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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**A FUNDAMENTAL STUDY OF
CHROMIUM DEPOSITION AND
POISONING AT CATHODES OF SOLID
OXIDE FUEL CELLS**

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School of Mechanical & Aerospace Engineering

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OXIDE FUEL CELLS**

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ABSTRACT

Intermediate-temperature solid oxide fuel cells (IT-SOFCs) have received considerable attention due to the improved stability, reliability and reduced cost compared with high temperature solid oxide fuel cells (HT-SOFCs). One important advantage of IT-SOFCs lies in the use of metallic materials with better properties and lower cost to replace ceramic materials as the interconnect. However, gaseous chromium species will be vaporized from the Cr_2O_3 oxide layer formed on the most widely used chromia-forming alloys under SOFC working conditions and thus cause the performance degradation of the cathode, i. e., chromium poisoning effects. Fundamental understanding of chromium deposition and poisoning is very important in the development of IT-SOFCs based on metallic interconnect. The objectives of this project are to investigate chromium deposition and poisoning processes at selected cathodes of SOFCs and to develop chromium-tolerant cathodes for metallic-interconnect based SOFCs.

$(\text{La}_{0.8}\text{Sr}_{0.2})_{0.95}(\text{Mn}_{1-x}\text{Co}_x)\text{O}_{3\pm\delta}$ (LSMC, $0.0 \leq x \leq 1.0$) and $(\text{La}_{0.6}\text{Sr}_{0.4-x}\text{Ba}_x)(\text{Co}_{0.2}\text{Fe}_{0.8})\text{O}_{3-\delta}$ (LSBCF, $0.0 \leq x \leq 0.4$) cathode systems were selected for the systematic study of the chromium deposition and poisoning. In the case of LSMC cathodes, the electrochemical activity of the cathodes for the O_2 reduction reaction increased as B-site Mn was substituted by Co due to the increased oxygen exchange coefficient and oxygen diffusion coefficient as a result of the increased oxygen vacancies of the LSMC perovskite. However, in the presence of

the chromia-forming metallic interconnect, the chromium deposition on the electrolyte surface in contact with the LSMC electrode decreased while on the electrode surface it increased as the Co content in LSMC perovskite increased from 0.0 to 1.0. On the other hand, the chromium poisoning effects as measured by the increase in the overpotential and electrode polarization resistance were most pronounced for the LSMC cathode with $x=0.4$. The results clearly indicated that the increase in the electrochemical activity of the cathode did not necessarily lead to the reduction in the chromium deposition. Similarly, the chromium deposition on the surface of LSBCF cathodes decreased significantly as the A-site Sr was substituted by Ba despite the fact that the electrochemical activity of LSBCF cathodes was almost independent of Sr/Ba ratio in this study. Chromium deposition was closely related to the chemical affinity and stability of the manganese and strontium species, which significantly depended on the Co/Mn ratio in the case of LSMC cathodes and Sr/Ba ratio in the case of LSBCF cathodes.

Chromium deposition and poisoning were also affected by the nature of metallic interconnect and operating conditions such as humidity in the air stream. Chromium poisoning at the $(\text{La,Sr})\text{MnO}_{3+\delta}$ (LSM) cathode was greatly suppressed when using the Ni-Mo-Cr alloy (developed by Huazhong University of Science and Technology, China) as the interconnect. The suppressed chromium poisoning effects could be attributed to the low Cr content and Cr-free NiMn_2O_4 layer formed on the interconnect surface, which substantially decreased the chromium vaporization. On the other hand, chromium deposition and poisoning at the LSM

cathode were significantly accelerated when using humidified air as the oxidant gas. Therefore, the humidity level in the air stream for practical SOFC systems should be kept as low as possible.

Finally, a new single-phased $(\text{La}_{0.24}\text{Sr}_{0.16}\text{Ba}_{0.6})(\text{Co}_{0.5}\text{Fe}_{0.44}\text{Nb}_{0.06})\text{O}_{3\pm\delta}$ (LSBCFN40) cathode was developed by simple calcination of the mixture of 40% $(\text{La,Sr})(\text{Co,Fe})\text{O}_{3-\delta}$ (LSCF) and 60% $\text{Ba}(\text{Co}_{0.7}\text{Fe}_{0.2}\text{Nb}_{0.1})\text{O}_{3\pm\delta}$ (BCFN) at 1100 °C as the chromium-tolerant cathode. The polarization resistance for the LSBCFN40 cathode was about $0.02 \Omega \text{ cm}^2$ at 800 °C, $0.05 \Omega \text{ cm}^2$ at 700 °C and $0.23 \Omega \text{ cm}^2$ at 600 °C, much smaller than those of the constituent LSCF and BCFN cathodes. The LSBCFN40 cathode had the best chromium-tolerance among all the cathodes studied so far, and the increases in electrode polarization resistance and overpotential for the oxygen reduction reaction in the presence of a Fe-Cr metallic interconnect were negligible under standard test conditions of 200 mA cm^{-2} at 900 °C for 1200 min. The 100 h stability test in the presence of the Fe-Cr metallic interconnect confirmed that the LSBCFN40 cathode was the most promising chromium-tolerant cathode for metallic-based IT-SOFCs.

Keywords: Intermediate-temperature solid oxide fuel cells; interconnect; cathode; chromium deposition and poisoning; chromium-tolerant.

LIST OF PUBLICATIONS

Journal paper

- [1] X.B. Chen, L. Zhang, and S.P. Jiang, *Chromium deposition and poisoning on $(La_{0.6} Sr_{0.4-x} Ba_x) (Co_{0.2} Fe_{0.8}) O_3$ ($0 \leq x \leq 0.4$) cathodes of solid oxide fuel cells*. Journal of The Electrochemical Society, 2008. **155**(11): p. B1093-B1101.
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- [3] X.B. Chen, B. Hua, J. Pu, J. Li, L. Zhang, and S.P. Jiang, *Interaction between $(La, Sr)MnO_3$ cathode and Ni-Mo-Cr metallic interconnect with suppressed chromium vaporization for solid oxide fuel cells*. International Journal of Hydrogen Energy, 2009. **34**(14): p. 5737-5748.
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- [7] X.B. Chen, K.F. Chen, and S.P. Jiang, *Novel cathode materials with good performance and improved chromium – tolerance for intermediate-temperature solid oxide fuel cells* (In preparation).

Conference paper

- [8] X.B. Chen, and S.P. Jiang. *Chromium depositions and poisoning effects at $(La_{0.8}Sr_{0.2})(Mn_{1-x}Co_x)O_{3\pm\delta}$ (LSMC) $(0.0\leq x\leq 1.0)$ cathodes for SOFCs.* International Conference on Electronic Materials 2010, Korea, Aug. 22-27, 2010.

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CHAPTER 1 INTRODUCTION

1.1 Introduction of Fuel Cells

Recently, energy crisis is becoming increasingly serious due to the limited reservation of fossil fuels. The extensive use of conventional energy resources, such as oil, natural gas and coal, also causes significant environmental pollution and global warming. As the conventional fossil fuels decrease every year and will be eventually consumed in the near future, exploitation of new renewable energy sources is becoming increasingly important [*Boudghene Stambouli and Traversa 2002; Henne 2007; Arif 2008*]. Fuel cells are the most efficient energy conversion devices in which chemical energy is directly converted into electrical energy without combustion. Compared with conventional energy conversion technologies like internal combustion engines (ICE), fuel cells have significant advantages, such as high energy conversion efficiency, much lower emissions of sulfur and nitrogen oxides and hydrocarbon oxides, and greatly reduced CO₂ emissions.

According to the chemical nature of the electrolytes used as ionic conductors, fuel cells can be generally categorized into five types, including alkaline fuel cell (AFC), phosphoric acid fuel cell (PAFC), polymer electrolyte membrane fuel cell (PEMFC), molten carbonate fuel cell (MCFC) and solid oxide fuel cell (SOFC). The primary features of different kinds of fuel cells are listed in Table 1.1 [*Ormerod 2003; Wee 2007; Kajikawa, Yoshikawa et al. 2008; Mulder, Coenen et al. 2008*].

The materials science at present has made the fuel cells a reality in some specialized applications. So far researches on fuel cells primarily focus on PEMFCs, suitable for cars and mass transportation, and SOFCs, suitable for large scale distributed power generation (hundreds of MW).

Table 1.1 Features of different types of fuel cell.

Type	AFC	PAFC	PEMFC	MCFC	SOFC
Electrolyte	Aqueous alkaline solution	Phosphoric acid	Polymer membrane	Molten potassium lithium carbonate	Solid oxide
Conduction species	OH^-	H^+	H^+	CO_3^{2-}	O^{2-}
Fuel	H_2	H_2	H_2	$\text{H}_2, \text{CH}_4, \text{CO}$	$\text{H}_2, \text{CH}_4, \text{CO}$
Operating temperature	$\sim 70^\circ\text{C}$	$\sim 200^\circ\text{C}$	$\sim 80^\circ\text{C}$	$\sim 650^\circ\text{C}$	$600\text{-}1000^\circ\text{C}$
Efficiency	50-55%	40-50%	40-50%	50-60%	45-60%

1.2 Solid Oxide Fuel Cells (SOFCs)

1.2.1 Working principle

Solid oxide fuel cells have the highest energy conversion efficiency, compared with other types of fuel cells [Liu, Co et al. 2006; Wu, Jiang et al. 2008]. The working principle of solid oxide fuel cells is illustrated in Figure 1.1. A solid oxide

fuel cell is composed of dense oxygen ion conductive electrolyte, porous cathode and porous anode. The oxidant gas, normally air or oxygen, travels to the cathode/electrolyte interface, where it combines with the electrons from the external circuit to form oxygen ions. Then the oxygen ions travel through the oxygen ion conductive electrolyte to arrive at the anode/electrolyte interface, where they react with the fuels, such as H_2 or CH_4 , and release electrons to the external circuit. The electrons travel from the anode to the cathode through the load in the external circuit and form the electric current [Ormerod 2003]. Electricity is generated as long as the fuel and oxidant gas are provided.

Figure 1.1 Working principle of SOFCs.

1.2.2 Stack design

The most widely used stack design of SOFCs are planar and tubular SOFCs. The stack designs of the planar and tubular SOFCs are illustrated in Figure 1.2.

Figure 1.2 Stack designs of SOFCs: (a) Planar SOFCs, and (b) Tubular SOFCs.

Planar SOFC stacks are under development by many companies, with Fuji Electric as the primary leader. In the stack, the cells are flat-plates bonded together and placed one on top of the other. During operation, hydrogen and air travel through the channels of the interconnect, where each electrode surface is in contact with the respective reactant gases. The tubular SOFC stack, constructed by an array of tubes composed of the electrolyte and electrode ‘sandwich’, operates with the fuel on the outside surfaces of the bundle of tubes, and the oxidant on the inside [Stambouli and Traversa 2002].

1.3 Chromium poisoning effect at cathodes of SOFCs

In the planar SOFC stack, interconnect is one important component in contact with both the cathode and anode (Figure 1.2a). For the high temperature SOFCs (800-1000°C), ceramic interconnect materials $\text{La}_{1-x}(\text{Sr}, \text{Ca})_x\text{CrO}_3$ are used. For the

intermediate-temperature SOFCs (IT-SOFCs) operated at 600-800°C, metallic interconnect materials, especially the chromia-forming alloys, are developed. Although the metallic interconnect materials have numerous advantages over ceramic interconnect materials, they still cannot overcome the chromium poisoning effects associated with the vaporization of chromium species [*Geng and Zhu 2006; Gannon, Gorokhovskiy et al. 2007*].

At the high operating temperature above 600°C, gaseous chromium species, i.e., CrO_3 (g) and $\text{CrO}_2(\text{OH})_2$ (g), will evaporate from the Cr_2O_3 oxide layer and react with the cathode materials to form solid chromium depositions under the SOFC operation conditions, which can cause serious cathode performance—chromium poisoning effects. It greatly limits the application of metallic interconnects and threatens the long-term stability of the SOFC stacks. Therefore, this project focuses on the chromium poisoning effects at different cathodes of SOFCs under the SOFC operation conditions.

1.4 Challenges

Chromium deposition and poisoning have been widely observed by different research groups [*Fujita, Hashimoto et al. 2004; Paulson and Birss 2004; Jiang, Zhang et al. 2005; Konyshcheva, Penkalla et al. 2006; Tucker, Kurokawa et al. 2006*]. However, there are still some uncertainties. The challenges in this field include the following aspects:

1. The chromium deposition mechanism at different cathodes of SOFCs-whether it happens through an electrochemical deposition process or a chemical process;
2. The reason for different chromium deposition behaviors at maganite and cobaltite materials-whether they are caused by the difference in electrochemical performance or in material chemistry;
3. Influence of different conditions, such as interconnect composition and humidity in air, on chromium deposition and poisoning at the cathodes;
4. Strategies to improve the chromium-tolerance of cathode materials.

1.5 Objectives

The mechanism of chromium deposition and poisoning is one of the most critical issues in the development of SOFC stacks with high performance and long-term stability. Therefore, the objectives of this project are as follows:

1. Fundamental investigation of chromium deposition and poisoning mechanism by studying the characteristics of chromium deposition and poisoning at different SOFC cathodes, especially the widely used cobaltite cathode materials for IT-SOFCs;
2. Systematic study of the effects of working condition, interconnect composition and cathode composition on the chromium deposition and

poisoning effects in order to minimize the chromium poisoning effects on the cathode performance and stability.

1.6 Scope

The scope of this project is outlined below:

1. Study of the chromium deposition and poisoning effects at different cathode materials for SOFCs, in particular
 - Chromium deposition and poisoning effects at $(\text{La}_{0.8}\text{Sr}_{0.2})_{0.95}(\text{Mn}_{1-x}\text{Co}_x)\text{O}_{3\pm\delta}$ (LSMC, $0.0 \leq x \leq 1.0$) cathodes;
 - Chromium deposition and poisoning effects at $(\text{La}_{0.6}\text{Sr}_{0.4-x}\text{Ba}_x)(\text{Co}_{0.2}\text{Fe}_{0.8})\text{O}_3$ (LSBCF, $0.0 \leq x \leq 0.4$) cathodes.
2. Study of the effects of operating condition, interconnect composition and cathode composition on chromium deposition and poisoning, in particular
 - The effect of novel Ni-Mo-Cr interconnect materials with lower Cr content on the chromium deposition and poisoning effects at LSM cathodes;
 - The effect of humidity on the chromium deposition and poisoning effects at the LSM cathodes;
 - Development of novel cathode materials with high chromium-tolerance.

