly consisted of chromia (Cr_2O_3) and spinel phases ($(\text{Cr,Mn})_3\text{O}_4$). On the other hand, the oxide scale on the RA600 alloy surface was composed of NiO and chromia. The lack of the $(\text{Cr,Mn})_3\text{O}_4$ spinel phase formation on the RA600 surface is most likely due to the very low Mn content in the alloy (Table 3.1). Studies have shown that the addition of Mn element in Cr-containing alloy would lead to the formation of $(\text{Cr,Mn})_3\text{O}_4$ spinel phase in the oxide scale [Brylewski, 2001; Yang, 2004]. The formation of $(\text{Cr,Mn})_3\text{O}_4$ spinel increases the scale electrical conductivity [Brylewski, 2001; Quadackers, 2000] and decreases the chromium

Fig.9.5 XRD patterns of the oxide scales formed on the chromia-forming alloys after oxidation at 900°C for 500 h in air.

volatility of the scale [Abellán, 2002]. The significant difference of the magnitude of $\Delta E_{\text{Cathode}}$ for the O_2 reduction reaction on identical LSM electrodes between the RA600, RA446 and Crofer22 APU alloys confirms that the formation of $(\text{Cr,Mn})_3\text{O}_4$ spinel phase on the oxide scale of a Fe-Cr alloy reduces the chromium volatility. The transpiration results of Cr evaporation rate also demonstrated that the evaporation of volatile Cr species in case of $(\text{Cr,Mn})_3\text{O}_4$ spinel forming alloys was much lower than that of a pure chromia-forming alloy (such as $\text{Cr5Fe1Y}_2\text{O}_3$ alloy) [Gindorf, 2001]. For example, the measured Cr evaporation rates of $\text{Cr5Fe1Y}_2\text{O}_3$ and 446 alloys were about 4.9×10^{-10} and $0.057 \times 10^{-10} \text{ kg m}^{-2} \text{ s}^{-1}$ in air at 950°C. The measured evaporation rates are in agreement with present results based on the electrochemical testing method.

Fig.9.6 is the SEM micrographs of cross-sections and the element distribution profiles of the Fe-Cr alloys after oxidation treatment at 900°C in air for 500 h. There is no spallation of the oxide scale, indicating the good adhesion between the scale and the alloys. However, the thickness of the oxide scale appears to depend on the composition

Fig.9.6 SEM micrographs of cross sections and the element distribution profiles of the Fe-Cr alloys after oxidation treatment at 900°C in air for 500 h. (a) and (b) RA600, (c) and (d) RA446 alloy, (e) and (f) Crofer22 APU alloy.

of the alloys. The oxide scale of superalloy RA600 was very thin, $\sim 3 \mu\text{m}$. The thickness of the oxide scale of Crofer22 APU is $\sim 5 \mu\text{m}$, smaller than $\sim 9 \mu\text{m}$ of the oxide scale formed on the RA446. This may be related with the alloying additives, such as La and Ti, in the Crofer22 APU alloy, which improves the adherence between the oxide scale and the alloy and reduces the growth rate of the chromium oxide scale [Abellán, 2002]. In the case of RA446 and Crofer22 APU alloys, the content of Cr in the oxide scale close to the alloy was much higher than that of Mn and the element profiles of Cr and Mn became closely matched at the top surface layer of the scale (Fig.9.6d and f). From the XRD and EDS results, it was clear that the top layer was mainly composed of an $(\text{Mn,Cr})_3\text{O}_4$ spinel phase, and sublayer mainly consisted of chromia. Similar results were also reported by Yang et al [2004]. The content of Ni on the oxide scale of the RA600 alloy is very small in comparison to that of Cr. This again confirms that the oxide scale formed on the RA600 alloy is dominated by Cr_2O_3 phase. Although the compositions of the oxide scales formed on the RA446 and Crofer22 APU alloy are similar (Fig.9.5), the $\Delta E_{\text{Cathode}}$ increase for the reaction on the LSM electrode in contact with the Crofer22 APU alloy is significantly smaller than that in contact with the RA446 alloy (Fig.9.3). The reason could be related to the denser, void-free and thinner oxide scale of Crofer22 APU alloy as compared to that of RA446 alloy. This indicates that $\Delta E_{\text{Cathode}}$ is also sensitive to the microstructure of the oxide scale in addition to the composition.

Fig.9.7 shows the SEM micrographs of YSZ electrolyte surface in contact with LSM electrode coating after cathodic polarization at 900°C for 20 h in the presence of

Fig.9.7 SEM micrographs of LSM/YSZ interface after cathodic polarization at 900°C and 200 mA cm⁻² for 20 h in the presence of (a) RA600 alloy, (b) RA446 alloy and (c) Crofer22 APU alloy. The YSZ surface in contact with LSM coating after cathodic polarization for 4 h at 900°C and 200 mA cm⁻² in the absence of metallic interconnect is shown in (d). The LSM coating was removed by HCl acid treatment.

different Fe-Cr alloy interconnects. The YSZ surfaces shown in the figure were taken on the area under the rib of the metallic interconnect and the LSM electrode coating was removed by 20% HCl acid treatment. In comparison, the LSM electrode/YSZ electrolyte interface after cathodic polarization for 4 h in the absence of metallic interconnect at 200 mA cm⁻² and 900°C is also shown in Fig.9.7d. The details of the O₂ reduction on the LSM electrode in the absence of chromia-forming alloy could be found in Chapter 4 and Chapter 6. Clearly, for the O₂ reduction at LSM electrode in the presence of metallic interconnect, there was significant deposition of Cr species between LSM grains on the YSZ electrolyte surface. The deposition of Cr species at

the LSM/YSZ interface for the reaction in the presence of RA600 alloy appears to be much more significant than that in the presence of RA446 and Crofer22 APU alloys, indicating again that the amount of the gaseous Cr species from the Cr_2O_3 -forming RA600 alloy is significantly higher than that from the $(\text{Cr,Mn})_3\text{O}_4$ spinel-forming alloys, i.e., RA446 alloy and Crofer22 APU alloy.

9.4 Conclusion

The interaction between three types of chromia-forming alloys and the LSM electrodes has been investigated at 900°C under cathodic polarization. It was found that the chromia-forming alloy causes a rapid degradation of electrochemical performance of LSM electrodes for O_2 reduction reaction. However, the magnitude of performance degradation caused is related with the microstructure and composition of oxide scale formed on the surface of alloys. The formation of $(\text{Cr,Mn})_3\text{O}_4$ spinel on Crofer22 APU alloy and RA446 alloy was effective to reduce the generation of volatile Cr species and led to a significant decrease of electrochemical degradation as compared to RA600 alloy. The result demonstrates the feasibility to assess the generation of volatile Cr species from alloys by a simple electrochemical evaluation of LSM electrodes under identical testing conditions.

CHAPTER 10.

CONCLUSIONS AND RECOMMENDATIONS

10.1 Conclusions

The object of this project is to fundamentally understand the interaction reaction mechanisms between the chromia-forming alloy interconnects and the cathodes under the SOFC operating conditions. The following conclusions can be drawn from this study.

1. The interaction between the chromia-forming alloy interconnects and the most promising cathodes, LSM and LSCF cathodes, caused significant Cr species deposition at the cathodes, resulting in a rapid degradation of the electrochemical performance for the O_2 reduction reaction. The deposition processes of Cr species at the LSM and LSCF cathodes were investigated under cathodic polarization conditions. In the chromia-forming alloy interconnect/LSM electrode/YSZ electrolyte system, Cr species deposition took place preferentially at the YSZ electrolyte surface with the formation of fine Cr_2O_3 and large $(Cr,Mn)_3O_4$ spinel phases. On the hand, in the chromia-forming alloy interconnect/LSCF electrode/GDC electrolyte system, the deposition of Cr species preferentially occurred on the LSCF electrode surface, forming $SrCrO_4$ spinel and Cr_2O_3 phases.

Significant deposition of Cr species on the LSCF electrode surface also occurred under open circuit at 900°C. The results conclusively demonstrated that the deposition of Cr species at the SOFC cathodes was not an electrochemical reduction reaction of high valent Cr species to solid Cr₂O₃ in competition with O₂ reduction at the three-phase boundary region. The deposition of Cr species is essentially a chemical reaction on re-deposition. The driving force for the deposition process is related to the nucleation reaction between the gaseous Cr species and the nucleation agent. At the LSM electrode, the nucleation agent is the Mn²⁺ ions generated under cathodic polarization while at the LSCF electrode, the nucleation agent is the SrO species enriched originally at the LSCF electrode surface. The deposition processes of Cr species in the LSM/YSZ system and LSCF/GDC system can be written as follows.