CHAPTER 2 LITERATURE REVIEW

In this chapter, development of intermediate-temperature SOFCs (IT-SOFCs), and study on the chromium deposition and poisoning effects at different cathodes for IT-SOFCs are reviewed.

2.1 Development of IT-SOFCs

2.1.1 Challenges of IT-SOFCs

To reduce the cost and improve the stability of SOFC systems, it is necessary to reduce the operating temperature of SOFCs from the high-temperature range (800-1000°C) to the intermediate temperature range (600-800 °C). Compared with the HT-SOFCs, IT-SOFCs have the following advantages [*Gannon, Gorokhovsky et al. 2007; Zhu, Geng et al. 2007; Fu, Sun et al. 2008*]:

- (1) Utilization of metallic materials with lower cost, higher electronic conductivity, better mechanical strength and thermal conductivity as interconnect materials;
- (2) Simplification of the design and materials requirements of the balance of plant;
- (3) Reduction in thermal shock and thermal stress during thermal cycles;
- (4) Improved component stability and increase in material selection.

However, the IT-SOFCs also face some new challenges. One challenge associated with the reduction in operating temperature is the cell performance decrease caused by the decrease in the ionic conductivity of the electrolyte. The actual cell voltage (V) under the operation condition can be expressed according to the equation below [Tarancón 2009]:

$$V = E_{\text{emf}} - IR_{\Omega} - \eta_a - \eta_c \quad (2.1)$$

$$E_{\text{emf}} = E^{\circ} + \frac{RT}{2F} \ln \left(\frac{p_{H_2} p_{O_2}^{1/2}}{p_{H_2O}} \right) \quad (2.2)$$

where E_{emf} is the electromotive force given by the Nernst equation 2.2, R_{Ω} is the ohmic resistance of the cell arising from the electrolyte and electrode, and η_a and η_c are the overpotential of the electrode reaction at the anode and cathode.

Figure 2.1 shows the temperature dependence of ionic conductivities of the common used electrolyte materials [Kharton, Marques *et al.* 2004; Tsipis and Kharton 2008]. The ionic conductivity of the traditional 8 mol% yttria stabilized zirconia (8YSZ) electrolyte decreases quickly as the temperature decreases, which will cause significant ohmic resistance loss of the cell in the intermediate temperature range. To resolve this problem, many methods, including fabricating anode-supported cell with thin electrolyte film and exploiting new electrolyte materials like Sr and Mg-doped LaGaO₃ (LSGM) and doped ceria materials with higher ionic conductivity in the intermediate temperature range [Lin and Barnett

2008; Liu and Zhang 2008; Wang, Sun et al. 2008].

Figure 2.1 Temperature dependence of ionic conductivities of electrolytes [Steele 2000; Chourashiya, Patil et al. 2008; Liu and Zhang 2008].

Different methods, including electrochemical vapor deposition (EVD) [Schoonman, Dekker et al. 1991; Dekker, van Dieten et al. 1992; Sasaki, Otoshi et al. 1994], spray pyrolysis [Setoguchi, Sawano et al. 1990; Kelder, Nijs et al. 1994], DC-sputtering [Hobein, Tietz et al. 2001], plasma spraying [Lang, Henne et al. 2001; Fedtke, Wienecke et al. 2004], pulsed laser deposition (PLD) [Hobein, Tietz et al. 2002], tape-casting [Jones and Irvine 2002; Ivanov, Lipilin et al. 2006], spin-coating [Xu, Xia et al. 2005], screen-printing [Von Dollen and Barnett 2005; Ge, Huang et al. 2006], and so on, have been extensively studied for the fabrication of thin film YSZ electrolyte in the anode supported cell. For example, Souza [1997] et al. reported an anode-supported cell with YSZ film of $\sim 10 \mu\text{m}$ achieved a

maximum powder density as high as 1.8 W cm^{-2} at 800°C . Despite the high power density of thin-film YSZ-based SOFCs at 800°C , it decreases quickly with the decreasing temperature. Therefore, there is great need for the exploitation of other oxide-ion electrolyte with higher oxygen ionic conductivity to enable SOFCs to operate at or below 700°C [Huang, Wan et al. 2001].

Among the newly developed electrolyte materials, doped ceria and LaGaO_3 -based materials are the most widely used and studied electrolyte materials. Although the ionic conductivities of doped ceria are approximately an order of magnitude larger than stabilized zirconia, ceria have an electronic conductivity at the reducing environment. This will lead to a n-type electronic conductivity and thereby cause internal short-circuit of the cell, generate lattice expansion, and lead to mechanical failure [Faro, Rosa et al. 2009]. Pervoskite LaGaO_3 -based materials, especially Sr and Mg-doped LaGaO_3 (LSGM), have received a lot of attention and been widely studied as promising electrolyte materials. Huang [1998; 1998] et al. reported the highest ionic conductivity of 0.17 S cm^{-1} at 800°C and 0.08 S cm^{-1} at 700°C , much higher than that of YSZ electrolytes, for $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{2.85}$ with the oxygen partial pressure ranging from 1 to 1×10^{-22} atm. The thermal expansion coefficient of the LSGM materials is similar to that of the YSZ materials. Disadvantages of LSGM-based electrolytes lie in the high cost of gallium oxide, the difficulty in achieve pure LSGM phase, possible reduction and vaporization of gallium oxide, significant reactivity with pervoskite cathode materials in the

oxidizing atmosphere and reactivity with metal anode in reducing atmosphere [Kharton, Marques *et al.* 2004; Jacobson 2010].

The second challenge with IT-SOFCs comes from the low electrochemical activity of the traditional LSM cathode as the operating temperature decreases. The main problem with the traditional LSM cathodes results from their low ionic conductivity, which greatly limit the electrochemical activity for the oxygen reduction reactions. Therefore, much effort has been devoted to increasing the ionic conductivity of cathode materials by different methods, including fabricating composite cathode materials by doping the cathode materials with ionic conductive electrolyte materials and development of novel cathode materials with mixed ionic and electronic conductivities (MIEC). The development of cathode materials will be reviewed in next section. Another problem with the IT-SOFCs is the serious chromium poisoning effects caused by the chromium vaporization from the Fe-Cr metallic interconnects. Studies of the chromium deposition and poisoning effects will be reviewed in this chapter.

2.1.2 Development of cathode materials

Cathodes for solid oxide fuel cells (SOFCs) have to possess many properties including high electrical conductivity, high catalytic activity for oxygen reduction, and compatibility with other cell components. In the cathode, the oxygen reduction reactions require the presence of oxygen and electrons and the possibility for

generated oxide ions to be transported from the reaction site into the bulk of the electrolyte. When the electrode materials and the electrolyte materials possess only electronic and ionic conductivity, these criteria are fulfilled in the vicinity of the triple-phase boundary (TPB) between the electrode, electrolyte, and oxidant gas. Therefore, the oxygen reduction reactions are generally thought to be confined closely to the electrode/electrolyte interface, where the gas has simultaneous access to both electronically conductive cathode and the ionically conductive electrolyte.

To improve the cathode performance, two approaches are generally used by extending the TPB area. One strategy is to replace LSM with a single-phase mixed conductor (material which conducts both oxygen ions and electrons), such as $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ (LSCF). By introducing bulk ionic transport, oxygen can be reduced to O^{2-} over a significant portion of the electrode surface, thereby extending the size of the active region and improving the kinetics at temperatures below 800°C. The other one is to add ionically conductive electrolyte materials into the electronically conductive cathode materials like LSM to form the composite cathode structure to increase the active region for cathode reduction reactions [Adler 2004; Jingbo Liu, Anne C. Co et al. 2006; Kawada, Sase et al. 2006; N. Caillol, M. Pijolat et al. 2007]. Figure 2.2 illustrates the mechanism of improving the cathode performance.

Figure 2.2 Mechanism of strategies used for improving cathode performance [Adler 2004].

Pure electronic conductive materials, including noble metals like Pt, Pd and Ag, and perovskite type LSM cathode materials, have been studied as the cathode materials for SOFCs [Lewis and Gomer 1968; Verkerk and Burggraaf 1983; Robertson and Michaels 1990; Wang 1990; A. M. Svensson, S. Sunde et al. 1996; J. Deseure, Y. Bultel et al. 2006]. However, noble metals such as platinum, palladium, or silver, are not suitable for applications due to their prohibitive cost (and insufficient long-term stability). The lanthanum manganite (LaMnO_3)-based perovskite structure is the most commonly studied cathode materials for SOFC. The lattice structure of perovskite, ABO_3 , is shown in Figure. 2.3 below.

Figure 2.3 Lattice structure of perovskite ABO_3 [Subhash C Singhal and Kendal 2003].

This oxide is composed of three elements, the large cations, A^{n+} , the small

cations, $B^{(6-n)+}$, and the oxide ions, O^{2-} , where n is the positive charge on the A ions. Cations $B^{(6-n)+}$ are surrounded by 6 oxide ions, whereas cations A^{n+} have 12 oxide ion coordinates: the sites with 12 coordinates are often called the A sites, and the sites with 6 coordinates the B sites. The geometrical fitting of cations and anions to this structure is measured with the Goldschmidt tolerance factor defined as follows:

$$t = (r_A + r_O) / [2^{1/2}(r_B + r_O)] \quad (2.3)$$

where r_A , r_B and r_O are the effective ionic radii of A, B and O ions, respectively. Usually, this factor is evaluated from Shannon's ionic radii [Shannon 1976] for respective coordination numbers. When the tolerance factor is near unity, the structure is the ideal cubic one. Otherwise, orthorhombic or rhombohedral distortions will appear.

The undoped stoichiometric LaMnO_3 materials have the orthorhombic structure at 25 °C and experience a structure transformation from orthorhombic to rhombohedral structure at about 600 °C, which is caused by the oxidation of some Mn^{3+} to Mn^{4+} ions [Tofield and Scott 1974]. Therefore, the crystallographic transformation temperature is closely related to the oxygen stoichiometry, and hence to the mean manganese valence. With increasing oxygen content, the transformation temperature decreases rapidly. Substitution of La with lower valence cations (such as Sr^{2+} and Ca^{2+}) or A-site deficiency increases the concentration of Mn^{4+} in the LaMnO_3 lattice. It eventually decreases the

transformation temperature. Although the cubic structure does not appear in pure LaMnO_3 , it appears around 1000 °C in $(\text{La}_{0.7}\text{Sr}_{0.3})\text{MnO}_3$. Zheng and Pederson [1999; 1999] systematically studied the phase behavior of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ with various Sr doping content and A/B cation ratio. The perovskite structure shows an orthorhombic distortion when the Sr content is increased to $x=0.2$ and it transforms into a monoclinic or hexagonal structure with $0.2 \leq x \leq 0.3$. The structure returns to orthorhombic symmetry when the Sr content increases to $x=0.3$. Compared with the influence Sr doping content, the influence of the A/B cation ratio on the lattice constants and cell volume of the perovskite phase appears much less significant. However, A/B cation ratio has significant influence on the minor phases formed in the prepared materials. In the case of $A/B < 1$, the main minor phases observed were Mn_3O_4 while the secondary phase La_2O_3 and its hydrated product $\text{La}(\text{OH})_3$ were observed with $A/B = 1$ and $A/B > 1$. Excess La_2O_3 is also known to react with YSZ to form a highly resistive lanthanum zirconate phase at the LSM/YSZ interface [Jiang, Love *et al.* 1999]. LSM with A-site nonstoichiometric compositions (e.g., $A/B = 0.9$) is preferred for the cathodes of SOFCs at high operating temperature.

Despite the high electronic conductivity of the LSM materials at the high operating temperature, nevertheless; their relatively low oxygen ionic conductivity greatly limits their use in the SOFC operated at the intermediate temperature range due to the low oxygen diffusion coefficient and limited TPB

area. The high polarization in the LSM cathodes will cause serious power loss of the cell stacks in the intermediate temperature range. Therefore, there are significant efforts in the search of new cathode materials with high oxygen ionic conductivities and electronic conductivities. Doped lanthanum cobaltite is a mixed conductive oxide and has been studied extensively as cathode materials of SOFCs. The material shows a large oxygen deficiency at high temperatures. Studies have shown that, LaCoO_3 has an intrinsic p-type conductivity, which can be enhanced by substituting a lower-valence ion like strontium or calcium at the A site. LaCoO_3 is rhombohedral from room temperature to 1000°C . The phase structure of perovskite LSCF depends on the dopant level as well as the temperature. In the $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ system, it is rhombohedral at room temperature and orthorhombic for $0 \leq y \leq 0.7$ and $0.8 \leq y \leq 1$, respectively [Tai, Nasrallah et al. 1995]. For $y = 0.8$, i.e., $\text{La}_{1-x}\text{Sr}_x\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$, the orthorhombic/ rhombohedral transition at room temperature occurs at $x = 0.3$. When Sr content increased to $x \geq 0.6$, a second phase was observed, while the main phases were rhombohedral for $0.6 < x < 0.8$ and cubic for $x > 0.8$ [Tai, Nasrallah et al. 1995].

The primary advantages of Sr-doped LaCoO_3 for SOFC cathode materials lie in their both high electronic conductivity and high ionic conductivity. However, the thermal expansion coefficient of Co-rich perovskites is generally much higher than both YSZ and doped CeO_2 electrolytes. An alternative to the Co-rich perovskites is the Sr-doped LaFeO_3 which has a lower thermal expansion

coefficient and a superior chemical compatibility with doped CeO_2 electrolyte. The TEC values at 700°C are 14.2 , 14.1 , and $13.8 \times 10^{-6} \text{ K}^{-1}$ for $\text{La}_{0.6-z}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ with $z = 0.05$, and $\text{La}_{0.6}\text{Sr}_{0.4-z}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$, with $z = 0.1$ and 0.2 , respectively. The TEC of stoichiometric $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ is $15.3 \times 10^{-6} \text{ K}^{-1}$ at 700°C , compared with the TEC of 11.5 to $11.9 \times 10^{-6} \text{ K}^{-1}$ for GDC electrolyte [Kharton, Figueiredo et al. 2001].

The oxygen self-diffusion coefficient of cobaltite-based materials is several orders of magnitude higher than that of the manganites. The oxygen ion conductivity is 1.20 and 0.18 S cm^{-1} at 900°C for $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$ and $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$. Substitution of 20% Co with Ni and Cu will increase the ionic conductivity as compared with $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ with the increase of the ionic conductivity in the order of $\text{Fe} < \text{Co} < \text{Cu} < \text{Ni}$.

Table 2.1 summarizes the oxygen diffusion coefficient, surface exchange coefficient and oxygen ionic conductivities for lanthanum cobaltite ferrite-based and lanthanum manganite-based perovskite cathodes measured by electron blocking technique [Ishigaki, Yamauchi et al. 1984; Ishigaki, Yamauchi et al. 1988; Teraoka, Nobunaga et al. 1991; Carter, Selcuk et al. 1992; Yasuda, Ogasawara et al. 1996; Kharton, Viskup et al. 1997]. Compared with the lanthanum magnetite-based perovskite, the lanthanum cobaltite ferrite-based cathode materials have much higher ionic conductivities, which makes them promising cathode materials for the IT-SOFCs.

Table 2.1 Oxygen diffusion coefficient, surface exchange coefficient and oxygen ionic conductivity for lanthanum cobaltite ferrite-based and lanthanum manganite-based perovskite cathodes.

Composition	T/ °C	$D^*/\text{cm}^2 \text{ s}^{-1}$	$k/\text{cm s}^{-1}$	$\sigma_i/\text{S cm}^{-1}$	Ref.
$\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$	900	4×10^{-8}	2×10^{-5}		[Carter, Selcuk et al. 1992]
	800	2×10^{-8}	5×10^{-6}		
	700	1×10^{-8}	4.3×10^{-6}		
LaFeO_3	1000	5.28×10^{-12}	1.67×10^{-7}		[Ishigaki, Yamauchi et al. 1984]
	900	9.84×10^{-13}	3.89×10^{-8}		
LaCoO_3	900	5.31×10^{-9}			[Ishigaki, Yamauchi et al. 1984]
	800	2.41×10^{-11}	3.47×10^{-7}		
	700	9.20×10^{-13}	4.57×10^{-9}		
$\text{La}_{0.9}\text{Sr}_{0.1}\text{CoO}_3$	800	1.99×10^{-10}	1.54×10^{-8}		[Ishigaki, Yamauchi et al. 1988]
$\text{La}_{0.9}\text{Sr}_{0.1}\text{FeO}_3$	900	2.65×10^{-9}	3.60×10^{-7}		
$\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$	900			1.20	[Teraoka, Nobunaga et al. 1991]
$\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$	900			0.18	[Teraoka, Nobunaga et al. 1991]
	900	3×10^{-7}	4×10^{-5}		
	800	1×10^{-7}	2×10^{-5}		
	700	2×10^{-8}	4×10^{-6}		
$\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Cu}_{0.2}\text{O}_3$				2.00	[Teraoka, Nobunaga et al. 1991]
$\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Ni}_{0.2}\text{O}_3$				3.16	
$\text{La}_{0.95}\text{Sr}_{0.05}\text{MnO}_3$	900	2.44×10^{-13}		1.10×10^{-7}	[Yasuda, Ogasawara et al. 1996]
$\text{La}_{0.90}\text{Sr}_{0.10}\text{MnO}_3$	1000	4.78×10^{-12}		2.09×10^{-6}	
$\text{La}_{0.80}\text{Sr}_{0.20}\text{MnO}_3$	1000	1.33×10^{-11}		5.76×10^{-6}	
$\text{La}_{0.50}\text{Sr}_{0.50}\text{MnO}_3$	900	3×10^{-12}	9×10^{-8}		

The (Ba, Sr)(Co, Fe)O_{3-δ} (BSCF) materials represent a new kind of cathode materials, which were first studied and adopted as cathode materials with high performance for SOFCs by Zongping Shao and Haile [*Shao and Halle 2004*]. The BSCF cathode showed an area specific resistance (ASR) of 0.055-0.071 Ω cm² at 600 and 0.51-0.60 Ω cm² at 500 °C, smaller than those of other cathode materials under similar conditions. However, the BSCF cathode materials has a high thermal expansion coefficient of $19.7 \times 10^{-6} \text{ K}^{-1}$ in air, indicating that the thermal compatibility of the BSCF materials may be a problem for its application [*Wei, Lü et al. 2005*]. Another issue associated with the BSCF cathode materials lies in their low electronic conductivity of only 43 S cm⁻¹ at 800 °C in air [*Wang, Wang et al. 2007*], which will lead to the increase in ohmic resistance of the cell and difficulties in current collection. To address this problem, Wei Zhou [2007] made composite cathode with BSCF and LaCoO₃ with high electronic conductivity and the results showed that the composite cathode reached a maximum conductivity of $\sim 300 \text{ S cm}^{-1}$ at 300 °C. Other cobaltite-based materials, such as Ba (Co, Fe, Nb)O_{3±δ} (BCFN), and Sr (Co, Nb) O_{3±δ} (BCN), have also been studied as cathode materials for IT-SOFCs [*Huang, Chen et al. 2010; Wang, Zhou et al. 2010*].

LaNiO₃ has been reported to be another kind of perovskite cathode materials with high electronic conductivity at room temperature [*Rajeev and Raychaudhuri 1992*]. Chiba [1999] et al. studied the system of La(Ni, M)O₃ (M = Al, Cr, Mn, Fe, Co, Ga) and found that LaNi_{1-x}Fe_xO_{3-δ} has both high electronic conductivity and

good TEC match with the YSZ electrolytes. The stability of the $\text{LaNi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ is improved as the x value increases and the structure shifts from rhombohedral with $x=0.4$ to orthorhombic with $x \geq 0.5$. The highest electronic conductivity of $11.4 \times 10^{-6} \text{ K}^{-1}$ is achieved with the materials with $x=0.4$ for totally dense specimen at 800°C . The electronic conductivity of $\text{LaNi}_{0.6}\text{M}_{0.4}\text{O}_3$ ($\text{M} = \text{Al}, \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ga}$) in the temperature range of 600 to 1000°C decreases in order: $\text{Co} > \text{Fe} > \text{Cr} > \text{Ga} > \text{Mn} > \text{Al}$. Lanthanum strontium manganese chromite (LSCM) is another kind of typical cathode materials, which can be used for IT-SOFCs. Raj [2006] et al. investigated the oxygen diffusion and surface exchange on $(\text{La}_{0.75}\text{Sr}_{0.25})_{0.95}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_3$, indicating that the oxygen tracer diffusion coefficient of LSCM is $1.0 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ at 900°C , two orders of magnitude higher than that of LSM. Furthermore, the LSCM also has good chemical stability with the YSZ electrolyte materials, enabling its application as cathode materials for the cathode-supported SOFCs.

2.1.3 Metallic interconnect materials for IT-SOFCs

The interconnect plays a highly important role and has several functions in an SOFC stack, which requires that the interconnect materials must meet the following requirements [Piccardo, Gannon et al. 2007]:

1. High electrical conductivity. The area specific resistance for the interconnect should be lower than $0.1 \Omega \text{ cm}^2$;

2. Good stability in the operating conditions. The interconnects should have adequate stability in terms of dimensions, microstructures, chemistry and phases at operating temperature around 800°C in both oxidizing and reducing environments;
3. Good imperviousness. The interconnects should have excellent imperviousness for oxygen and hydrogen to prevent direct combination of oxidant and fuel during operation;
4. Appropriate thermal expansion coefficient (TEC). The TEC of interconnects should match those of electrodes and electrolytes to avoid the thermal stresses developed during start-up and shut down;
5. High thermal conductivity. The thermal conductivity of interconnects should be larger than $20 \text{ W m}^{-1} \text{ K}^{-1}$ to ensure uniform heat distribution in the stack. The interconnect materials provide the major thermal conduction path for heat distribution in the fuel cell stack;
6. Low chemical reactivity. The interconnects should have excellent oxidation, sulfidation and carbon cementation resistance. No reaction or inter-diffusion is allowed between the interconnects and their adjacent components.
7. Good mechanical resistance. The interconnects should have adequate strength and creep resistance at elevated temperatures;

8. Satisfactory machinability. The interconnects should be easy to be fabricated and shaped into the desired structure;
9. Low cost. The cost of interconnects should be low enough for the commercialization of SOFCs.

Generally, the interconnect materials can be categorized into two different groups, including LaCrO₃-based ceramic and metallic interconnect materials. Compared with the ceramic interconnect materials, the metallic interconnect materials have the advantages of higher electronic and thermal conductivities, lower cost, better mechanical properties and easier processing. Therefore, metallic interconnect materials are widely studied and used for the IT-SOFCs [M. P. Brady, B. A. Pint *et al.* 2006]. The metallic interconnect materials usually contain Cr, Si or Al element to form Cr₂O₃, SiO₂ or Al₂O₃ protective layer at the operating temperature to decrease the oxidation rate of the metallic materials [Badwal, Deller *et al.* 1997]. There are mainly three groups of metallic interconnect materials so far, including Cr-based, Fe-based and Ni-based alloys.

Compared with Cr-based and Fe-based alloys, the Ni-based alloys can work at higher temperature of $\sim 1200^{\circ}\text{C}$ and have higher hardness at the high temperature. The oxidation products of both NiO and Cr₂O₃ formed in the Ni-Cr based alloys can decrease the oxygen diffusion rate, improving the oxidation resistant property of the materials. However, the Ni-based alloys usually have a thermal expansion

coefficient (TEC) of $17\text{-}20 \times 10^{-6} \text{K}^{-1}$, much higher than that the TEC value of $9\text{-}12 \times 10^{-6} \text{K}^{-1}$ for YSZ electrolyte. The TEC mismatch between the interconnect and electrolyte will lead to thermal stresses during the heating and cooling process, resulting in the cracking of the electrolyte. Therefore, the Ni-based alloys have not been widely used for the interconnect materials for planar IT-SOFCs.

SOFC stacks developed by Sanyo and Fuji Electric used nickel-based alloys such as Inconel 600 and Ni 22Cr respectively as the interconnect materials [De Larramendi, Ortiz et al. 2007; van Alphen, Kunz et al. 2008]. According to the report, electrical resistance of the Ni 22Cr alloy coated with $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ did not change significantly and maintained a value below $10 \text{ m}\Omega \text{ cm}^2$ during the long-term exposure experiment of 12, 000h despite the SrCrO_4 formed at the interface. However, the mismatch in TEC with other cell components led to cracks at the interconnect /electrode interfaces, thereby resulting in voltage drops during the thermal cycling. Linderoth et al. investigated the oxidation resistance and the corrosion products of Fe-Cr-Ni steels (Haynes 230, Inconel 601), Ni-Cr steel (Inconel 657), Fe-Cr-Al steel (APM-Kanthal), and the Plansee Ducrolloy. The Haynes 230 had the best oxidation resistance and the Cr_2O_3 and spinel oxide layer formed on the surface had better electronic conductivity than pure chromia scale [Linderoth, Hendriksen et al. 1996]. Thin foils of Ni-based superalloys (Inconel 625, Inconel 718, Hastelloy X, and Haynes 230) have been studied by England and Virkar as possible metallic interconnect materials [England and Virkar 1999;

England and Virkar 2001]. Similar to the previous report, they also observed the slowest oxidation kinetics for Haynes 230 and Cr-Mn spinel at the outer surface led to the depletion of Mn in the inner part the foil.

The Cr-based alloys are the most widely used and studied interconnect materials because the Cr_2O_3 oxide layer formed is electrically conductive. Furthermore, they also possess good corrosion and oxidation resistant properties in addition to their better TEC match with YSZ electrolytes [*M. P. Brady, B. A. Pint et al. 2006*]. However, the vaporization rate of the Cr species will increase significantly when the temperature is above 700 °C, thereby accelerating the formation of the oxide layer and decreasing the electronic conductivity. Outward diffusion of chromium ions will lead to the growth of chromia scales and it will result in the formation of porosity at the alloy-scale interface. The significant grow stresses together with the porosity will cause the scale cracking and spallation [*Kofstad and Bredesen 1992*]. At high temperatures, the chromia formed on the surface of the interconnect will be oxidized to gaseous chromium species like CrO_3 or $\text{CrO}_2(\text{OH})_2$, leading to higher oxidation rates.

The oxidation behavior can be improved with the addition of oxygen-active elements, which can improve scale adherence, decrease the scale growth rate and improve the scale morphology. Furthermore, the vaporization of chromium can also be decreased by the addition of alloying elements like manganese and titanium that form oxides outside the chromia layer to reduce the chromium vaporization.

The amount of aluminum and silicon must be kept low enough to avoid the formation of the insulating oxide layer and elements such as molybdenum and tungsten can be added to improve the TEC match of the alloy to other components of the stack [Fergus. 2005].

Compared with Cr-based alloys, ferritic steels possess the advantages of lower cost, easier processing and fabrication, better weldability and thermal expansion match with the anode substrate. Ferritic steel interconnect materials have been used in several SOFC stacks while the long-term tests indicated that the power density of the stacks degraded significantly. Currently, the widely studied ferritic steels primarily include Fe-Cr-Mo, Fe-16Cr, and ZMG232 materials, where the Cr content is near 17%. The active elements contained in the ferritic alloys will form relatively stable oxide layer and reduce the chromium vaporization; however, the chromium vaporization still comprise a significant problem for application of Fe-based metallic materials [Ivers-Tiffée, Weber et al. 2001; Horita, Xiong et al. 2003]. Huang et al. studied the oxidation kinetics of Fe-26Cr-Mo alloys coated with LSM ($\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_{3+\delta}$) + LSGM ($\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.83}\text{Mg}_{0.17}\text{O}_{2.815}$) and LSCo ($\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\sigma}$), respectively. The results showed that the growth rate of the oxide layer for the interconnect with LSCo coating is four times that of the interconnect without coating while that with LSM+LSGM coating has the same oxide growth rate as the interconnect without coating [Huang, Hou et al. 2000; Matsuzaki and Yasuda 2000; Yang, Wen et al. 2000; Jiang, Zhang et al. 2002].