At LSM electrode,

At LSCF electrode,

The kinetics of the deposition process is strongly affected by the flux of the gaseous Cr species and temperature.

2. The dependence of the Cr deposition process on the nature of the materials is also supported by the chemical interaction between the Fe-Cr alloy and the constituent oxides of LSM material such as La_2O_3 , SrO and Mn_2O_3 under open circuit. The interaction between the Fe-Cr alloy and La_2O_3 and Mn_2O_3 oxide coatings primarily resulted in the formation of LaCrO_3 and $(\text{Cr}, \text{Mn})_3\text{O}_4$ while in the case of SrO oxide coating, Cr_2O_3 was the main product. In the case of LSM coating, the formation of $(\text{Cr}, \text{Mn})_3\text{O}_4$ and Cr_2O_3 was identified. The results indicate that the chemical interaction between the Fe-Cr alloy and LSM material is most likely related to the surface oxide species such as SrO and MnO_x initially enriched or segregated on the surface of LSM particularly in the early stage of the reaction.
3. The interaction between the chromia-forming alloy interconnect and the LSM/YSZ composite and GDC-impregnated LSM cathodes were also studied in this project. The LSM/YSZ composite and GDC-impregnated LSM cathodes showed much higher electrochemical activity and performance stability as compared to that of the pure LSM cathode. There is no preferential deposition of Cr species at the electrode and electrolyte interface region for the reaction on the LSM/YSZ composite cathode with high YSZ content ($\geq 30\text{wt}\%$) and a GDC-impregnated LSM composite cathode. The results demonstrate that LSM/YSZ composite and GDC-impregnated LSM electrodes have high tolerance towards the Cr species poisoning.

4. The effect of Cr species on the O₂ reduction reaction at the LSM cathode was identified through the comparative studies of the reactions in the absence and presence of chromia-forming alloy interconnect. The O₂ reduction is strongly inhibited by the existence of Cr species, leading to a significant increase in the polarization potential. Similar to that in the absence of chromia-forming alloy, the O₂ reduction at the LSM cathode in the presence of chromia-forming alloy is limited by two electrode processes, the adsorption and diffusion of oxygen on the LSM cathode surface and the incorporation of oxygen ions into the YSZ electrolyte, corresponding to the low- and high-frequency arcs in the impedance spectrum, respectively. In the presence of chromia-forming alloy interconnect, the surface diffusion process of oxygen species is strongly inhibited by the gaseous Cr specie generated at high temperature while the migration process of oxygen ions into the YSZ electrolyte is limited by the Cr₂O₃/(Cr,Mn)₃O₄ solid species deposition on the YSZ electrolyte surface. The solid Cr species layer formed at the LSM electrode/YSZ electrolyte interface increases with the polarization time, which not only significantly affects the kinetics but also changes the mechanism for the O₂ reduction at the LSM electrode.
5. A simple electrochemical method was developed to qualitatively evaluate chromia-forming alloys for the potential application as interconnect in SOFC. Three types of commercial chromia-forming alloys with different Cr content and alloying elements were evaluated by the measurement of the electrochemical performance degradation of LSM cathodes. The magnitude of the performance

degradation is found to relate to the generation of gaseous Cr species, which is closely related with the microstructure and composition of oxide scale formed on the surface of alloys. It was found that the formation of dense $(\text{Cr,Mn})_3\text{O}_4$ spinels on Crofer22 APU and RA446 alloys is effective to reduce the generation of gaseous Cr species, leading to a significantly low electrochemical degradation as compared to RA600 alloy.

10.2 Major achievements

1. Systematically investigated the interaction reaction between the chromia-forming alloy interconnect and the LSM, LSCF and LSM/YSZ composite cathodes of SOFC. The deposition of Cr species at SOFC cathodes is essentially a chemical dissociation process on re-deposition. The driving force for the deposition of Cr species is associated with the nucleation reaction between the nucleation agent and gaseous Cr species. The results clearly indicate the significant dependence of the Cr deposition process on the nature of the electrode materials. Reaction mechanisms between the chromia-forming alloy interconnect and SOFC cathodes are proposed.
2. Studied in details the effect of Cr specie on the O_2 reduction reaction on the LSM cathode. Gaseous Cr species plays a predominant role in the inhibiting of the oxygen diffusion on the LSM electrode surface while the solid Cr species deposits layer formed at the LSM electrode/YSZ electrolyte interface significantly inhibits the migration process of oxygen ions into the YSZ electrolyte.

3. Demonstrated that the composite electrodes have much higher tolerance towards the Cr species poisoning as compared to the pure LSM cathode. GDC-impregnated LSM and LSM/YSZ with high content of YSZ composite electrodes show stable performance and small amount of Cr species deposition for the O₂ reduction in the presence of chromia-forming alloy interconnect. The results indicate the feasibility of the development of composite electrodes in the prevention of Cr poisoning of chromia-forming alloy interconnect for SOFC.
4. Demonstrated the feasibility of an electrochemical evaluation method to characterize the metallic interconnect. The conventional approaches to evaluation of the alloys for SOFC interconnect are to examine the oxidation resistance and the electrical conductivity at high temperatures. However, it is difficult to determine the Cr volatility of alloys. The results in the present project indicate that the Cr volatility of Fe-Cr alloys could be assessed by the measurement of the magnitude of the performance degradation of LSM cathodes under certain SOFC testing conditions.

10.3 Recommendations

1. Development of composite protective coatings for metallic interconnect

The composite materials have shown to have high tolerance towards the Cr poisoning as compared to the single-phase electrode. This indicates that composite coating may be effective to prevent the Cr evaporation from the chromia-forming alloy interconnect. Currently most studies on the protective coating for the metallic

interconnect are focusing on the development of single-phase material. The novel concept of composite coating includes a matrix of electronic conductor with addition of ionic conducting phases, which could have high tolerance towards the Cr poisoning with no reduction in electronic conductivity.

2. Investigation of the effect of Cr species on the O₂ reduction reaction at the GDC-impregnated LSM cathode

Although GDC-impregnated LSM composite cathode has shown high electrochemical activity for the O₂ reduction and high tolerance towards the Cr poisoning, it still needs more study especially under long-term operation conditions. One of the important issues regarding the ion impregnation treatment is to optimize the distribution of oxygen ion conducting particles within the LSM matrix. Moreover, the mechanism of O₂ reduction reaction on the GDC-impregnated in the presence of chromia-forming alloy as well as that in the absence of chromia-forming alloy is still unclear.

3. Study of the interaction reaction between the metallic interconnect and anodes

This project has mainly focused on the investigation of the interaction reaction between the chromia-forming alloy metallic interconnect and the cathode materials. Similar to that in the oxidant atmospheres, oxide scale would be formed on the chromia-forming alloy surface under the anode atmospheres [[Horita, 2003a and 2003b](#)]. Although the gaseous Cr species generated under reduced atmospheres can be negligible [[Hilpert, 1996](#)], it is possible that the chemical interaction between the

chromia oxide scale and the anode material would take place at high temperatures. Thus, it is also important to study the interaction between the metallic interconnect and the anode materials under SOFC operation conditions before the successful usage of metallic interconnect in SOFC.

4. Further development of quick and adequate electrochemical evaluation method for metallic interconnect

In this project, an electrochemical method has been proposed and is successfully to evaluate the gaseous Cr species from different commercial chromia-forming alloys. The following aspects still need to be investigated. One is to set up the relationship between the degree of performance degradation and the amount of gaseous Cr species from the alloys. The other is to determine the evaporation rate of Cr species at high temperatures. One approach is to use oxide to capture the gaseous Cr species at high temperatures based on the chemical reaction and then to analyze the content of Cr in the oxide.