2.2 Chromium deposition and poisoning effects

Chromium deposition and poisoning effects at the cathode for SOFCs have been widely studied, including thermodynamics of chromium vaporization, transportation kinetics of gaseous chromium species, deposition of chromium species at cathodes and influence of chromium species on the cathode electrochemical performance. It has been well known that performance of the cathode degrades seriously in the presence of chromia-forming metallic interconnect materials due to the chromium poisoning effects; however, disagreements exist regarding the driving force of the chromium deposition mechanism. Here, results and reports on chromium poisoning effects and depositions are reviewed.

2.2.1 Vaporization of gaseous chromium species

The basic reason for the Cr volatility is the thermodynamic instability of the chromia scales formed on the chromia-forming alloys at high temperature, forming gaseous species through the following reactions [Hilpert, Das et al. 1996]:

The volatile Cr species from the chromia scale are strongly dependent on the partial pressure of oxygen and the water content. It has been shown that the vapor pressure is much higher in air than that in the fuel (the oxygen partial pressure in the SOFC anode side is in the range between 10^{-12} and 10^{-7} Pa) [Hilpert, Das et al. 1996]. Thus, the vaporization of Cr species on the SOFC anode will not be discussed here.

Ebbinghaus [1993] et al. studied the possible equilibrium composition of fifteen gaseous chromium species over Cr_2O_3 at fixed partial pressures of oxygen (0.01 atm) and water (0.1 atm) in the temperature range from 800 to 1600K. Their results from thermodynamics calculation predict that $\text{CrO}_2(\text{OH})_2(\text{g})$ is the dominant vapor species with a small fraction of $\text{CrO}_3(\text{g})$, $\text{CrO}(\text{OH})_3(\text{g})$, $\text{CrO}_2\text{OH}(\text{g})$ and $\text{CrO}(\text{OH})_2(\text{g})$ under normal incineration conditions within the temperature range studied (Figure 2.4). The chromium volatility is maximized when both $\text{O}_2(\text{g})$ and $\text{H}_2\text{O}(\text{g})$ are present in about equal quantities and the overall pressure of chromium species will reduce dramatically if either $\text{O}_2(\text{g})$ and $\text{H}_2\text{O}(\text{g})$ partial pressure becomes small. Thus, de-humidification or drying of the inlet air in SOFCs would be important to minimize the vaporization of Cr species, particularly the chromium oxyhydroxides. Opila [2007] et al. studied the vaporization of gaseous chromium species over Cr_2O_3 in humidified air (water content $\geq 4\%$) at 873K by transpiration technique. The study on the pressure dependence of the gaseous chromium species on water and oxygen indicated that the x and y values in

equation (2.7) are equal to $3/2$ and 2 , confirming that the gaseous chromium species was primarily composed of $\text{CrO}_2(\text{OH})_2$ (g). The thermodynamic data predicted that formation of CrO_3 (g) and $\text{CrO}_2(\text{OH})$ (g) would become significant for Cr_2O_3 in oxygen and water containing atmosphere at the temperature above 1173 K.

Figure 2.4 Partial pressures of the chromium oxide and oxyhydroxide vapor species above Cr_2O_3 (s) as a function of temperature under conditions where $p(\text{H}_2\text{O})=0.1$ atm and $p(\text{O}_2)=0.1$ atm [Ebbinghaus 1993].

Hilpert [1996] et al. have systematically investigated the chromium vaporization over solid oxide fuel cell interconnect materials by thermodynamic modeling. The study on the dependence of partial pressures of different gaseous chromium species on the oxygen partial pressure and the humidity found the predominant gaseous chromium species is CrO_3 at 1223K at high oxygen partial pressure (Figure 2.5). The predominant gaseous chromium species is $\text{CrO}_2(\text{OH})_2$ at 1223K when the partial pressure is higher than 10^2 Pa (H_2O content $>0.1\%$) (Figure

2.6). Therefore, it has been widely agreed that the predominant gaseous chromium species is $\text{CrO}_3(\text{g})$ in dry air while in wet air it is $\text{CrO}_2(\text{OH})_2$. The reactions occur through the equations below:

Figure 2.5 Partial pressures of gaseous chromium species over $\text{Cr}_2\text{O}_3(\text{s})$ at 1223K and different O_2 partial pressures [Hilpert, Das et al. 1996].

Figure 2.6 Partial pressures of gaseous chromium species over $\text{Cr}_2\text{O}_3(\text{s})$ as a function of water partial pressure at 1223K [Hilpert, Das et al. 1996].

Graham [1971] et al. established a mass transport model which involves diffusion through a stagnant boundary layer of the gaseous reaction product to describe the oxidation/vaporization behavior of Cr_2O_3 (s). In their model, the flux J_{CrO_3} of CrO_3 (g) away from Cr_2O_3 (s) obeys the following equation:

$$J_{\text{CrO}_3} = \frac{2k_1}{M_{\text{Cr}_2\text{O}_3}} \quad (2.10)$$

where $M_{\text{Cr}_2\text{O}_3}$ is the molecular weight of Cr_2O_3 , k_1 is the linear rate constant of equation 2.4 and represents the rate of weight loss of Cr_2O_3 per unit area. k_1 is defined by equation 2.7 below:

$$k_1 = \frac{M_{\text{Cr}_2\text{O}_3} D_{\text{CrO}_3}}{2\delta RT} K_{\text{eq}}^{1/2} P_{\text{O}_2}^{3/4} \frac{\text{g}}{\text{cm}^2\text{s}} \quad (2.11)$$

where D_{CrO_3} is the diffusivity of CrO_3 , T is the absolute temperature, δ is the thickness of the diffusion boundary layer, K_{eq} is the equilibrium constant for reaction 2.3, and P_{O_2} is the equilibrium partial pressure of O_2 . The study on the flow rate and total pressure dependencies based on their model indicated that the mass transport through the gaseous boundary layer is the rate-controlling step in the oxidation/vaporization of Cr_2O_3 . Evaporation coefficients defined by the ratio of the observed J_{CrO_3} to the maximum possible vapor loss (J_{max}) for the loss of CrO_3 (g) under their experimental conditions were below 0.01.

Vaporization of Cr species from chromia-forming alloys is not only dependent on the temperature and humidity but also related to the scale compositions.

According to Gindorf [1999; 2001], the transportation or vaporization rate of Cr species from iron-based alloy is much lower than that from chromium-based alloy due to the formation of Fe-rich oxides on the surface of the iron-based alloy. The formation of $(\text{Cr,Mn})_3\text{O}_4$ spinel top layer in the oxide scale also significantly reduces the vaporization of volatile Cr species. For example, the manganese-containing alloys form a spinel phase in the scale, leading to an increase scale electric conductivity [Brylewski, Nanko *et al.* 2001; Yang, Hardy *et al.* 2004; Yang, Xia *et al.* 2005] and decrease scale volatility [Konysheva, Penkalla *et al.* 2006]. Applying a protective coating to the chromia-forming alloy metallic interconnect can also effectively reduce the oxidation rate and volatility of chromium and the poisoning effects on the cathode performance [Qu, Li *et al.* 2004; Chen, Hou *et al.* 2005; Collins, Lucas *et al.* 2006]. However, in practice, a complete dense, well adherent and highly conductive oxide coating on the metal surface is hard to achieve under long-term SOFC operating conditions due to the significant difference between the thermal and physical properties of the oxide coating and the metallic interconnect substrate.

2.2.2 Chromium deposition and poisoning at LSM cathode

Perovskite-type oxide LSM is the most important materials widely used for cathodes in SOFC stacks. Therefore, investigations on the chromium poisoning effects and depositions at LSM cathodes bear great significance for the development of SOFCs.

Badwal [1997] et al. studied the interaction between chromia-forming alloy and LSM cathodes of SOFCs by the electrochemical test of cells in the absence and presence of the $\text{Cr}_5\text{Fe}_1\text{Y}_2\text{O}_3$ interconnect materials, respectively. The results showed that the cell, composed of LSM/3YSZ/Ni-zirconia, kept a nearly constant cell voltage and showed very little degradation during the 2500h test in the absence of the metallic interconnect. Meanwhile, the cell voltage decreased quickly from 0.8 V to 0.4 V in 16 h in the presence of the metallic interconnect, which was attributed to the increase in the overpotential losses caused by the formation of $(\text{Cr}, \text{Mn})_3\text{O}_4$ spinel depositions across the electrode/electrolyte interface.

Matsuzaki [2000] use the electrochemical impedance spectroscopy to investigate on the electrochemical properties of the LSM/3YSZ composite cathodes in contact with the chromium-containing alloy interconnect by drawing comparisons between the cathode performance in the presence of Sr-doped LaCrO_3 materials and the Inconel 600 materials (Figure. 2.7). In the equivalent circuit, R_e is the resistance of the charge-transfer reaction, Z_d is the R-type Warburg impedance, R_b is the ohmic resistance of electrolyte and lead wires, W is a semi-infinite-length diffusion impedance known as Warburg impedance, C_{dl} is the double layer capacitance, and L is the inductance of lead wires. Comparing the spectrum after 30 min with the initial one, the size of arcs decreased for the doped LaCrO_3 but increased for the alloy. The fitted results showed that R_b slightly decreased, while R_e and R_d greatly increased with time when the alloy was used as the current collector,

indicating that the chromium poisoning effects were caused both by the gaseous chromium species around the surface of the cathodes, inhibiting the dissociation and diffusion of oxygen on the electrode surface, and the solid chromium depositions, hampering the charge transfer process across the cathode/electrolyte interface.

Figure 2.7 Complex impedance spectra of the electrode measured under polarization at the current density of 0.3 A cm⁻²: (a) With the doped LaCrO₃, (b) with the alloy as interconnect, and (c) equivalent circuit used for fitting [Matsuzaki and Yasuda 2000].

Taniguchi [1995] et al. studied the degradation phenomena at the La_{0.9}Sr_{0.1}MnO₃ cathode with an Inconel 600 interconnect. The results indicated that the increase in the cathode polarization during the discharging process is due to the chromium filling the pores at the cathode/electrolyte interface, restricting diffusion

of oxygen gas and decreasing the number of electrode reaction sites. The chromium displacement at the cathode/electrolyte interface is caused by the decrease in the oxygen activity at the cathode/electrolyte interface during the discharge process.

Yokokawa [2006] et al. investigated the thermodynamics of chromium deposition at the LSM cathodes in terms of the valence stability of the transition metal ions in binary oxide and perovskite, which showed that the high valence stability of Mn^{4+} in LSM leads to the oxygen excess region, where the oxide ion vacancies are small and oxide ion conductivity is small. The high stability of Mn^{4+} also gives rise to the A-site deficiency, which affects the reactivity against YSZ electrolyte. Under a large cathodic polarization; however, the manganese oxides can be precipitated from the B-site of LSM and react with the chromium species to form the solid chromium depositions. Tucker [2006] et al. studied the chromium depositions on LSM cathodes at different temperatures. In their study, chromium depositions were not observed on LSM cathodes at 700 or 800 °C while the depositions were observed at 1000 °C, indicating that chromium deposition at LSM cathodes is temperature dependent and the chromium poisoning effects may be alleviated by lowering the operating temperature of SOFCs. Moreover, the results also clearly showed that the chromium contamination at the LSM cathode occurred through a chemical mechanism, and the contamination caused by surface diffusion of Cr from the stainless steel was much more significant than that used by the vapor deposition of Cr from the atmosphere.

Jiang has made systematic investigations on the chromium poisoning effects at both the LSM and LSM/YSZ composite cathodes. According to the study, the chromium poisoning effects on the LSM cathodes mainly have two causes, the gaseous chromium species around the surface of cathodes, inhibiting the dissociation and transportation of oxygen at the cathodes, and the solid chromium depositions like $(\text{Cr,Mn})_3\text{O}_4$, which hampers the charge transfer at the cathode/electrolyte interface [Jiang, Zhang *et al.* 2000; Jiang, Zhang *et al.* 2002; Jiang, Zhang *et al.* 2005; S. P. Jiang, Y. D. Zhen *et al.* 2006; Zhen, Jiang *et al.* 2006; Zhen, Li *et al.* 2006]. According to the study (Figure 2.8), the activation energy of the charge transfer process in the presence of the chromia-forming alloy is 163 kJ mol^{-1} , much higher than that of 109 kJ mol^{-1} for the process in the absence of the alloy, which can be attributed to the solid chromium depositions at the cathode/electrolyte interface. Meanwhile, the activation energy of the adsorption and diffusion of oxygen in the presence of the alloy is 293 kJ mol^{-1} , compared with that of 274 kJ mol^{-1} for the process in the absence of the alloy, indicating the inhibiting effect of the gaseous chromium species on the oxygen diffusion process. The O_2 reduction reaction in the absence of the alloy can be described in the equations below:

while the oxygen ions diffuse through a different path from equation (2.12) in the presence of the chromia-forming alloy according to the equations below:

Figure 2.8 Dependence of electrode resistance on the temperature for O_2 reduction in the absence and presence of chromia-forming alloy [Jiang, Zhang et al. 2000].

In the presence of solid chromium deposits, the oxygen species have to diffuse through the Cr deposit layer before entering the electrolyte. The oxygen

self-diffusion coefficient in Cr_2O_3 single crystals is $10^{-18} \text{ cm}^2 \text{ s}^{-1}$ and is $10^{-13} \text{ cm}^2 \text{ s}^{-1}$ in Cr_2O_3 poly-crystals at 1100°C [Sabioni, Lesage et al. 1992; Liang, Chen et al. 2008; Hua, Pu et al. 2009]. In comparison, the oxygen self-diffusion coefficient in doped ZrO_2 electrolyte is in the range of 10^{-8} to $10^{-7} \text{ cm}^2 \text{ s}^{-1}$ at 900°C [Packer, Skinner et al. 2006; Montero, Tietz et al. 2009]. Therefore, the electrode processes of migration of oxygen ions into the electrolyte would be increasingly dominated by the diffusion of oxygen through the solid chromium deposit, leading to a significant increase in the electrode resistance of the migration of oxygen ions.

Jiang [2000; 2001] also studied the time behavior of the cathodic polarization potential (E_{cathode}) at the LSM cathode in the absence and presence of the metallic interconnect (Figure 2.9). In the absence of the interconnect, the change in E_{cathode} is characterized by two well-defined potential regions, as shown in Figure. 2.9a. E_{cathode} decreased quickly with the current passage in region I, followed by a region II, where the decrease in E_{cathode} is much slower. In the presence of the interconnect (Figure 2.9b), the change in E_{cathode} can also be characterized by two regions, but the change in E_{cathode} with current passage is just in the opposite direction of that in the absence of interconnect. E_{cathode} increases quickly in region I, reaching a plateau, where the increase becomes much slower (region II). In the absence of interconnect, the change of E_{cathode} in region I is not recoverable, while it is almost fully reproducible in the presence of the interconnect, indicating that chromium poisoning at the initial stage of polarization is most likely due to the gaseous

chromium species rather than the Cr deposits on the electrolyte surface. The significant different in the trend and magnitude of E_{cathode} also indicates that the inhibiting effect of the gaseous chromium species on the electrode process in region I is much larger than that in region II. The value of $\Delta E_{\text{cathode}}$ can be used to characterize the chromium volatility of the chromia-forming metallic interconnect materials [Jiang, Zhen et al. 2006].

Figure 2.9 Polarization curves of the LSM electrodes under a cathodic current passage of 200 mA cm^{-2} at 900°C in air in the absence (a) and presence (b) of RA446 interconnect [Jiang, Zhen et al. 2006].

2.2.3 Chromium deposition and poisoning at other cathodes

Novel materials, including $(\text{La,Sr})(\text{Co,Fe})\text{O}_{3-\delta}$ (LSCF), $(\text{La,Ba})(\text{Co,Fe})\text{O}_{3-\delta}$ (LBCF), $\text{La}(\text{Ni,Fe})\text{O}_{3-\delta}$ (LNF), $(\text{La,Sr})\text{CoO}_{3-\delta}$ (LSC) and so on, are developed and studied as cathode materials for SOFCs [Lee, Baek et al. ; Himeko Orui, Kimitaka Watanabe et al. 2004; Bevilacqua, Montini et al. 2006; Komatsu, Arai et al. 2007; Yan, Maragou et al. 2007; Zhao, Peng et al. 2008; Zhen and Jiang 2008; Zhou, Ran et al. 2008]. Chromium deposition and poisoning effects at these cathodes have also been studied.

Konysheva [2006] et al. studied the chromium poisoning effects at the LSCF cathodes using the $\text{Cr}_5\text{Fe}_1\text{Y}_2\text{O}_3$ interconnect at 800 °C and reported that the chromium depositions primarily happened on the surface of the LSCF cathodes, forming a complete SrCrO_4 layer on the electrode surface, as confirmed by EDX, XPS and XRD. They attributed the difference between the chromium depositions at LSM and LSCF cathodes to the significant oxygen ion conductivity of the LSCF cathodes.

Jiang [2002; 2006; 2008] et al. studied the chromium poisoning effects both at the LSCF and LBCF cathodes and reported LBCF as cathode materials with higher chromium-tolerance than LSCF. Very different from the chromium depositions at the LSM cathodes, chromium depositions at the LSCF cathodes primarily occur on the surface while the chromium deposition at the LBCF cathode

is very small and showed much less significant poisoning effects for the O_2 reduction reactions (Figure 2.10). Under a current passage of 200 mA cm^{-2} at 900°C in the presence of RA 446 interconnect, R_E of the LSCF cathode increased quickly from 0.21 to $0.79 \Omega \text{ cm}^2$ during the 1200 min test while R_E for the LBCF cathode almost maintained at $0.1 \Omega \text{ cm}^2$, indicating the much better chromium tolerance of LBCF cathodes than LSCF cathodes. η of the LBCF cathode increased by only 144 mV during the test, comparing an increase of 322 mV for the LSCF cathode. It also confirms the high chromium tolerance of LBCF cathodes.

Figure 2.10 Plot of R_E and η for LBCF and LSCF cathode during 20h current passage at 900°C and under a current density of 200 mA cm^{-2} in the presence of RA446 interconnect [Zhen and Jiang 2008].

A complete layer of chromium depositions composed of Sr and Cr was formed on the surface of LSCF cathode. The depositions were closely related to the Sr species contained in the cathodes and they acted as the nuclei for the chromium depositions. No observable chromium depositions can be found on the surface of

LBCF cathodes; however, EDS analysis detected the presence of chromium depositions on the surface of LBCF cathodes. Chromium depositions at the LBCF cathodes were related to the segregated BaO on the surface of the cathodes. The solid chromium depositions at the LSCF and LBCF cathodes take place through a chemical process according to the equations below:

At LSCF cathodes:

At LBCF cathodes:

Zhen [2006] et al. studied the chromium poisoning effects at the LSM/YSZ composite cathodes and GDC-impregnated LSM cathodes. In contrast to the serious chromium depositions at pure LSM cathodes, chromium deposition on the electrolyte surface at the LSM/YSZ composite cathodes decreased significantly. Moreover, the electrochemical test results prove the feasibility of using gaseous

chromium species to investigate the kinetics of cathode reactions. The results showed that there is an electrochemical transition from the dominant electronic conducting LSM electrode to the mixed ionic and electronic conducting oxides like LSCF in the composite cathodes as the YSZ content increased, which is in agreement with the previous studies.

In addition to LSM, LSCF and LBCF, Pt and $\text{La}(\text{Ni}, \text{Fe})\text{O}_{3-\delta}$ (LNF) are interesting materials for the study of the effect of Fe-Cr alloy interconnect. Pt is a metallic electrode while LNF is a mixed ionic and electronic conductor with very different compositions from that of LSM and LSCF.

Figure. 2.11 shows the SEM micrographs of a Pt electrode in contact with a Fe-Cr alloy interconnect after polarization at 200 mA cm^{-2} and 900°C for 22 h [Jiang, Zhang *et al.* 2005]. The large sphere-like particles on the YSZ electrolyte surface were Pt particles. EDS analysis of the small particles on the YSZ electrolyte surface also show the presence of Pt only (Figure. 2.11c). Very different from that observed on the LSM and LSCF cathodes, there was no Cr deposition or Cr deposits either on the YSZ electrolyte surface or on the Pt electrode surface under conditions studied. This indicates that the deposition of Cr species at Pt electrodes in the presence of Fe-Cr alloy interconnect is kinetically inhibited.

Figure 2.11 SEM micrographs of a Pt electrode in contact with a Fe-Cr alloy interconnect after polarization at 200 mA cm^{-2} and 900°C for 22 h (a&b). EDS pattern of large and small particles on the YSZ electrolyte surface is shown in (c) [Jiang, Zhang *et al.* 2005].

The interaction between $\text{LaNi}_{0.4}\text{Fe}_{0.6}\text{O}_{3-\delta}$ (LNF) cathode and Fe-Cr alloy interconnect was studied in a similar fashion as that for LSM and LSCF electrodes [Zhen, Tok *et al.* 2007; Yongda Zhen, A. I. Y. Tok *et al.* 2008]. Figure 2.12 shows the SEM micrographs of the surface and cross-sections of the LNF electrode after cathodic current passage at 200 mA cm^{-2} and 900°C for 20 h in the presence of a Fe-Cr alloy interconnect. LNF electrode was sintered at 1100°C for 2 h in air. The microstructure of LNF electrode was characterized by uniformly distributed LNF particles with grain size of $\sim 0.5 \mu\text{m}$. Very different from that of LSCF cathode, the surface of the LNF cathode is generally clean with no visible Cr deposits. Similarly,

very different from that of the LSM cathode, the LNF/YSZ interface region is also clean without visible Cr deposition (Figure. 2.12b). The YSZ electrolyte surface in contact with LNF electrode shows the formation of clusters of fine particles (Figure 2.12c). EDS analysis of the clusters of fine particles shows no Cr elements. This indicates that clusters of the fine particles are not due to the Cr deposits. Chiba [1999] et al. and Orui [2004] et al. reported that stoichiometric LNF reacts with YSZ to form the $\text{La}_2\text{Zr}_2\text{O}_7$ phase at the LNF/YSZ interface when the sintering temperature exceeds 1000°C . As the present LNF was sintered at 1100°C , the clusters of fine particles formed on the YSZ electrolyte surface are most likely due to the formation of $\text{La}_2\text{Zr}_2\text{O}_7$ resistive phase. The electrolyte areas between the clusters are clean, indicating no preferential Cr deposition on the electrolyte surface (Figure 2.12 c).

Komatsu [2006] *et al.* studied the effect of Cr poisoning on cells which consist of either $\text{LaNi}_{0.6}\text{Fe}_{0.4}\text{O}_{3+\delta}$ (LNF) or $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3+\delta}$ (LSM) as a cathode in the presence of a chromia-forming alloy (Inconel 600). Very different from that of the LSM cathode, the cell performance with LNF cathode was very stable and did not change significantly in the presence and absence of the Fe-Cr alloy. The electron probe microanalysis (EMPA) showed very low Cr species distribution in the LNF cathode and there was no Cr accumulation at the cathode/YSZ electrolyte interface.

Figure 2.12 SEM micrographs of (a) the surface and (b) cross-section surface of the LNF electrode after cathodic current passage at 200 mA cm^{-2} and 900°C for 20 h in the presence of a Fe-Cr alloy interconnect. The YSZ electrolyte surface in contact with the LNF electrode and EDS of the particles on the YSZ electrolyte surface are shown in (c) and (d) [Zhen, Tok et al. 2007; Yongda Zhen, A. I. Y. Tok et al. 2008].

2.2.4 Chromium deposition mechanism

The interaction between metallic interconnect and cathodes of SOFCs has been extensively investigated recently and a great deal of information is available. However, there are still considerable disagreements on the poisoning mechanism of the chromium deposition on the O_2 reduction reaction. The driving force for the deposition of chromium is generally discussed in terms of chemical or electrochemical reactions [Fergus 2007]. The first chromium deposition mechanism is named the electrochemical deposition mechanism, which regards that the chromium depositions are closely related to the cathodic polarization and

attributes the chromium depositions to the electrochemical reduction of the chromium-containing gas species to solid Cr_2O_3 at the TPB of cathodes in competition with the oxygen reaction reactions [Taniguchi, Kadowaki *et al.* 1995; Badwal, Deller *et al.* 1997; Matsuzaki and Yasuda 2000; Fujita, Ogasawara *et al.* 2004; Simner, Anderson *et al.* 2005; Konysheva, Penkalla *et al.* 2006]. The rationale behind the electrochemical deposition mechanism is the thermodynamic compatibility of the electrochemical reduction of high valent Cr species and O_2 reduction reaction under the SOFC operation conditions [Hilpert, Das *et al.* 1996]. According to this mechanism, the solid chromium depositions occur through either of the equations below:

if CrO_3 is the predominant Cr-containing species or,

if $\text{CrO}_2(\text{OH})_2$ is the predominant Cr-containing gas species. The process of chromium depositions by the electrochemical process is illustrated in Figure 2.13.

Figure 2.13 Electrochemical deposition of Cr_2O_3 at TPB [Fergus 2007].

The electrochemical mechanism explains some of the phenomena observed in the studies; however, confusions about the chromium depositions still exist and cannot be explained by the electrochemical deposition mechanism. Therefore, another mechanism named chemical deposition mechanism was proposed by Jiang et al.. According to the chemical deposition mechanism, nuclei are first formed at the cathodes and then react with the gaseous chromium species to form the solid chromium depositions. Owing to the mobility of some nuclei, such as manganese species, the chromium depositions can be formed at areas away from the TPB area for the cathode reduction reactions. Fig. 2.14 illustrates the process of chromium depositions according to the chemical deposition mechanism.

The evidence for the chemical deposition mechanism include: (1) chromium depositions occur in the absence of the polarization; (2) chromium depositions happen both under cathodic or anodic polarizations; and (3) the area of chromium depositions have been found to be much larger than the estimated TPB area of cathodes; and (4) chromium poisoning effects can be greatly reduced by fabricating cathodes with materials without the elements like Mn, Sr, Ca, Ba, which can form nuclei for chromium depositions.

Figure 2.14 Chemical deposition of Cr_2O_3 on LSM [Fergus 2007].

Jiang [2005; 2008; 2008] et al. have studied the chromium depositions at the LSM, LSCF, LBCF and LNF cathodes, respectively. At the nonstoichiometric LSM cathodes, the Mn element will form nuclei for chromium deposition. The Mn ions on the surface of LSM cathodes was first reduced from the Mn^{3+} to Mn^{2+} under the cathodic polarization, and then the Mn^{2+} ions will move from the cathode surface to the electrolyte surface, where they will react with the gaseous chromium species to form the solid chromium depositions like Cr_2O_3 and $(\text{Cr},\text{Mn})_3\text{O}_4$ [Jiang, Zhang et al. 2000]. The equations for the formation of the solid chromium depositions at the LSM cathodes are listed below:

It is well known that in the LSM/YSZ electrode/electrolyte cells, Cr deposition occurs at the electrode/electrolyte interface under cathodic polarization, as shown by numerous studies [Taniguchi, Kadowaki *et al.* 1995; Badwal, Deller *et al.* 1997; Jiang, Zhang *et al.* 1999; Jiang, Zhang *et al.* 2000; Jiang, Zhang *et al.* 2000; Matsuzaki and Yasuda 2000; Jiang, Zhang *et al.* 2001; Matsuzaki and Yasuda 2001; Jiang, Zhang *et al.* 2002; Paulson and Birss 2004; Jiang, Zhang *et al.* 2005; Konyshova, Penkalla *et al.* 2006]. Jiang [2006] *et al.* also observed chromium depositions at the LSM/YSZ cells under the anodic polarization, as shown in Figure 2.15. After the anodic polarization under a current passage of 200 mA cm^{-2} for 6 h at 900°C and 11.5 h at 800°C , the LSM electrode was peeled away and it can be clearly observed that the YSZ electrolyte surface was covered by fine grains, which were confirmed to be chromium depositions by the EDS analysis. That is, chromium deposition of Cr species occurred in the LSM/YSZ system under both cathodic and anodic polarization conditions, indicating that the deposition of Cr species is independent of polarization direction and thus is not dominated by the electrochemical reduction of high valence Cr species.