REFERENCE

- Abellán J.P., Tidt F., Shemet V., Gil A., Ledwein T., Singheiser L., Quadackers W.J. (2002), "Long term oxidation behaviour and compatibility with contact materials of newly developed ferrite interconnect steel", in Proceedings of Fifth European Solid Oxide Fuel Cell Forum, p.248-256
- Adler S.B., Lane J.A., Steele B.C. (1996), "Electrode kinetics of porous mixed-conducting oxygen electrodes", J. Electrochem. Soc., **143**, 3554-3564
- Akashi T., Maruyama T., Goto T. (2003), "Transport of lanthanum ion and hole in LaCrO_3 determined by electrical conductivity measurements", Solid State Ionics, **164** (3-4), 177-183
- Armstrong, T.R., Stevenson, J.W., Pederson, L.R., Raney P.E. (1995), In Proceedings of the Fourth International Symposium on Solid Oxide Fuel Cells (SOFC-IV), p.944
- Armstrong T.R., Stevenson J.W., Pederson L.R., Raney P.E. (1996), "Dimensional instability of doped lanthanum chromite", J. Electrochem. Soc., **143** (9), 2919-2925
- Armstrong, T.R., Hardy, J.S., Simner, S.P., Stevenson, J.W. (1999), "Optimizing lanthanum chromite interconnect for solid oxide fuel cells", In Proceedings of the Sixth International Symposium on Solid Oxide Fuel Cells (SOFC-VI), p.706
- Badwal S.P.S., Deller R., Foger K., Ramprakash Y., Zhang J.P. (1997), "Interaction between chromia forming alloy interconnects and air electrode of solid oxide fuel cells", Solid State Ionics, **99**, 297-310
- Basu R.N., Tietz F., Teller O., Wessel W., Buchkremet H.P., Stöver D. (2003), " $\text{LaNi}_{0.6}\text{Fe}_{0.4}\text{O}_3$ as a cathode contact material for solid oxide fuel cells", J. Solid State Electrochem., **7**, 416-420
- Batawi E., Honegger K., Diethelm R. and Wettstein M. (1996), "The selection and optimisation of thermally sprayed perovskite-based coatings for improved long-term electrochemical performance", in Proceedings of Second European Solid Oxide Fuel Cell Forum, p.307-314
- Batawi E., Glatz W., Kraussler W., Janousek M., Doggwiler B. and Diethelm R. (1999), "Oxidation resistance & performance in stack tests of near-net-shaped chromium-based interconnects", in Proceedings of the Sixth International Symposium on Solid Oxide Fuel Cells (SOFC VI), p.731-736
- Batawi E., Plas A., Straub W., Honegger K., Diethelm R. (1999a), "New cost-effective ceramic oxide phases used as protective coatings for chromium-based interconnects, in Proceedings of the Sixth International Symposium on Solid Oxide Fuel Cells (SOFC VI), p.767-773
- Benson S.J., Waller D. and Kilner J.A. (1999), "Degradation of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$ in carbon dioxide and water atmospheres", J. Electrochem. Soc., **146**, 1305-1309
- Brylewski T., Nanko M., Maruyama T., Przybylski K. (2001), "Application of Fe-16Cr ferritic alloy to interconnect for a solid oxide fuel cell", Solid State Ionics, **143**, 131-150

- Brylewski T., Przybylski K., Morgiel J. (2003), "Microstructure of Fe-25Cr/(La,Ca)CrO₃ composite interconnector in solid oxide fuel cell operating conditions", Mater. Chem. Phys., **81**, 434-437
- Burriel M., Garcia G., Santiso J., Hansson A.N., Linderöth S., Figueras A. (2005), "Co₃O₄ protective coatings prepared by pulsed injection metal organic chemical vapour deposition", Solid Thin Film, **473**, 98-103
- Chen C.C., Nasrallah M.M., Anderson H.U. (1993), in Proceedings of the Third International Symposium on Solid Oxide Fuel Cells (SOFC III), p.252
- Chen X.J., Khor K.A. and Chan S.H. (2003), "Identification of O₂ reduction processes at yttria stabilized zirconia/doped lanthanum manganite interface", J. Power Sources, **123**, 17-25
- Chen X., Hou P.Y., Jacobson C.P., Visco S.J., De Jonghe L.C. (2004), "Protective coating on stainless steel interconnect for SOFCs: oxidation kinetics and electrical properties", Solid State Ionics, **176**, 425-433
- Chen X.J., Chan S.H. and Khor K.A. (2004a), "Defect chemistry of La_{1-x}Sr_xMnO₃ under cathodic polarization", Electrochem. Solid State Lett., **7**, A144
- Chen X.J., Khor K.A. and Chan S.H. (2004b), "Electrochemical behavior of La(Sr)MnO₃ electrode under cathodic and anodic polarization", Solid State Ionics, **167**, 379-387
- Chiba R., Yoshimura F. and Sakurai Y. (2002), "Properties of La_{1-y}Sr_yNi_{1-x}Fe_xO₃ as a cathode material for a low-temperature operating SOFC", Solid State Ionics, **152-153**, 575-582
- Chick L.A., Kiu J., Stevenson J.W., Armstrong T.A., McCready D.E., Maupin G.D., Coffey G.W., Coyle C.A. (1997), "Phase transitions and transient liquid-phase sintering in calcium-substituted lanthanum chromite", J. Am. Ceram. Soc., **80** (8), 2109-2120
- Ciacchi F.T., Crane K.M., Badwal S.P.S.. (1994), "Evaluation of commercial zirconia powders for solid oxide fuel cells", Solid State Ionics, **73**, 49-61
- Cox M.G.E., McEnaney B. and Scott V.D. (1972), "a chemical diffusion model for partitioning of transition elements in oxide scales on alloys", Philos. Mag., **26**, 839-851
- Decorse P., Caboche G. and Dufour L.C. (1999), "A comparative study of the surface and bulk properties of lanthanum-strontium-manganese oxide La_{1-x}Sr_xMnO_{3±δ} as a function of Sr-content, oxygen potential and temperature", Solid State Ionics, **117**, 161-169
- Ebbinghaus B.B. (1993), "Thermodynamics of Gas Phase Chromium Species: The Chromium Oxides, the Chromium Oxyhydroxides, and Volatility Calculations in Waste Incineration Processes", Combustion and Flame, **93**, 119-137
- England D.M., Virkar A.V. (1999), "Oxidation Kinetics of Some Nickel-Based Superalloy Foils and Electronic Resistance of the Oxide Scale Formed in Air Part I", J. Electrochem. Soc., **146** (9), 3196-3202
- England D.M., Virkar A.V. (2001), "Oxidation Kinetics of Some Nickel-Based Superalloy Foils in Humidified Hydrogen and Electronic Resistance of the Oxide Scale Formed Part II", J. Electrochem. Soc., **148** (4), A330-A338

- Esquirol A., Brandon N.P., Kilner J.A., Mogenson M. (2004), "Electrochemical characterization of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ cathodes for intermediate-temperature SOFCs", *J. Electrochem. Soc.*, **151** (11), A1847-A1855
- Flandermeyer B.F., Nasrallah M.M., Sparlin D.M., Anderson H.U. (1985), "High temperature stability of magnesium-doped lanthanum chromite", *High Temp. Sci.*, **20** (3), 256-269
- Fergus J.W. (2005), "Metallic interconnects for solid oxide fuel cells", *Mater. Sci. Engin. A*, **397**, 271-283
- Fujita K., Ogasawara K., Matsuzaki Y., Sakurai T. (2004), "Prevention of SOFC cathodes degradation in contact with Cr-containing alloy", *J. Power Sources*, **131**, 261-269
- Fujita K., Hashimoto T., Ogasawara K., Kamede H., Matsuzaki Y., Sakurai T. (2004a), "Relationship between electrochemical properties of SOFC cathode and composition of oxide layer formed on metallic interconnects", *J. Power Sources*, **131**, 270-277
- Gannon P.E., Trip C.T., Knospe A.K., Ramana C.V., Deibert M., Smith R.J., Gorokhovskiy V., Shutthanandan V., Gelles D. (2004), "High-temperature oxidation resistance and surface electrical conductivity stainless steels with filtered arc Cr-Al-N multiplayer and/or superlattice coatings", *Surf. Coat. Technol.*, **188-189**, 55-61
- Gharbage B., Tagnier T., Mammou A. (1994), "Oxygen Reduction at $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ Thin Film/Yttria-Stabilized Zirconia Interface Studied by Impedance Spectroscopy", *J. Electrochem. Soc.*, **141**, 2118-2122
- Gindorf C., Singheiser L., Hilpert K., Schroeder M., Martin M., Greiner H., Richter F. (1999), "Chromium vaporization from metallic interconnect and retention by perovskite layers", in *Proceedings of the Sixth International Symposium on Solid Oxide Fuel Cells (SOFC VI)*, p.774-782
- Gindorf C., Hilpert K., Nabielek H., and Singheiser L. (2000), "Chromium release from metallic interconnects with and without coatings", in *Proceedings of Fourth European Solid Oxide Fuel Cell Forum*, p.845-854
- Gindorf C., Hilpert K. and Singheiser L. (2001), "Determination of chromium vaporization rates of different interconnect alloys by transpiration experiments", in *Proceedings of the Seventh International Symposium on Solid Oxide Fuel Cells (SOFC VII)*, p.793-802.
- Glatz W., Batawi E., Janousek M., Kraussler W., Zach R., Zobl G. (1999), "A new low cost mass production route for metallic SOFC-interconnectors", in *Proceedings of the Sixth International Symposium on Solid Oxide Fuel Cells (SOFC VI)*, p.783-790
- Gödicke M., Sakaki K., Gauckler L.J. and Riess I. (1997), "Electrochemical characteristics of cathodes in solid oxide fuel cells based on ceria electrolytes", *J. Electrochem. Soc.*, **144**, 1635.
- Gorte R. J., Kim H. and Vohs J. M. (2002), "Novel SOFC anodes for the direct electrochemical oxidation of hydrocarbon", *J. Power Sources*, **106**, 10-15
- Graham H.G. and Davis H.H. (1971), "Oxidation/vaporization kinetics of Cr_2O_3 ", *J. Am. Ceram. Soc.*, **54**, 89