Figure 2.15 SEM micrographs of the exposed YSZ electrolyte surface after the LSM electrode was anodically polarized at 200 mAcm^{-2} for 6 h at 900°C (a) and 11.5 h at 800°C (b). EDS analysis of the fine grains in (a) is shown in (c) [Jiang, Zhang *et al.* 2000].

In addition, deposition of Cr species took place preferentially on the zirconia electrolyte surface with a deposition ring far greater than the TPB area. The deposition ring was calculated to be $60 \mu\text{m}$ for the LSM/YSZ cell after polarized at 900°C for 50 h and $89 \mu\text{m}$ for the cell after polarized for 129 h. The width of the deposition ring is much larger than the estimated length of three phase boundary of $0.03\text{-}0.07 \mu\text{m}$. It indicates that solid chromium depositions at the LSM/YSZ cell are not limited to the three phase boundary, which is contradictory with the electrochemical deposition mechanism. Finally, the polarization and impedance responses measured under open circuit conditions for O_2 reduction at LSM

electrodes in the presence of chromia-forming alloys behave differently. Despite the increase in the overpotential, the impedance curve under the open circuit condition decreases, illustrating that the TPB area is not decreased due to the chromium deposition.

The spinel $(\text{Cr,Mn})_3\text{O}_4$ chromium depositions are attributed to the dissolution of Mn in the YSZ electrolyte. Previous studies on the oxide-manganese oxide phase diagram found that 10-14% manganese can dissolve in Cr_2O_3 and the spinel $(\text{Cr,Mn})_3\text{O}_4$ is stable in the SOFC operating temperature [Matraszek, Miller *et al.* 2004]. Chen [2005] *et al.* calculated the solubility of MnO_x in YSZ at different temperatures (Figure 2.16), which is in good agreement with the experiment results by Kawada [2009] *et al.*. According to their results, the solubility of MnO_x in YSZ increases monotonously from 4% to 6% as the temperature increases from 1200K to 1800K. In addition, they also studied the solubility of Mn^{2+} and Mn^{3+} ions in YSZ, as shown in Figure 2.17. According to their results, the solubility limit of Mn^{3+} in YSZ is much lower than Mn^{2+} , which can be attributed to the difference in the radius and valence state between Mn^{2+} and Mn^{3+} ions.

Wang [2008] *et al.* studied the effect of Mn doping on the chromium depositions at Pt/YSZ cathode interfaces and found that the Pt electrode with the Mn-doped YSZ electrolyte surface degraded much more rapidly than the electrode with the pure YSZ electrolyte after cathodic polarization for 25 h in moist air at 800 °C. It indicates that the chromium depositions at the cathodes are closely related to

the dissolved Mn in the electrolyte, further explaining the reason for the formation of spinel $(\text{Mn,Cr})_3\text{O}_4$ deposition. However, the mechanism of the Mn transportation from the cathode to the electrolyte surface is still not very clear.

Figure 2.16 MnO_x solubility in YSZ in air [Chen, Hallstedt et al. 2005].

Figure 2.17 Solubility of MnO_x in YSZ at 1273K as a function of oxygen partial pressure [Chen, Hallstedt et al. 2005].

According to the study of Jiang [2006] et al., the increase in the electrode potential (E_{cathode}) for LSCF is much smaller compared with the Pt and LSM electrodes. The change of E_{cathode} with current passage time is almost fully

reproducible, indicating the strong inhibiting effects of the gaseous Cr species on the surface process like dissociative adsorption and diffusion reaction on the electrode surface. The analyses are in agreement with the chromium deposition phenomena observed on the surface of the LSCF electrodes that the surface is fully covered by a layer of chromium crystals. In their study, the surface of LSCF cathodes is still covered by a layer of chromium depositions after being heated for 140h in contact with the interconnect at 900 °C in the absence of the cathodic polarization, demonstrating that the chromium depositions at the LSCF cathodes is a chemical deposition process rather than an electrochemical deposition process. EDS and XRD results show that the chromium depositions on the surface of the LSCF electrodes is primarily composed of SrCrO_4 , which is closely related to the segregated Sr species on the surface of the cathodes. At the LBCF cathode, the chromium depositions are much less than those at the LSCF cathode. EDS analysis shows that the chromium deposits are primarily composed of Ba, Cr, and O, closely related to the segregated BaO on the cathode surface. However, further study on the chromium deposition mechanism at cobaltite cathode materials is needed to explain difference in the chromium poisoning and depositions observed at the LSCF and LBCF cathode.

2.3 Summary

The previous studies have shown that chromium deposition behavior at the cobaltite materials is different from that observed at the manganite cathode

materials. It seems that the B-site element in the pervoskite structure has great influence on the chromium deposition behaviors, but further study is still needed to provide evidence and reveal the relationship. Furthermore, the LBCF cathode shows much higher chromium-tolerance than the LSCF cathode, which indicates that the chromium-tolerance of cathode materials can be enhanced by substituting the A-site Sr with Ba, which shed lights on the development of chromium-tolerance cathode materials. However, the reason for this is still not very clear. Different phenomena were observed by distinct research groups, which may be attributed to the difference in the research conditions, such as the humidity in air, interconnect composition, cathode composition and so on. Nonetheless, it needs further study to clarify the influence of working conditions on the chromium depositions in detail.

CHAPTER 3 EXPERIMENTAL PROCEDURES

In this chapter, the experimental procedures such as fabrication of the metallic interconnect, preparation of the cathode materials, fabrication of the cathode, and characterization techniques used in this study are detailed.

3.1 Sample preparation

3.1.1 Metallic interconnect

The metallic interconnect materials used in this study are the commercial chromium-containing alloys RA446 (23-27% Cr, 1.5% Mn, 1% Si, 0.2% C, 0.12% N and the remaining Fe; Rolled Alloy Co., Ontario, Canada) and Ni-Mo-Cr interconnect (Huazhong University of Science & Technology, China).

For electrochemical test, the alloys were machined into coupons (12 mm×12 mm×4 mm) with channels (1.2 mm×1.2 mm) cut on one side and holes in the center of each channel. The samples were also grounded with 400-grit sand paper and cleaned in ultrasonic cleaner with isopropanol. The design of the interconnect used for the electrochemical test is shown in Figure 3.1.

Figure 3.1 Design of metallic interconnect.

3.1.2 Electrode materials

The electrode materials used in this study, including the $(\text{La}_{0.8}\text{Sr}_{0.2})_{0.95}(\text{Mn}_{1-x}\text{Co}_x)\text{O}_{3\pm\delta}$ (LSMC, $0.0 \leq x \leq 1.0$), $(\text{La}_{0.6}\text{Sr}_{0.4-x}\text{Ba}_x)(\text{Co}_{0.2}\text{Fe}_{0.8})\text{O}_{3-\delta}$ (LSBCF) ($0.0 \leq x \leq 0.4$) and $(\text{La}_{0.8}\text{Sr}_{0.2})_{0.9}\text{MnO}_{3+\delta}$ (LSM), were synthesized via a glycine-nitrate process (GNP). Detailed steps for the GNP method are shown in Figure 3.2.

For the preparation of LSMC ($0.0 \leq x \leq 1.0$) cathode materials, stoichiometric amounts of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Sr}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (analytical grade, all from Sigma-Aldrich) were dissolved in distilled water with glycine added as the fuel. The mixture was heated at 60°C to evaporate the water and combustion was carried out in a beaker on a hot plate. Subsequently, the powders produced from the spontaneous combustion were collected and heated at 1100°C for 6 h. For the preparation of LSBCF ($0.0 \leq x \leq 0.4$) materials, $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Ba}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Sr}(\text{NO}_3)_2$

(analytical grade, all from Sigma-Aldrich) were used as the raw materials. Similar steps were followed during the whole process and the powders produced from the spontaneous combustion were heated at 1100 °C for 6h to get the cathode materials. For the preparation of LSM materials, stoichiometric amounts of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Sr}(\text{NO}_3)_2$, and $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (analytical grade, all from Sigma-Aldrich) were used as the materials. Powders collected from the spontaneous combustion are heated at 1000 °C for 6h to get the cathode materials.

Figure 3.2 Procedures for preparing cathode powders by GNP process.

The $\text{Ba}(\text{Co}_{0.7}\text{Fe}_{0.2}\text{Nb}_{0.1})\text{O}_{3\pm\delta}$ (BCFN) materials were prepared by solid state reaction method because of the unavailability of niobium nitrate due to the low solubility of niobium oxide in acid solutions. Stoichiometric amount of BaCO_3 , Co_3O_4 , Fe_3O_4 , and Nb_2O_5 oxides were mechanically mixed, calcined at 950 °C for 6h, and then ball-milled for 20h to achieve the BCFN cathode powders. All the materials, including $(\text{La}_{0.36}\text{Sr}_{0.24}\text{Ba}_{0.4})(\text{Co}_{0.4}\text{Fe}_{0.56}\text{Nb}_{0.04})\text{O}_{3\pm\delta}$ (LSBCFN60 with 60 wt. % LSCF), $(\text{La}_{0.3}\text{Sr}_{0.2}\text{Ba}_{0.5})(\text{Co}_{0.45}\text{Fe}_{0.5}\text{Nb}_{0.05})\text{O}_{3\pm\delta}$ (LSBCFN50), $(\text{La}_{0.24}\text{Sr}_{0.16}\text{Ba}_{0.6})(\text{Co}_{0.5}\text{Fe}_{0.44}\text{Nb}_{0.06})\text{O}_{3\pm\delta}$ (LSBCFN40), and $(\text{La}_{0.18}\text{Sr}_{0.012}\text{Ba}_{0.7})(\text{Co}_{0.55}\text{Fe}_{0.38}\text{Nb}_{0.07})\text{O}_{3\pm\delta}$ (LSBCFN30), were prepared by mechanically mixing corresponding weight percent of LSCF and BCFN powders, which were calcined at 1100 °C for 4h and ball-milled for 20h to achieve the LSBCFN cathode powders. The powders were examined with X-ray diffraction.

3.1.3 Electrolyte materials

Two kinds of materials including 8YSZ and gadolinium-doped ceria ($\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$, GDC) were used as the electrolytes. The 8YSZ electrolyte materials were supplied by Tosoh Corporation, Japan. The GDC electrolytes were prepared by the solid-state reaction methods. Stoichiometric amounts of CeO_2 (99.9%, Sigma-Aldrich) and Gd_2O_3 (99.9%, Sigma-Aldrich) were mixed and ball-milled in iso-propanol with yttria-stabilized zirconia medium for 24 h. After drying, the mixture was uniaxially pressed into disks under a uniaxial pressure of 50 MPa and sintered at 1600 °C for 6h in air to form the electrolyte pellets, which

were ~ 1 mm in thickness and ~ 20 mm in diameter.

3.1.4 Preparation of test cells

For the electrochemical characterization, both three-electrode system, composed of the working electrode (WE), counter electrode (CE) and reference electrode (RE), forming one polarization circuit and one measuring circuit, and two-electrode system, composed of WE and CE, acting as both the polarization and measuring circuit, were used in this project.

(1) Half cell for the three-electrode system test.

The configuration of the half cell used in three-electrode system, is illustrated in Figure 3.3. Detailed procedures for the preparation of the three electrode system are shown in Figure 3.4. The mixed powders of electrolyte materials and ~ 1.5 wt% polyvinyl-butylal (PVB) binder were first uniaxially pressed into disks under a pressure 50 MPa followed by high temperature sintering to form the dense electrolyte pellets. Pt paste (Ferro Corporation, USA) was painted onto one side of the electrolyte pellets to serve as the RE and CE, respectively. The counter electrode was symmetrically located at the center, opposite to WE. The reference electrode was painted as a circular ring around CE with a distance of ~ 4 mm to CE. WE, made by the cathode materials investigated with binders, was screen-printed onto the other side of the electrolyte pellet with an area of ~ 0.50 cm². Then the cathode was sintered at a high temperature to form the desired porous structure.

Figure 3.3 Configuration of test cell.

Figure 3.4 Preparation procedure for half cells.

(2) Full cell for two-electrode system test

The configuration of the full cell composed of the anode support layer, anode functional layer, thin GDC electrolyte layer, and cathode layer are illustrated in Figure 3.5. Detailed procedures for the fabrication of the anode-supported cell are shown in Figure 3.6. The anode-supported full cell was fabricated by the spin-coating method. Powders for the anode support layer were prepared by ball-milling NiO powders (J. T. Baker, US), which were heated at 750 °C for 2 h to coarsen the microstructure, and GDC powders (GDC10-TC, Nextech) at a weight ratio of 60:40 with 6 wt. % of graphite added as the pore former. The mixed powders were die-pressed under a pressure of 100 MPa into discs of ~ 24 mm in diameter, which were pre-sintered at 1000 °C for 2 h to form the anode substrates. The suspension used for the fabrication of anode functional layer was prepared by dispersing 4 wt. % GDC and 6 wt. % NiO powders in isopropanol with certain organic additives. The suspension was spin-coated onto the anode support layer at 2500 rpm for 20 s. After drying at room temperature for ~ 15 min, the spin-coating process was repeated once more to achieve the desired thickness of the anode functional layer. For the GDC electrolyte layer, the suspension used was prepared by dispersing 2 wt. % GDC powders into iso-propanol with certain organic additives. The suspension was spin-coated onto the anode functional layer at 2500 rpm for 20 s and the process was repeated for several times to achieve the desired thickness of the electrolyte. Then disc with prepared anode and electrolyte layers

was sintered at 1500 °C for 4 h. The LSBCFN40 cathode was applied to the GDC electrolyte by screen-printing method and sintered at 1050 °C for 2 h. Later a thin layer of Pt paste was screen-printed onto both the cathode and anode surface as the current collector. The Pt paste was sintered at 900 °C for 2 h.

Figure 3.5 Configuration of anode supported cell.

3.2 Electrochemical characterization

3.2.1 Electrochemical test design

For characterizing the chromium poisoning effects at different cathodes, the three-electrode system was adopted to characterize the electrochemical performance of each cathode both in the absence and presence of the metallic

interconnect based on the special requirements for the investigation of the chromium poisoning effects. By drawing comparisons between the electrochemical performance of cathodes in the absence and presence of the interconnect, the chromium poisoning effects can be effectively characterized. The electrochemical test designs for the cathodes in the absence and presence of the interconnect are illustrated in Figure 3.6 and 3.7, respectively.

Figure 3.6 Electrochemical test design for cathode in the absence of metallic interconnect.

Figure 3.7 Electrochemical test design for cathode in the presence of metallic interconnect.

The three-electrode set-up was used in both arrangements and can be measured at open circuit and polarization conditions. Current was passed through WE and CE to provide polarization of the cathode while potential difference between RE and WE was measured using a separate Pt wire as voltage probe. Overpotential at WE was determined as the measured potential difference between RE and WE minus the voltage drop related to ohmic resistance of the system.

As shown, the testing cell was located in the furnace with WE exposed in controlled flow air of $\sim 100 \text{ ml min}^{-1}$ while CE and RE were exposed in static air. For the measurements in the absence of the metallic interconnect, Pt mesh was used as the current collector for both WE and CE. For the measurements in the presence of metallic interconnect, the metallic interconnect was directly in contact with WE. Two Pt wires were spot-welded to the sides of the metallic interconnect to serve as voltage and current probes, respectively. No extra Pt mesh was placed between the

metallic interconnect and the electrode coating. In this design, the metallic interconnect also served 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.

For the full cell test, two-electrode setup was adopted and the arrangement for the test is illustrated in Figure 3.8. In the two-electrode system, anode served as WE and hydrogen was provided as the fuel at a flow rate of 40 ml min^{-1} . The alumina tube at the anode side was sealed by the glass sealant to avoid direct contact between air and hydrogen. The cathode, exposed in static air, served as CE, which was connected with RE during the test. On both side, a layer of Pt paste was fabricated onto the electrode for current collection.

Figure 3.8 Electrochemical design for cell performance test.

3.2.2 Electrochemical impedance test

(1) Basic theory

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. The technique has been in use in aqueous electrochemistry for a long time. For ionically conducting materials, the technique was first applied by Bauerle in 1969 to analyze the response of zirconia-based solid electrolyte cells to sinusoidal perturbations. Since then this technique has been widely used to investigate a range of ionic conductors which include polymers, ceramics and glasses.

The EIS technique in general involves the measurement of current through a solid electrolyte cell when a sinusoidal voltage of low amplitude is applied. The sine wave is used in impedance measurements because for a sinusoidal signal (irrespective of its amplitude and frequency), the inputs and outputs have the same form and the 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 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 the amplitude and phase from the voltage signal

may occur depending on the elements in the circuit and can be represented by:

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

where Φ is the phase angle, ΔE is the amplitude of the voltage and ΔI the amplitude of the current signal. For a pure resistor, the phase shift is zero.

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

$$Z(\omega) = E(t)/I(t) = Z \exp(-j\Phi) \quad (3.3)$$

$$= Z \cos \Phi - j Z \sin \Phi = Z_R - j Z_I \quad (3.4)$$

where j is a complex number with value of $\sqrt{-1}$, Z_R and Z_I are real and imaginary parts of the impedance. The relationships between various terms are as follows:

$$\Phi = \tan^{-1}(Z_I/Z_R) \quad (3.5)$$

$$Z = \sqrt{Z_R^2 + Z_I^2} \quad (3.6)$$

For a pure resistor (R), capacitor (C) and an inductor (L), the impedance is given by the following relations respectively:

$$Z = R + 0j \quad (3.7)$$

$$Z=0-j/\omega c \quad (3.8)$$

$$Z=0+j\omega L \quad (3.9)$$

Though impedance of a capacitor or an inductor has the same units as the resistor, however; it differs from the impedance of a resistor in that it is dependent on the frequency of the AC signal applied.

Apart from impedance, three other different representations are used to display data in the complex plane. These are admittance (Y), permittivity (ϵ) and modulus (M). Both admittance and permittivity are parallel functions whereas impedance and modulus are series functions. The relationship between the four basic immittance functions are given below.

Admittance:

$$Y=1/Z=G+jB \quad (3.10)$$

$$G=Z_R/(Z_R^2+Z_I^2) \quad (3.11)$$

$$B= Z_I/(Z_R^2+Z_I^2) \quad (3.12)$$

Permittivity:

$$\epsilon=\epsilon_R-j\epsilon_I=Y/(j\omega C_o) \quad (3.13)$$

Modulus:

$$M=\epsilon^{-1}=M_R+jM_I \quad (3.14)$$

In these equations, C_0 is the vacuum capacitance of the measuring cell in the absence of the material of interest, G is the conductance and B the susceptance. From these four different equations, impedance and admittance representations are commonly used for analyzing the response of solid electrolyte systems and are more useful in separating the response of systems for which the time constants of various processes differ as a result of different capacitances. The complex permittivity and modulus representations are generally used for analyzing the dielectric response of systems.

The fundamental laws governing the relationship between the charge and potential and the properties of linear systems are similar in passing from electronic to ionic materials. Therefore as a first approximation, it is reasonable to assume that a direct connection exists between the behavior of a real electrochemical system and that of an electrical circuit consisting of discrete components (resistors, capacitors, inductors). Randles suggested that various processes in an electrochemical system can be represented by an electrical circuit which would depict the way in which various conducting elements in the electrochemical cell are connected. The equivalent circuit approach in data analysis is even more popular in the study of solid ionic materials as detailed microscopic models of all possible electrode and electrolyte processes are generally not available or are extremely complex. Fig. 3.9 shows the electrochemical impedance spectroscopy and equivalent circuit of LSM cathodes with YSZ as the electrolyte at 900 °C. The

kinetics of the cathode reactions, including the charge transfer process and the gas phase transportation process, can be separated and studied in detail by EIS analyses. In this project, EIS was also used for the study of the chromium poisoning effects of the Fe-Cr metallic interconnect on the electrochemical performance of the cathodes.

Figure 3.9 Electrochemical impedance spectroscopy of LSM cathode on YSZ electrolyte at 900 °C : (a) Nyquist plot and fitted curve, and (b) equivalent circuit for fitting.

(2) EIS test

In this project, a Solatron 1260 frequency response analyzer in conjunction with a 1287 electrochemical interface was used for the EIS measurement in the frequency range from 100 kHz to 0.1 Hz with the amplitude of 10 mV at open circuit. Electrode ohmic resistance (R_{Ω}) was measured from the high frequency

intercept and the electrode interface (polarization) resistance (R_E) was obtained from the differences between the high-frequency and the low-frequency intercepts on the impedance spectra.

3.2.3 Steady-state polarization test

The electrochemical performance of the cathode under the current passage was investigated by the polarization test using the three-electrode method. Polarization test of cathodes in the absence and presence of the metallic interconnect was carried on under a constant current density of 200 mA cm^{-2} within the temperature range studied. The electrode potential (E_{cathode}) was measured against the Pt air reference electrode. The cathodic current passage was interrupted from time to time to make the EIS measurements. Overpotential (η) was obtained from E_{cathode} and R_Ω by the following equation:

$$\eta = E_{\text{cathode}} - j R_\Omega \quad (3.15)$$

where j is the current density.

3.2.3 Cell performance test

Two-electrode setup was used for testing the power-generating performance of the anode-supported cell with thin film GDC electrolyte at different operating temperature. Potentiodynamic technique was adopted to achieve the Current-voltage (I - V) curve and power density of the whole cell at a scan rate of 5 mV s^{-1} .

3.3 Material characterization

3.3.1 X-ray diffraction (XRD)

In this project, X-ray diffraction (XRD, Philips MPD 1880) using Cu K α 1 radiation ($=1.54060\text{\AA}$) at room temperature was adopted for phase determination. X-ray scans were run over a 2θ range of $20\text{--}80^\circ$ at a scan rate of $0.02^\circ/\text{sec}$, and plots of X-ray intensity against 2θ were obtained. For the cathode materials prepared by the GNP method, XRD was used to determine the phase composition of the powders. XRD was also used to study the chemical compatibility of the cathode materials with the electrolyte materials after high temperature sintering. In addition, it was also used to determine the phase composition of the solid chromium depositions at the cathodes after the long term electrochemical test at 900°C .

3.3.2 Scanning electron microscopy (SEM) / energy dispersive spectroscopy (EDS)

In this project, scanning electron microscopy (SEM, JEOL 6360, Japan) with X-ray energy dispersion spectroscopy (EDS, Oxford, UK) was used for the study of the morphology and element distribution of the on the electrode surface, inside the bulk of the electrode and on the electrolyte interface in contact with the electrode before and after the electrochemical test. To examine the electrolyte surface in contact with the cathode coating, the cathode coating was removed by 20% HCl acid treatment in an ultrasonic bath at room temperature. Then the samples were

washed with distilled water and desiccated. Chemical compositions of the samples were quantitatively determined by EDS using point microanalysis or mapping. The samples were coated with Pt or Au before SEM examination.

3.3.3 Conductivity test

Conductivity is a very important property for the cathode materials for SOFCs. Therefore, conductivity of the materials was tested by the four-probe method with a sourcemeter. The LSCF, BCFN, and LSBCFN40 materials were die-pressed into rectangular bars and sintered at 1400 °C, 1100 °C, and 1100 °C for 4 h to measure the conductivities using the four-terminal DC method. The measurement was carried out in air in the temperature range of 400-900 °C with an interval of 50 °C between two measurements. Before each measurement, 30 min is allowed for the stabilization of the samples. The measured conductivities of the materials were corrected using the equation below :

$$\sigma_{corr} = \frac{\sigma_{app}}{2(d_{rel} / 100 - 0.5)} \quad (3.16)$$

where σ_{corr} is the porosity-corrected conductivity, d_{rel} is the relative density and σ_{app} is the measured apparent conductivity.

CHAPTER 4 CHROMIUM DEPOSITION AND POISONING AT LSMC ($0.0 \leq x \leq 1.0$) CATHODES

Previous studies showed that the manganite-based $(\text{La,Sr})\text{MnO}_{3+\delta}$ (LSM) cathode and cobaltite-based $(\text{La,Sr})(\text{Co,Fe})\text{O}_{3-\delta}$ (LSCF) cathode had different chromium deposition behavior in the presence of the Fe-Cr metallic interconnect [Jiang, Zhang *et al.* 2002]. Chromium deposition at the LSM cathode occurred preferentially on the electrolyte surface in the form of $(\text{Cr,Mn})_3\text{O}_4$ crystals, closely related to the segregation of MnO at the electrode/electrolyte interface, while at the LSCF cathode it occurred on the electrode surface in the form of SrCrO_4 crystals, closely related to the segregation of SrO on the electrode surface. De Souza and Kilner [1998; 1999] studied oxygen transport properties in $\text{La}_{1-x}\text{Sr}_x\text{Mn}_{1-y}\text{Co}_y\text{O}_{3\pm\delta}$ (LSMC) perovskites and showed that as the Co content at the B-site increases from 0.0 to 1.0, the LSMC materials change from a pure electronic conductor to a mixed ionic and electronic conductor with $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ (LSC) displaying the highest oxygen diffusion coefficient and $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3+\delta}$ displaying the lowest oxygen diffusion coefficient. Thus, the LSMC ($0.0 \leq x \leq 1.0$) system is taken as an ideal system in this chapter to investigate the fundamental relationship between the Cr deposition and poisoning and the electrocatalytic activity (i.e., oxygen surface exchange and diffusion coefficients) under SOFC operation conditions.

4.1 Experimental

The chromia-forming alloy interconnect used in this study was the commercially available RA446 interconnect and GDC was used as the electrolyte. Details on the fabrication of the testing cell can be found in Chapter 3. Polarization behaviors of the LSMC ($0.0 \leq x \leq 1.0$) were studied under a constant current passage of 200 mA cm^{-2} at 900°C . The electrode potential (E_{cathode}) was measured against the Pt air reference electrode. Current passage was interrupted from time to time for the EIS measurements at the open circuit condition. The EIS test was carried out in the frequency range of 0.1 Hz to 100 kHz with a signal amplitude of 10 mV. SEM and EDS were used to examine the chromium deposition at the LSMC ($0.0 \leq x \leq 1.0$) cathodes.

Figure 4.1 illustrates the different parts of LSMC electrode and GDC electrolyte for the chromium deposition characterizations, including (1) LSMC electrode surface under the rib of the Fe-Cr interconnect, (2) LSMC electrode surface under the channel of the Fe-Cr interconnect, (3) GDC electrolyte surface in contact with LSMC electrode under rib of the Fe-Cr interconnect, and (4) GDC electrolyte surface in contact with LSMC electrode under channel of the interconnect. For the characterization of chromium depositions on the electrolyte surface, the LSMC cathode was removed by 20 % HCl etching, followed by washing with de-ionized water.

Figure 4.1 Areas and terminologies of LSMC electrode and GDC electrolyte examined by SEM for chromium deposition.

4.2 Results and discussion

4.2.1 XRD pattern of cathode powders

Figure 4.2 shows the XRD patterns of the $(\text{La}_{0.8}\text{Sr}_{0.2})_{0.95}(\text{Mn}_{1-x}\text{Co}_x)\text{O}_{3\pm\delta}$ (LSMC, $0.0 \leq x \leq 1.0$) cathode powders after calcined at 1100°C for 6 h. The lattice parameter and unit volume of the LSMC powders are given in Table 4.1. All the major peaks in the XRD pattern belong to the perovskite structure, indicating that the rhombohedral perovskite phase has been formed as the primary phase in the LSMC powders within the composition range studied. There is a gradual shift in the XRD peak position to a higher diffraction angle with the substitution of the B-site Mn by Co, as shown in the enlarged region for peak (024). The shift in the XRD peak indicates the decrease in the lattice parameter as x changes from 0.0 to 1.0. The LSMC ($x=0.0$) powders have a unit parameter of $5.488 \text{ \AA}$, and a unit volume of

165.3 Å³, which decreased to 5.473 Å and 163.9 Å³ for the LSMC ($x=0.4$). In the case of LSMC with $x=1.0$ the lattice parameters are 5.437 Å and 160.7 Å³, respectively. The discrepancy of the lattice parameter for LSMC ($x=0.8$) from the trend can be attributed to the error in the fitting and refining process to get the parameters. The ion radius of Co³⁺ (0.61 Å for HS Co³⁺ and 0.55 Å for LS Co³⁺) are lower than that of Mn³⁺ (0.65 Å) [Shannon 1976]. Thus the substitution of Mn ions by Co ions would lead to the decrease in the lattice parameters and unit volume. As the Co content increases, the LSMC materials would shift from the oxygen excessive region to the oxygen deficient region, which would also contribute to the decrease in the unit volume [Wandekar, Wani et al. 2009].