- Hatchwell C.E., Sammes N.M., Tompsett G.A. and Brown I.W.M. (1999), "Chemical compatibility of chromium-based interconnect related materials with doped cerium oxide electrolyte", J. Euro. Ceram. Soc., **19**, 1697-1703
- Hibino T., Hashimoto A., Yano M., Suzuki M., Yoshida S., Sano M. (2002), "High performance anodes for SOFCs operating in methane-air mixture at reduced temperatures", J. Electrochem. Soc., **149** (2), A133-A136
- Hilpert K., Das D., Miller M., Peck D. H. and Weiß R. (1996), "Chromium Vapor Species over Solid Oxide Fuel Cell interconnect Materials and Their Potential for Degradation Processes", J. Electrochem. Soc., **143**, 3642-3647
- Hilpert K., Steinbrech R.W., Boroomand F., Wessel E., Meschke F., Zuev A., Teller O., Nickel H., Singheiser L. (2003), "Defect formation and mechanical stability of perovskites based on LaCrO_3 for solid oxide fuel cells (SOFC)", J. Eur. Ceram. Soc., **23**, 3009-3020
- Höfer H.E., Kock W.F. (1993), "Crystal chemistry and thermal behavior in the $\text{La}(\text{Cr,Ni})\text{O}_3$ perovskite system", J. Electrochem. Soc., **140** (10), 2889-2894
- Holt A., Kofstad P. (1994), "Electrical conductivity and defect structure of Cr_2O_3 . I. High temperatures ($>1000^\circ\text{C}$)", Solid State Ionics, **69**, 127-136
- Holt A., Kofstad P. (1994a), "Electrical conductivity and defect structure of Cr_2O_3 . II. Reduced temperatures ($<1000^\circ\text{C}$)", Solid State Ionics, **69**, 137-143
- Honegger K., Plas A., Diethelm R., Glatz W. (2001), "Evaluation of Ferritic Steel Interconnects for SOFC Stacks", in Proceedings of the Seventh International Symposium on Solid Oxide Fuel Cells (SOFC VII), p.803-810
- Horita T., Ishikawa M., Yamaji K., Sakai N., Yokokawa H., and Dokiya M. (1998), "Cation diffusion in $(\text{La,Ca})\text{CrO}_3$ perovskite by SIMS", Solid State Ionics, **108**, 383
- Hortia T., Yamaji K., Ishikawa M., Sakai N., Yokokawa H., Kawada T. and Kato T. (1998), "Active sites imaging for oxygen reduction at the $\text{La}_{0.9}\text{Sr}_{0.1}\text{MnO}_{3-x}/\text{Yttria-stabilized zirconia}$ interface by secondary-ion mass spectrometry", J. Electrochem. Soc., **145**, 3196-3202
- Horita T., Tsunoda T., Yamaji K., Sakai N., Kato T., Yokokawa H. (2002), "Microstructures and oxygen diffusion at the LaMnO_3 film/yttria-stabilized zirconia interface", Solid State Ionics, **152-153**, 439-446
- Horita T., Xiong Y., Yamaji K., Sakai N., Yokokawa H. (2003a), "Stability of Fe-Cr alloy interconnects under $\text{CH}_4\text{-H}_2\text{O}$ atmosphere for SOFCs", J. Power Sources, **118**, 35-43
- Horita T., Xiong Y., Yamaji K., Sakai N., Yokokawa H. (2003b), "Evaluation of Fe-Cr Alloys as Interconnects for Reduced Operation Temperature SOFCs", J. Electrochem. Soc., **150** (3), A243-A248
- Horita T., Xiong Y., Kishimoto H., Yamaji K., Sakai N., Yokokawa H. (2003c), in Proceedings of the Eighth International Symposium on Solid Oxide Fuel Cells (SOFC VIII), p.856-864
- Horita T., Xiong Y., Kishimoto H., Yamaji K., Sakai N., Yokokawa H. (2004a), "Application of

- Fe-Cr alloys to solid oxide fuel cells for cost-reduction oxidation behavior of alloys in methane fuel”, *J. Power Sources*, **131**, 293-298
- Horita T., Xiong Y., Kishimoto H., Yamaji K., Sakai N., Brito M.E., Yokokawa H. (2004b), “Imaging of mass transports around the oxide scale/Fe-Cr alloy interfaces”, *Solid State Ionics*, **174**, 41-48
- Hou P.Y., Huang K., Bakker W.T. (1999), “Performance and problems with metallic interconnects for reduced temperature solid oxide fuel cells”, in Proceedings of the Sixth International Symposium on Solid Oxide Fuel Cells (SOFC VI), p.737-748
- H. Hu and M. Liu (1998), “Interfacial studies of solid-state cells based on electrolytes of mixed ionic–electronic conductors”, *Solid State Ionics*, **109**, 259-272
- Huang K., Hou P.Y., Goodenough J.B. (2000), “Characterization of iron-based alloy interconnects for reduced temperature solid oxide fuel cells”, *Solid State Ionics*, **129**, 237-250
- Huang K., Hou P.Y., Goodenough J.B. (2001), “Reduced area specific resistance for iron-based metallic interconnects by surface oxide coatings”, *Mater. Research Bulletin*, **36**, 81-95
- Ishihara T., Matsuda H. and Takita Y. (1994), “Doped-LaGaO₃ perovskite type oxide as a new oxygen ionic conductor”, *J. Amer.Chem. Soc.*, **116**, 3801-3803
- Jiang S.P., Love J.G., Badwal S.P.S. (1997), “Electrochemical Techniques in Studies of Solid Ionic Conductors”, *Key Engineering Material*, **125-126**, 81-132
- Jiang S.P., Zhang J.P., Apateanu L., Foger K. (1999), “Deposition of chromium species on Sr-doped LaMnO₃ cathodes in solid oxide fuel cell”, *Electrochem. Commun.*, **1**, 394-397
- Jiang S.P., Love J.G., Zhang J.P., Hoang M., Ramprakash Y., Hughes A.E. and Badwal S.P.S. (1999a), “The electrochemical performance of LSM/zirconia-yttria interface as a function of a-site non-stoichiometry and cathodic current treatment”, *Solid State Ionics*, **121**, 1-10
- Jiang S.P., Zhang J.P., Apateanu L. and Foger K. (2000), “Deposition of Chromium Species at Sr-Doped LaMnO₃ Electrodes in Solid Oxide Fuel Cells I. Mechanism and Kinetics”, *J. Electrochem. Soc.*, **147** (11), 4013-4022
- Jiang S.P., Zhang J.P. and Foger K. (2000a), “Deposition of Chromium Species at Sr-Doped LaMnO₃ Electrodes in Solid Oxide Fuel Cells II. Effect on O₂ Reduction Reaction”, *J. Electrochem. Soc.*, **147** (9), 3195-3205
- Jiang S.P., Zhang J.P., Ramprakash Y., Milosevic, Wilshier K. (2000b), “An investigation of shelf-life of strontium doped LaMnO₃ materials”, *J. Mater. Sci.*, **35**, 2735-2741
- Jiang S.P., Zhang J.P. and Foger K. (2001), “Deposition of Chromium Species at Sr-Doped LaMnO₃ Electrodes in Solid Oxide Fuel Cells III. Effect of Air Flow”, *J. Electrochem. Soc.*, **148** (7), C447-C455
- Jiang S.P. and Love J.G. (2001a), “Origin of the initial polarization behavior of Sr-doped LaMnO₃ for O₂ reduction in solid oxide fuel cells”, *Solid State Ionics*, **138**, 183-190
- Jiang S.P. (2001b), “Use of gaseous Cr species to diagnose surface and bulk process for O₂

- reduction in solid oxide fuel cells”, *J. Applied Electrochem.*, **31**, 181-192
- Jiang S.P., Zhang J.P., Zheng X.G. (2002), “A comparative investigation of chromium deposition at air electrodes at solid oxide fuel cells”, *J. Euro. Ceram. Soc.*, **22**, 361-373
- Jiang S.P. (2002a), “A comparative of O₂ reduction reactions on porous (La,Sr)MnO₃ and (La,Sr)(Co,Fe)O₃ electrodes”, *Solid State Ionics*, **146**, 1-22
- Jiang S.P., Love J.G. and Ramprakash Y. (2002b), “Electrode behaviour at (La,Sr)MnO₃/Y₂O₃-ZrO₂ interface by electrochemical impedance spectroscopy”, *J. Power Sources*, **110**, 201-208
- Jiang S. P. (2003), “Issues on development of (La,Sr)MnO₃ cathode for solid oxide fuel cells”, *J. Power Sources*, **124**, 390-402
- Jiang S.P. and Love J.G. (2003a), “Observation of structure change induced by cathodic polarization on (La,Sr)MnO₃ electrodes of solid oxide fuel cells”, *Solid State Ionics*, **158**, 45-53
- Jiang S.P., Leng Y.J., Chan S.H. and Khor K.A. (2003b), “Development of (La,Sr)MnO₃-based cathodes for intermediate temperature solid oxide fuel cells”, *Electrochem. Solid-State Lett.*, **6**, A67-A70
- Jiang S.P., Zhang S., and Zhen Y.D. (2005), “Early interaction between Fe-Cr alloy metallic interconnect and Sr-doped LaMnO₃ cathodes of solid oxide fuel cells”, *J. Mater. Res.*, **20**, 747-758
- Jiang S.P., Wang W. (2005a), “Effect of polarization on the interface between (La,Sr)MnO₃ electrode and Y₂O₃-ZrO₂ electrolyte”, *Electrochem. Solid State Lett.*, **8**, A115
- Jiang S.P., Wang W. (2005b), “Fabrication and performance of GDC-impregnated (La,Sr)MnO₃ cathodes for intermediate temperature solid oxide fuel cells”, *J. Electrochem. Soc.*, **152** (7), A1398-A1408
- Jiang Y., Wang S., Zhang Y., Yan J. and Li W. (1998), “Kinetic Study of the Formation of Oxygen Vacancy on Lanthanum Manganite Electrodes”, *J. Electrochem. Soc.*, **145**, 373-378
- Johnson C., Gemmen R., Orlovskaya N. (2004), “Nano-structured self-assembled LaCrO₃ thin film deposited by RF-magnetron sputtering on a stainless steel interconnect steel”, *Composite: Part B*, **35**, 167-172
- Jørgensen M. J. and Mogensen M. (2001), “Impedance of solid oxide fuel cell LSM/YSZ composite cathodes”, *J. Electrochem. Soc.*, **148**, A433-A442
- Kamata H., Hosaka A., Mizusaki J., Tagawa H. (1998), “High temperature electrocatalytic properties of the SOFC air electrode La_{0.8}Sr_{0.2}MnO₃/YSZ”, *Solid State Ionics*, **106**, 237-245
- Kim J.D., Kim G.D., Moon J.W., Park Y., Lee W.H., Kobayashi K., Nagai M., Kim C.E. (2001), “Characterization of LSM-YSZ composite electrode by ac impedance spectroscopy”, *Solid State Ionics*, **143**, 379-389
- Kofstad P. (1996), “High temperature oxidation of chromium and chromia-forming alloys”, in *Proceedings of Second European Solid Oxide Fuel Cell Forum*, p.479-490
- Krogh, B., Brustad, B., Dahle, M., Eilertsen, J.L., Odegard, R. (1997), in *Proceedings of the Fifth*

International Symposium on Solid Oxide Fuel Cells (SOFC-V), p.1234

Kurokawa H., Kawamura K., Maruyama T. (2004), "Oxidation behavior of Fe-16Cr alloy interconnect for SOFC under hydrogen potential gradient", Solid State Ionics, **168**, 13-21

Larring Y., Norby T. (2000), "Spinel and perovskite functional layers between planese metallic interconnect (Cr-5 wt% Fe-1 wt% Y₂O₃) and ceramic (La_{0.85}Sr_{0.15})_{0.91}MnO₃ cathode materials for solid oxide fuel cells", J. Electrochem. Soc., **147** (9), 3251-3256

Lee H. G. (2000), Chemical Thermodynamics for Metals and Materials

Lee H.Y., Cho W.S., Oh S.M., Wiemhofer H. D. and Gopel W. (1995), "Active Reaction Sites for Oxygen Reduction in La_{0.9}Sr_{0.1}MnO₃/YSZ Electrodes", J. Electrochem. Soc., **142**, 2659-3065

Leng Y.J., Chan S.H, Khor K.A., and Jiang S.P. (2004)," Development of LSM/YSZ composite cathode for anode-supported solid oxide fuel cells", J. Appl. Electrochem., **34**, 409-415

Liebert B. E. (1999), "Electrical characterization of a chromium alloy interconnect material", in Proceedings of the Sixth International Symposium on Solid Oxide Fuel Cells (SOFC VI), p.722-730

Linderoth. S., Hendriksen P.V., Mogensen M. (1996), "Investigation of metallic alloy for use as interconnect in solid oxide fuel cell stacks", J. Mater. Sci., **31**, 5077-5082

Liu M., Wu Z. (1998), "Significance of interfaces in solid-state cells with porous electrodes of mixed ionic–electronic conductors", Solid State Ionics, **107**, 105-110

Majkic G, Mironova M., Wheeler L.T., and Salama K. (2004), "Stress-induced diffusion and defect chemistry of La_{0.2}Sr_{0.8}Fe_{0.8}Cr_{0.2}O_{3-δ}: 2. Structural, elemental and chemical analysis", Solid State Ionics, **167**, 243-254

Matsuzaki Y., Yasuda I. (2000), "Electrochemical properties of a SOFC cathode in contact with a chromium-containing alloy separator", Solid State Ionics, **132**, 271-278

Matsuzaki Y. and Yasuda I. (2001), "Dependence of SOFC Cathode Degradation by Chromium-Containing Alloy on Compositions of Electrodes and Electrolytes", J. Electrochem. Soc., **148** (2), A126-A131

McIntosh S., Vohs J.M., Gorte R.J. (2003), "Effect of Precious-metal dopants on SOFC anodes for direct utilization of hydrocarbons, Electrochem. Solid-State Lett., **6**, A240–A243

McIntosh S., Adler S.B., Vohs J.M., Gorte R.J. (2004), "Effect of polarization on and implications for characterization of LSM-YSZ composite cathodes", Electrochem. Solid-State Lett., **7** (5), A111-A114

Meulenberg W.A., Uhlenbruck S., Wessel E., Buchkremer H.P., Stöver D. (2003), "Oxidation behavior of ferrous alloys used as interconnecting material in solid oxide fuel cells", J. Mater. Sci., **38**, 507-513

Minh N.Q., Takahashi T. (1995), Science and Technology of Ceramic Fuel Cells, Elsevier, Amsterdam

- Minh N.Q. (2005), "Solid oxide fuel cell systems for stationary power generation applications", in: Singhal S.C., Mizusaki J. (Eds.), in Proceedings of the Ninth International Symposium on Solid Oxide Fuel Cells (SOFC IX), 76-81
- Mitterdorfer A. and Gauckler L.J. (1998), "La₂Zr₂O₇ formation and oxygen reduction kinetics of the La_{0.85}Sr_{0.15}Mn_yO₃, O₂(g)/YSZ system", Solid State Ionics, **111**, 185-218
- Miura N., Okamoto Y., Tamaki J., Morinaga K., and Yamazoe N. (1995), "Oxygen semipermeability of mixed-conductive oxide thick-film prepared by slip casting", Solid State Ionics, **79**, 195
- Mizusaki J., Saito T. and Tagawa H. (1996), "A chemical diffusion-controlled electrode reaction at the compact La_{1-x}Sr_xMnO₃/stabilized zirconia interface in oxygen atmosphere", J. Electrochem. Soc., **143**, 3065-3073
- Mizusaki J. Mori N., Takai H., Yonemura Y., Minamiue H., Tagawa H., Dokiya M., Inaba H., Naraya K., Sasamoto T., Hashimoto T. (2000), "oxygen nonstoichiometry and defect equilibrium in the perovskite-type oxides La_{1-x}Sr_xMnO_{3±δ}", Solid State Ionics, **129**, 163-177
- Mogensen M., Sammes N.M., Tompsett G.A. (2000), "Physical, chemical and electrochemical properties of pure and doped ceria", Solid State Ionics, **129**, 63-94
- Mori M., Hiei Y., Sammes N.M. (1999), "Sintering behavior and mechanism of Sr-doped lanthanum chromites with A site excess composition in air", Solid State Ionics, **123**, 103-111
- Mori M. and Sammes N.M. (2002), "Sintering and thermal expansion characterization of Al-doped and Co-doped lanthanum strontium chromites synthesized by the Pechini method", Solid State Ionics, **146**, 301-312
- Murray E.P., Tsai T., Barnett S.A. (1998), "Oxygen transfer processes in (La,Sr)MnO₃/Y₂O₃ stabilized ZrO₂ cathodes: an impedance spectroscopy study", Solid State Ionics, **110**, 235-243
- Murray E. P. and Barnett S. A. (2001), "(La,Sr)MnO₃-(Ce,Gd)O_{2-x} composite cathodes for solid oxide fuel cells", Solid State Ionics, **143**, 265-273
- Murray E. P., Sever M. J. and Barnett S. A. (2002), "Electrochemical performance of (La,Sr)(Co,Fe)O₃-(Ce,Gd)O₃ composite cathodes", Solid State Ionics, **148**, 27-34
- Nguyen B.C., Lin L., and Mason D.M. (1986), J. Electrochem. Soc., **133**, 1807
- Oishi N., Yamazaki Y. (1999), "The effect of rare earth element coatings on oxidation of alloys in SOFC operating atmosphere", in Proceedings of the Sixth International Symposium on Solid Oxide Fuel Cells (SOFC VI), p.759-766
- Park K., Olander D.R. (1991), "Oxygen Diffusion in Single-Crystal Tetragonal Zirconia", J. Electrochem. Soc., **138**, 1154-1159
- Paulik S.W., Baskaran S., Armstrong T.R. (1997), "Mechanical properties of calcium- and strontium-substituted lanthanum chromite", J. Mater. Sci., **33**, 2397- 2404
- Paulik S.W., J. Hardy, Stevenson J., Armstrong T.R. (2000), "Sintering of non-stoichiometric strontium doped lanthanum chromite", J. Mater. Lett., **19**, 863-865

- Paulson S.C., Birss V.I. (2004), "Chromium poisoning of LSM-YSZ SOFC cathodes", J. Electrochem. Soc., **151** (11), A1961-A1968
- Peck D.H., Miller M. and Hilpert K. (2001), "Vaporization and thermodynamics of $\text{La}_{1-x}\text{Sr}_x\text{CrO}_3$ investigated by Knudsen efficient mass spectroscopy", Solid State Ionics, **143**, 401-412
- Qu W., Li J., Ivey D.G. (2004), "Sol-Gel coatings to reduce oxide growth in interconnects used for solid oxide fuel cell", J. Power Sources, **138**, 162-173
- Quadackers W.J., Griner, H., Kock, W. (1994), "Metals and alloys for high temperature SOFC application", in Proceedings of the First European Solid Oxide Fuel Cell Forum, p.525
- Quadackers W.J., Greiner H., Hansel M., Pattanaik A., Khanna A. S., Mallener W. (1996), "Compatibility of perovskite contact layers between cathode and metallic interconnector plates of SOFCs", Solid State Ionics, **91**, 55-67
- Quadackers W.J., Malkow T., Abellán J.P., Flesch U., Shemet V., Singheiser L. (2000), "Suitability of ferritic steels for application as construction materials for SOFC interconnects", in Proceedings of Fourth European Solid Oxide Fuel Cell Forum, p.827-836
- Ralph J.M., Schoeler A.C., Krumpelt M. (2001), "Materials for lower temperature solid oxide fuel cells", J. Mater. Sci., **36**, 1161-1172
- Sabioni A.C.S., Huntz A.M., Millot F., Monty C. (1992), Philos. Mag. A, **66**, 361
- Sakai, N., Horita, T., Yokokawa, H., Dokiya, M., Kawada, T. (2000), in Proceedings of Fourth European Solid Oxide Fuel Cell Forum, p.531.
- Sauvet A. -L. and Fouletier J. (2001), "Catalytic properties of new anode materials for solid oxide fuel cells operated under methane at intermediary temperature", J. Power Source, **101**, 259-266
- Schulz O. and Martin M. (2000), "Preparation and characterization of $\text{La}_{1-x}\text{Sr}_x\text{Ga}_{1-y}\text{Mg}_y\text{O}_{3-(x+y)/2}$ for the investigation of cation diffusion processes", Solid State Ionics, **135**, 549
- Shao Z., Haile S.M. (2004), "A high-formance cathode for the next generation of solid-oxide fuel cells", Nature, **431**, 170-173
- Simner S.P., Anderson M.D., Xia G.G., Yang Z., Pederson L.R., and Stevenson J.W. (2005), "SOFC performance with Fe-Cr-Mn alloy interconnect", J. Electrochem. Soc., **152** (4), A740-A745
- Simpson L.A., Carter R.E. (1966), J. Am. Ceram. Soc., **49**, 139
- Speidel D. H. and Muan A. (1963), "The System Manganese Oxide- Cr_2O_3 in Air", J. Am. Ceram. Soc., **46**, 577-578
- Speidel D.H., Muan A. (1963), "The system manganese oxide- Cr_2O_3 in air", J. Am. Ceram. Soc., **46**, 577
- Stearns C.A., Kohl F.K., and Fryburg G.C. (1974), "Oxidative vaporization kinetics of Cr_2O_3 in oxygen from 1000 to 1300°C", J. Electrochem. Soc., **121**, 945
- Steele B.C.H. (1994), *Electrochemistry and clean energy*, Royal Society of Chemistry

- Steele B.C.H. (1999), "Running on natural gas", *Nature*, **400**, 619-621
- Steele B.C.H., Heinel A. (2001), "Materials for fuel cell technologies", *Nature*, **414**, 345-352
- Tai L.W., Lessing P.A. (1991), "Tape casting and sintering of strontium doped lanthanum chromite for a planar solid oxide fuel cell bipolar plate", *J. Am. Ceram. Soc.*, **74** (1), 155-160
- Takeda Y., Kanno R., Noda M., Tomida Y. and Yamamoto O. (1987), "Cathodic polarization phenomena of perovskite oxide electrodes with stabilized zirconia", *J. Electrochem. Soc.*, **132**, 2656-2661
- Taniguchi S., Kadowaki M., Kawamura H., Yasuo T., Akiyama Y., Miyake Y., Saitoh T. (1995), "Degradation phenomena in the cathode of a solid oxide fuel cell with an alloy separator", *J. Power Sources*, **55**, 73-79
- Tao S.W. and Irvine J.T.S. (2003), "A redox-stable efficient anode for solid-oxide fuel cells", *Nature Material*, **2**, 320-323
- Teller O., Meulenberg W.A., Tietz F., Wessel E. and Quadackers W. J. (2001), "Improved material combination for stacking of solid oxide fuel cells", in *Proceedings of the Seventh International Symposium on Solid Oxide Fuel Cells (SOFC VII)*, p.895-903
- Uchida H., Yoshida M., Watanabe M. (1999), "Effect of ionic conductivity of zirconia electrolytes on the polarization behavior of various cathodes in Solid Fuel Cells", *J. Electrochem. Soc.*, **146**, 1-7
- Ueda M., Taimatsu H. (2000), "Thermal Expansivity and High-Temperature Oxidation Resistance of Fe-Cr-W alloys Developed for a Metallic Separator of SOFC", in *Proceedings of Fourth European Solid Oxide Fuel Cell Forum*, p.837-843
- Uehara T., Ohno T., Toji A. (2002), "Development of Ferritic Fe-Cr Alloy for SOFC Separator", in *Proceedings of the Fifth European Solid Oxide Fuel Cell Forum*, p.281-288
- Urbanek J., Miller M., Schmidt H., and Hilpert K. (1996), "Reduction of the chromium vaporization from the metallic interconnect by perovskite coatings", in *Proceedings of Second European Solid Oxide Fuel Cell Forum*, p.503-512
- van Heuveln F. H and Bouwnesster H. J. M. (1997), "Electrode Properties of Sr-Doped LaMnO_3 on Yttria-Stabilized Zirconia I. Three-Phase Boundary Area", *J. Electrochem. Soc.*, **144**, 126-133
- van Heuveln F. H and Bouwnesster H. J. M. (1997a), "Electrode Properties of Sr-Doped LaMnO_3 on Yttria-Stabilized Zirconia II. Electrode Kinetics", *J. Electrochem. Soc.*, **144**, 134-140
- van der Heride P.A.W. (2002), "Systematic x-ray photoelectron spectroscopic study of $\text{La}_{1-x}\text{Sr}_x$ -based perovskite-type oxides", *Surf. Interface Anal.*, **33**, 414-425
- Vazquez-Navarro M.D., McAleese J., Kilner J.A. (1999), "Candidate Interconnect Materials: Oxidation Study of A Ni-Based Superalloy in Pure Oxygen at 800°C ", in *Proceedings of the Sixth International Symposium on Solid Oxide Fuel Cells (SOFC VI)*, p.749-758
- Viitanen M.M., v. Welzenis R.G., Brongersma H.H. and van Berkel F.P.F. (2002), "Silica poisoning of oxygen membranes", *Solid State Ionics*, **150**, 223-228

- Wang S.Z., Jiang Y., Zhang Y., Yan J., Li W. (1998), "The role of 8mol% yttria stabilized zirconia in the improvement of electrochemical performance of lanthanum manganite composite electrodes", J. Electrochem. Soc., **145**, 1932-1939
- Wang W., Jiang S.P. (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
- Weber A., Ivers-Tiffée E. (2004), "Materials and concepts for solid oxide fuel cells (SOFCs) in stationary and mobile applications", J. Power Sources, **127**, 273-283
- Uchida H., Yoshida M. and Watanabe M. (1999), "Effect of ionic conductivity of zirconia electrolyte on the polarization behavior of various cathodes in solid oxide fuel cells", J. Electrochem. Soc., **146**, 1-7
- Xia C., Liu M. (2002), "Microstructure, conductivity, and electrochemical properties of Ce_{0.9}Gd_{0.1}O₂ and GDC-Ni anodes for low-temperature SOFCs", Solid State Ionics, **152-153**, p423-430
- Xia C., Rauch W., Chen F., Liu M. (2002b), "Sm_{0.5}Sr_{0.5}CoO₃ cathodes for low-temperature SOFCs", Solid State Ionics, **149**, 11-19
- Yamamoto O., Arati Y., Takeda Y., Imanishi N., Mizutani Y., Kawai M. and Nakamura Y. (1995), "Electrical conductivity of stabilized zirconia with ytterbia and Scandia", Solid State Ionics, **79**, p137-142
- Yang Z., Weil K.S., Paxton D.M., Stevenson J.W. (2003), "Selection and evaluation of heat-resistant alloys for SOFC interconnect applications", J. Electrochem. Soc., **150** (9), A1188-A1201
- Yang Z., Walker M.S., Singh P., Stevenson J.W. (2003a), "Anomalous corrosion behavior of stainless steels under SOFC interconnect exposure conditions", Electrochem. Solid State Lett., **6** (10), B35-B37
- Yang Z., Hardy J.S., Walker M.S., Xia G., Simner S.P., Stevenson J.W. (2004), "Structure and conductivity of thermal grown scales on ferrite Fe-Cr-Mn steel for SOFC interconnect applications", J. Electrochem. Soc., **151** (11), A1825-A1831
- Yang Z., Walker M.S., Singh P., Stevenson J.W., Norby T. (2004a), "Oxidation behavior of ferrite stainless steels under SOFC interconnect exposure conditions", J. Electrochem. Soc., **150** (12), B669-B678
- Yang Z., Xia G., Stevenson J.W. (2005), "Mn_{1.5}Co_{1.5}O₄ spinel protection layers on ferritic stainless steels for SOFC interconnect applications", Electrochem. Solid State Lett., **8** (3), A168-A170
- Yasuda I., Ogasawara K., Hishinuma M., Kawada T., Dokiya M. (1996), "Oxygen tracer diffusion coefficient of (La, Sr)MnO_{3±δ}", Solid State Ionics, **86-88**, 1197-1201
- Yokokawa H., Sakai N., Kawada T., Dokiya M. (1991), "Chemical thermodynamic considerations in sintering of LaCrO₃-based perovskites", J. Electrochem. Soc., **138** (4), 1018-1027.
- Yoo Y., Dauga M. (2001), "The Effect of Protective Layers Formed by Electrophoretic Deposition

- on Oxidation and Performance of Metallic Interconnects”, in Proceedings of the Seventh International Symposium on Solid Oxide Fuel Cells (SOFC VII), p.837-846
- Youndblood G.E., Ruppel A.S., Pederson L.R., Bates J.L. (1993), in: Proceedings of the Third International Symposium on Solid Oxide Fuel Cells (SOFC III), p.585
- Yu C.J., Anderson H.U., Sparlin D.M. (1989), “High-temperature defect structure of Nb-doped LaCrO_3 ”, J. Solid State Chem., **78**, 242– 249
- Zeng Z., Natesan K. (2004), “ Corrosion of metallic interconnects for SOFC in fuel gases”, Solid State Ionics, **167**, 9-16
- Zhang J.P., Jiang S.P., Love J.G., Forger K., Badwal S.P.S. (1998), “Chemical interactions between strontium-doped praseodymium manganite and 3 mol% yttria-zirconia”, J. Mater. Chem., **8**, 2787-2794
- Zhu W.Z., Deevi. S.C. (2003), “Development of interconnect materials for solid oxide fuel cells”, Mater. Sci. Engin. A, **348**, 227-243
- Zhu J.H., Zhang Y., Basu A., Lu Z.G., Paranthaman M., Lee D.F., Payzant E.A. (2004), “ LaCrO_3 -based coatings on ferritic stainless steel for solid oxide fuel cell interconnect applications”, Surf. Coat. Technol., **177-178**, 65-72
- Zuev A., Singheiser L., Hilpert K. (2002), “Defect structure and isothermal expansion of A-site and B-sitesubstituted lanthanum chromites”, Solid State Ionics, **147**, 1 – 11

APPENDIX

THERMODYNAMIC CALCULATION OF GASEOUS Cr SPECIES OVER METALLIC INTERCONNECT

1. Procedure

Vaporization of the oxide scales (Cr_2O_3) formed on the surface of the chromia-forming alloy interconnect in different atmospheres is complex. Cr_2O_3 produces a number of volatile species, such as CrO_3 , CrO_2 and CrO by reacting with the oxygen. Several gaseous hydroxide and oxyhydroxide species would be generated if H_2O in addition to oxygen is present in the atmosphere. The possible gaseous Cr species formed under the conditions of cathode and anode of SOFC are listed in Table 1, followed by the chemical reaction equations.

Table 1. Gaseous chromium oxide, hydroxide and oxyhydroxide over Cr_2O_3

CrO	Cr(OH) ₃	CrOOH
CrO ₂	Cr(OH) ₄	CrO(OH) ₂
CrO ₃	Cr(OH) ₅	CrO(OH) ₃
	Cr(OH) ₆	CrO(OH) ₄
		CrO ₂ OH
		CrO ₂ (OH) ₂

where x, y are the stoichiometric coefficients of the reactants, respectively.

The following calculation is concentrated on the CrO_3 where the calculation procedures of other gaseous chromium species are similar. The total pressure (P^0) in the system is assumed to be constant, i.e. 1 bar.

For the reaction

At a given temperature (T) the total standard free energy change (ΔG_m^0) can be obtained from the Gibbs free energy change of every species according to the stoichiometric coefficients.

$$\Delta G_m^0(T) = \Delta G_m^0(T)_{\text{CrO}_3} - 1/2\Delta G_m^0(T)_{\text{Cr}_2\text{O}_3} - 3/4\Delta G_m^0(T)_{\text{O}_2} \quad (6)$$

For every species the Gibbs free energy change can be calculated from the heat capacity (C_p) of the species involved as a function of T and using values of both standard enthalpy of formation (ΔH_m) and standard entropy (ΔS_m) at one particular temperature, usually 298K.

$$\Delta H_m(T) = \Delta H_m^0 + \int_{298}^T C_p dT \quad (7)$$

$$\Delta S_m(T) = \Delta S_m^0 + \int_{298}^T \frac{C_p}{T} dT \quad (8)$$

The heat capacity of species, as a function of T , can be expressed as:

$$C_p(T) = A + BT + CT^{-2} + DT^2 \quad (9)$$

Therefore,

$$\Delta H_m(T) = \Delta H_m^0(298K) + A(T-298) + 1/2B(T-298)^2 - C(1/T - 1/298) + 1/3D(T-298)^3 \quad (10)$$

$$\Delta S_m(T) = \Delta S_m^0(298K) + A \ln(T/298) + B(T-298) - 1/2C(T-298)^{-2} + 1/2D(T-298)^2 \quad (11)$$

Then, for every species at a given temperature (T),

$$\Delta G_m(T)_i = \Delta H_m(T) - T\Delta S_m(T) \quad (12)$$

Therefore the standard free energy change of reaction (5) can be computed by equation (6). Meanwhile, for gaseous reaction the free energy change and the equilibrium constant had the following relationship:

$$\Delta G_m(T) = -RT \ln K \quad (13)$$

Then, the partial pressure of the product (CrO_3) can be calculated from the equilibrium constant (K).

$$K = (P_{\text{CrO}_3} / P^0) / (P_{\text{O}_2} / P^0)^{3/4} \quad (14)$$

The thermodynamic data of the gaseous chromium species listed in Table 1 are given in the publication by Ebbinghaus [1993], shown in the end of this section. While the heat capacities of solid Cr_2O_3 , gaseous H_2O and O_2 are obtained from other reference.

In order to study the interaction of $\text{H}_2\text{O}(\text{g})$ with $\text{Cr}_2\text{O}_3(\text{s})$ in air, the partial pressure of water, $P_{\text{H}_2\text{O}}$, is varied between its typical value in air and that present in the anode gas composed of $\text{H}_2(\text{g})$ and $\text{H}_2\text{O}(\text{g})$. The partial pressure of oxygen in the

cathode side, P_{O_2} , is kept at 2.13×10^4 Pa. This is in contrast to the anode gas with partial pressure P_{O_2} in the range of 10^{-11} - 10^{-7} Pa, which results by the use of different fuels and a varying percentage of each fuel burned downstream in the flowing gas [Hilpert, 1996]. Partial pressure of oxygen higher than 10^{-7} Pa are obtained by the mixing of cathode gas with the anode gas caused by possible leakage of seals or electrolytes. Such leakage also leads additionally high $H_2O(g)$ concentration in the cathode gas. The possible leakage and the $H_2O(g)$ content of normal air stimulate the calculation on the vaporization in air with different $H_2O(g)$ concentration. A special temperature of 900°C is selected for the calculations. In addition, calculations are carried out for temperatures in the range between 600°C and 1100°C in order to show the influence of a temperature decrease on the chromium vaporization.

2. Results of the calculation of partial pressure and discussion

Fig.1 shows the most abundant partial pressures of the gaseous Cr species over the oxide scales $Cr_2O_3(s)$ in dry air at different temperatures. The dominant vapor species is the high valent oxide, CrO_3 , in the cathode gas. The partial pressures of the gaseous chromium species decrease with the decrease of temperature. The partial pressure of the low valent oxide shows significant dependence on the temperature. The change of partial pressures of the gaseous species as a function of oxygen partial pressure (P_{O_2}) at 900°C is shown in Fig.2. The low valent oxides are dominating at the low partial pressure of oxygen in the anode gases. The partial pressure of $CrO(g)$ increases with the decrease of oxygen partial pressure, which is opposite to those of

$\text{CrO}_2(\text{g})$ and $\text{CrO}_3(\text{g})$.

Fig.1 Partial pressures of gaseous chromium species over $\text{Cr}_2\text{O}_3(\text{s})$ in dry air ($P_{\text{O}_2} = 2.13 \times 10^{-4}$ Pa) at different temperatures

Fig.2 Partial pressures of gaseous species over $\text{Cr}_2\text{O}_3(\text{s})$ at different O_2 partial pressures and 900°C

The partial pressures of the gaseous Cr-containing oxyhydroxides and Cr-containing hydroxides over $\text{Cr}_2\text{O}_3(\text{s})$ in humid air at different temperatures are shown Fig.3 and Fig.4, respectively. The partial pressure of H_2O is assumed to be

3×10^3 Pa, corresponding to air with a normal humidity of 60% at 25°C. The equilibrium calculation results show that in the humid gas, the partial pressures of most oxyhydroxides are much larger than those of the hydroxides. $\text{CrO}_2(\text{OH})_2(\text{g})$ is the dominant vapor species under these conditions. Compared to partial pressure of the gaseous Cr species in dry air at the same temperature, the partial pressures of vapors in humid air are much higher, showing that small amount of $\text{H}_2\text{O}(\text{g})$ in the gases would significantly increase the chromium vaporization. Similar to that in the dry air, the partial pressures of the oxyhydroxides and hydroxides decrease with the decrease of temperature.

Fig.3 Partial pressures of Cr-containing oxyhydroxide species over $\text{Cr}_2\text{O}_3(\text{s})$ in humid air at different temperatures ($P_{\text{O}_2} = 2.13 \times 10^4 \text{ Pa}$, $P_{\text{H}_2\text{O}} = 3 \times 10^3 \text{ Pa}$)

Fig.4 Partial pressures of Cr-containing hydroxide species over $\text{Cr}_2\text{O}_3(\text{s})$ in humid air at different temperatures ($P_{\text{O}_2}=2.13\times 10^4\text{Pa}$, $P_{\text{H}_2\text{O}}=3\times 10^3\text{Pa}$)

Fig.5 shows the relative amounts of the Cr-containing gaseous species in the presence of moisture at $P_{\text{O}_2}=2.13\times 10^4\text{Pa}$ and 900°C . With the increase of the partial pressure of H_2O , the partial pressures of the oxyhydroxides and hydroxides increase, while the partial pressures of the gaseous oxides are independent on the H_2O partial pressure. The most abundant vapor species under these conditions are $\text{CrO}_2(\text{OH})_2$, CrO_3 and CrO_2OH .

Fig.5 Partial pressures of gaseous chromium species over $\text{Cr}_2\text{O}_3(\text{s})$ in humid air ($P_{\text{O}_2}=2.13\times 10^4\text{Pa}$) at 900°C with different H_2O partial pressures

Appendix 1. The heat capacity as a function of temperature for the gaseous chromium oxyhydroxides [Ebbinghaus, 1993; Lee, 2000]

$C_p^o(T) = A + BT + CT^{-2} + DT^2$ (J mol ⁻¹ K ⁻¹)						
Species	T _{min}	T _{max}	A	10 ³ B	10 ⁻⁵ C	10 ⁶ D
CrOH (g)	298	1000	46.257	4.481	-3.712	0.905
	1000	3000	57.551	-3.581	-44.360	1.651
Cr(OH) ₂ (g)	298	1000	75.927	1.490	-4.877	5.520
	1000	3000	79.455	8.186	-41.899	-1.147
Cr(OH) ₃ (g)	298	1000	125.498	-11.748	-9.969	14.265
	1000	3000	121.163	12.443	-50.509	-1.759
Cr(OH) ₄ (g)	298	1000	163.111	-8.459	-15.716	14.132
	1000	3000	158.408	17.291	-61.172	-2.582
Cr(OH) ₅ (g)	298	1000	190.524	10.831	-20.470	6.706
	1000	3000	195.219	22.376	-83.022	-3.448
Cr(OH) ₆ (g)	298	1000	216.862	16.444	-16.812	10.647
	1000	3000	229.874	28.472	-120.177	-4.406
CrO (g)	298	1000	30.097	12.552	-0.626	-5.734
	1000	3000	40.555	-2.959	-17.472	-1.015
CrO ₂ (g)	298	1000	39.526	31.005	-4.916	-14.579
	1000	3000	56.696	0.235	-18.641	0.481
CrO ₃ (g)	298	1000	57.200	43.231	-8.578	-20.459
	1000	3000	82.569	0.308	-36.294	-0.044
CrOOH (g)	298	1000	74.175	-6.114	-5.5335	5.481
	1000	3000	72.053	3.070	-18.777	-0.309
CrO(OH) ₂ (g)	298	1000	109.525	1.124	-13.263	3.407
	1000	3000	109.250	7.946	-33.763	-1.138
CrO(OH) ₃ (g)	298	1000	137.098	19.710	-15.415	-3.532
	1000	3000	146.002	13.607	-53.386	-2.010
CrO(OH) ₄ (g)	298	1000	162.049	27.780	-13.302	-0.811
	1000	3000	180.650	19.164	-93.437	-2.967
CrO ₂ OH (g)	298	1000	83.724	29.246	-14.318	-14.340
	1000	3000	96.902	3.687	-26.766	-0.560
CrO ₂ (OH) ₂ (g)	298	1000	107.819	38.351	-10.272	-11.975
	1000	3000	131.457	9.842	-66.229	-1.527
Cr ₂ O ₃ (s)	-	-	119.4	9.31	-15.66	-
H ₂ O (g)	-	-	30.0	10.71	0.34	-
O ₂ (g)	-	-	29.96	4.18	-1.67	-

**Appendix 2. The standard entropy and standard enthalpy of formation ($P(\text{total})=1$ bar)
[Ebbinghaus, 1993]**

Species	$S^0(298)$ (J mol ⁻¹ K ⁻¹)	$\Delta H_f^0(298)$ (kJ mol ⁻¹)
CrOH (g)	260.4	78.9
CrO (g)	238.5	182.4
Cr(OH) ₂ (g)	316.1	-321.6
CrOOH (g)	307.7	-246.8
Cr(OH) ₃ (g)	378.9	-631.4
CrO ₂ (g)	265.5	-99.2
CrO(OH) ₂ (g)	350.3	552.4
Cr(OH) ₄ (g)	386.9	868.6
CrO ₂ OH (g)	315.1	438.0
CrO(OH) ₃ (g)	398.3	-792
Cr(OH) ₅ (g)	470.2	-1087.5
CrO ₃ (g)	269.3	-323.5
CrO ₂ (OH) ₂ (g)	357.4	-748.3
CrO(OH) ₄ (g)	428.5	-1012
Cr(OH) ₆ (g)	499.4	-1276
Cr ₂ O ₃ (s)	81.15	-1134.7
O ₂ (g)	205.152	0
H ₂ O (g)	188.834	-241.826