Figure 4.2 XRD patterns of the $(\text{La}_{0.8}\text{Sr}_{0.2})_{0.95}(\text{Mn}_{1-x}\text{Co}_x)\text{O}_{3\pm\delta}$ (LSMC, $0.0 \leq x \leq 1.0$) cathode powders after calcined at 1100 °C for 6 h.

Table 4.1 Lattice parameters of the LSMC ($0.0 \leq x \leq 1.0$) cathode materials prepared by GNP method, followed by heat treated at 1100 °C for 6h.

Composition	Structure	a, b, c (Å)	α (°)	V (Å ³)
$(\text{La}_{0.8}\text{Sr}_{0.2})_{0.95}\text{MnO}_{3+\delta}$	Rh	5.488	90.11	165.3
$(\text{La}_{0.8}\text{Sr}_{0.2})_{0.95}(\text{Mn}_{0.8}\text{Co}_{0.2})\text{O}_{3\pm\delta}$	Rh	5.493	90.25	165.7
$(\text{La}_{0.8}\text{Sr}_{0.2})_{0.95}(\text{Mn}_{0.6}\text{Co}_{0.4})\text{O}_{3\pm\delta}$	Rh	5.473	90.28	163.9
$(\text{La}_{0.8}\text{Sr}_{0.2})_{0.95}(\text{Mn}_{0.4}\text{Co}_{0.6})\text{O}_{3\pm\delta}$	Rh	5.446	90.21	161.6
$(\text{La}_{0.8}\text{Sr}_{0.2})_{0.95}(\text{Mn}_{0.2}\text{Co}_{0.8})\text{O}_{3\pm\delta}$	Rh	5.439	90.24	160.9
$(\text{La}_{0.8}\text{Sr}_{0.2})_{0.95}\text{CoO}_{3-\delta}$	Rh	5.437	90.29	160.7

4.2.2 Electrochemical behavior in the absence of metallic interconnect

Figure 4.3 shows the impedance and polarization curves of LSMC cathodes with $x=0.0, 0.4, 0.8$ and 1.0 under a cathodic current passage 200 mA cm^{-2} at 900°C in the absence of the Fe-Cr metallic interconnect. EIS was measured under open circuit. The LSMC with $x=0.0$, i.e., LSM cathode, showed significant activation effects under the current passage (Figure 4.3a&b), R_E and η decreased from $0.73 \Omega \text{ cm}^2$ and 144 mV to $0.39 \Omega \text{ cm}^2$ and 98 mV , respectively after polarized at 200 mA cm^{-2} for 240 min. The reduction in the electrode polarization resistance and overpotential is an indication of the activation effect of the cathodic polarization on the LSM cathodes, consistent with previous reports [Jiang and Wang 2005; Jiang 2006]. As the x value, i.e., the B-site Co content, increases, the activation effect

becomes much smaller. For the reaction at the LSMC ($x=0.4$) cathode, the decrease in R_E and η is relatively small, e.g., R_E decreased from $0.18 \Omega \text{ cm}^2$ to $0.10 \Omega \text{ cm}^2$, a reduction of $0.08 \Omega \text{ cm}^2$ after polarized for 240 min (Figure 4.3c). When the Co content increased to 0.8 and 1.0, the R_E , E_{Cathode} and η values remain more or less constant during the cathodic current passage treatment (Figure 4.3e-h), clearly showing the characteristics of MIEC cathode materials like LSCF and LSC [Jiang, Zhang *et al.* 2006; Jingbo Liu, Anne C. Co *et al.* 2006; Zhao, Peng *et al.* 2008]. The impedance and polarization behavior of the LSMC cathodes with the cathodic polarization treatment is consistent with the gradual change of the LSMC cathode materials from pure electronic conducting materials to MIEC materials as the Co content at the B-site of the LSMC perovskite increases.

Figure 4.4 summarizes the electrochemical behavior of the LSMC ($0.0 \leq x \leq 1.0$) cathodes under a current passage of 200 mA cm^{-2} at 900°C in the absence of the metallic interconnect. As the Co content increases in the B-site of the LSMC cathode, η decreases significantly (Figure 4.4a&b), indicating the enhanced electrochemical catalytic activity of the LSMC cathode towards the oxygen reduction reaction. The improved electrochemical performance of the LSMC cathodes can be attributed to the enhanced oxygen surface exchange and diffusion kinetics at the LSMC cathodes due to the substitution of the B-site Mn cations by Co cations [De Souza and Kilner 1998; 1999].

Figure 4.3 Impedance and polarization behaviors of the LSMC cathodes as a function of cathodic current passage time at 200 mAcm⁻² and 900°C in the absence of the Fe-Cr metallic interconnect: (a,b) $x=0.0$, (c,d) $x=0.4$, (e,f) $x=0.8$, and (g,h) $x=1.0$. Impedance curves were measured under the open circuit condition.

Figure 4.4 Plots of the overpotential, η , of LSMC ($0.0 \leq x \leq 1.0$) cathodes as a function of (a) current passage time at 200 mAcm^{-2} and (b) x value in LSMC composition measured at current passage time of 5 and 240 min at 900°C in the absence of the Fe-Cr metallic interconnect.

De Souza and Kilner [1998; 1999] and Cater [1992] et al. studied the change in oxygen tracer diffusion coefficient (D^*) and oxygen surface exchange coefficient (k^*) of the $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_{1-x}\text{Co}_x\text{O}_{3\pm\delta}$ and found that both parameters increase as Mn is substituted by Co. Substitution of 20 mol% Mn by Co will increase D^* by one order of magnitude. The k^* values for the cobaltites (10^{-5} - $10^{-7} \text{ cm s}^{-1}$) are much higher

than those of 10^{-8} - 10^{-7} cm s⁻¹ for manganites [Carter, Selcuk et al. 1992; Chater, Carter et al. 1992]. The B-site substitution of Mn by Co greatly facilitates the oxygen diffusion and exchange at the LSMC ($x=0.0$ - 1.0) cathode, which in turn increases the electrocatalytic activity of LSMC cathodes for the O₂ reduction reaction. The present results of the electrochemical behavior of the LSMC for the O₂ reduction reaction in the absence of the Fr-Cr metallic interconnect are consistent with the isotopic exchange/diffusion profile (IEDP) results on LSMC cathodes [De Souza and Kilner 1998; De Souza and Kilner 1999].

4.2.3 Electrochemical behavior in the presence of metallic interconnect

Figure 4.5 is the impedance curves of the LSMC ($0.0 \leq x \leq 1.0$) cathodes as a function of the cathodic polarization time at 200 mA cm⁻² and 900 °C in the presence of RA446 metallic interconnect. EIS was measured under the open circuit condition. Figure 4.6 gives the corresponding polarization curves of the LSMC cathodes. The size of the impedance arc (i.e., R_E) increases with the cathodic polarization time (Figure 4.5). In the present study, there was no interlayer or Pt mesh between the metallic interconnect and the LSMC electrode coating. The high frequency intercept (i.e., R_Ω) varied with the cathodic polarization time. Nevertheless, the R_Ω value generally increased after polarization treatment, indicating the increase of the electrode ohmic resistance most likely caused by the formation of the oxide scales on the surface of RA446 metallic interconnect [Jiang, Zhen et al. 2006]. Different to the decrease of R_E in the absence of the interconnect,

R_E measured in the presence of RA446 interconnect increased with the cathodic polarization time for the O_2 reduction reaction on the LSMC cathodes in the composition range studied, clearly indicating the chromium poisoning effects of the Fe-Cr metallic interconnect on the electrochemical activity of the LSMC cathodes.

Figure 4.5 Impedance curves of the LSMC ($0.0 \leq x \leq 1.0$) cathodes as a function of current passage time at 200 mAcm^{-2} and 900°C in the presence of a RA446 metallic interconnect: (a) $x=0.0$, (b) $x=0.2$, (c) $x=0.4$, (d) $x=0.6$, (e) $x=0.8$, and (f) $x=1.0$. Impedance curves were measured under the open circuit condition.

Figure 4.6 Polarization curves of the LSMC ($0.0 \leq x \leq 1.0$) cathodes as a function of current passage time at 200 mAcm^{-2} and 900°C in the presence of a RA446 metallic interconnect: (a) $x=0.0$, (b) $x=0.2$, (c) $x=0.4$, (d) $x=0.6$, (e) $x=0.8$, and (f) $x=1.0$. Electrode ohmic and polarization resistance, R_Ω and R_E , were taken from the impedance curves of Figure 4.5.

The polarization potential for the O_2 reduction at LSMC cathodes in the presence of RA446 metallic interconnect also behaves significantly different as compared to that in the absence of metallic interconnect (Figure 4.6). The electrode potential, polarization resistance and overpotential, E_{cathode} , R_E and η values increase significantly with the cathodic polarization time. E_{Cathode} increases rapidly

initially and reaches a plateau where the increase in E_{Cathode} is much slower, a characteristic phenomena of the Cr poisoning effect on the O_2 reduction reaction [Jiang and Love 2001; Jiang, Zhen et al. 2006]. However, the magnitude of increase in E_{Cathode} , R_E and η varies greatly with the LSMC composition. For example, for LSMC cathode with $x=0.0$ (i.e., LSM), the initial R_E and η at the end of the first 5 min polarization were $0.59 \Omega \text{ cm}^2$ and 260 mV, respectively and after cathodic polarization treatment for 1200 min, R_E and η increased to $0.79 \Omega \text{ cm}^2$ and 383 mV, respectively. The increase in R_E and η , i.e., ΔR_E and $\Delta \eta$, is $0.20 \Omega \text{ cm}^2$ and 123 mV, respectively. At the end of the test, the increase in the E_{Cathode} , i.e., $\Delta E_{\text{Cathode}}$, is 453 mV. In the case of the LSMC cathode with $x = 1.0$ (i.e., LSC), the corresponding ΔR_E , $\Delta \eta$, and $\Delta E_{\text{Cathode}}$ are $0.05 \Omega \text{ cm}^2$, 72 mV and 112 mV, respectively, considerably smaller than those observed on the LSMC cathode with $x=0.0$. This clearly indicates that the electrochemical activities of LSMC cathodes in the presence of Fe-Cr metallic interconnect also depend on the composition of the cathode.

The increase in the R_E and η , ΔR_E and $\Delta \eta$, can be taken as an indication for the chromium poisoning effect on the cathodes for the O_2 reduction reaction [Jiang and Love 2001]. Figure 4.7 shows the plots of ΔR_E and $\Delta \eta$ as a function of the Co content (i.e., x value) in the LSMC composition. It is interesting to note that both ΔR_E and $\Delta \eta$ increase initially with the increase in the Co content in the LSMC composition and decrease again when the Co content in LSMC is higher than $x = 0.4$. This indicates that the chromium poisoning effect on the electrochemical

activity of the LSMC cathode materials is most pronounced for the LSMC with $x = 0.4$.

Figure 4.7 Plots of the increase in the electrode polarization resistance and overpotential, $\Delta \eta$ and ΔR_E , as a function of x value in LSMC composition. $\Delta \eta$ and ΔR_E were obtained by the difference of η and R_E measured at current passage time of 5 and 1200 min at 900°C in the presence of RA446 metallic interconnect.

4.2.4 Chromium deposition on LSMC electrode surface

Figure 4.8 shows the SEM micrographs of the surface of the LSMC cathode ($0.0 \leq x \leq 1.0$) under the rib of RA446 interconnect (location ‘8’ in Figure 4.1) after polarized at 200 mAcm^{-2} and 900 °C for 1200 min, and Figure 4.9 is the corresponding EDS analysis taken on the surface of the LSMC cathodes.

The relative intensity ratio of the $\text{La}_{L\alpha}/\text{La}_{L\beta}$ can be taken as an effective criterion of the chromium depositions at the La-containing cathodes [Tucker, Kurokawa et al. 2006]. In the presence of chromium depositions, the K_α X-ray peak

of Cr overlaps with L_{β} peak for La, which leads to a decrease in the $La_{L\alpha}/La_{L\beta}$ ratio. Therefore, smaller $La_{L\alpha}/La_{L\beta}$ ratio indicates more serious chromium depositions at the cathode. In Figure 4.8a, the surface of the LSMC cathode with $x=0.0$, i.e., LSM, appears very clean with no visible chromium deposits. The corresponding EDS analysis also confirmed that no Cr deposits were detected (Figure 4.9a). The $La_{L\alpha}/La_{L\beta}$ ratio is 5.02, close to ~ 5.10 of the pure LSM. However, chromium deposition on the LSMC cathode surface increases as the x value in LSMC composition increases. For the LSMC cathode with $x=0.2$, i.e., $(La_{0.8}Sr_{0.2})_{0.95}(Mn_{0.8}Co_{0.2})O_3$, some crystalline particles can be observed on the electrode surface (Figure 4.8b), and the corresponding $La_{L\alpha}/La_{L\beta}$ ratio is 4.76 (Figure 4.9b), lower than ~ 5.10 of the pure LSM. The reduction in the $La_{L\alpha}/La_{L\beta}$ ratio is due to the overlapping of the K_{α} X-ray peak of Cr, $Cr_{K\alpha}$, with the L_{β} peak for La, $La_{L\beta}$. The amount and size of the chromium deposits on the electrode surface increase with the increase in the Co doping at the B-site of LSMC, and the pores on the electrode surface are increasingly filled by the chromium deposits. For the LSMC cathodes with $x = 0.4, 0.6, 0.8$, and 1.0 , the corresponding $La_{L\alpha}/La_{L\beta}$ ratio measured on the electrode surface is 1.28, 0.83, 0.45, and 0.44, respectively (Figure 4.9c-f). The significant reduction in the $La_{L\alpha}/La_{L\beta}$ ratio corresponds to the significant coverage of the LSMC electrode surface by chromium deposits (Figure 4.8). In the case of the LSMC with $x=1.0$ (i.e., LSC) cathode, the surface is almost completely covered by large crystals and the original LSMC particles can be hardly seen (Figure 4.8f), very similar to that observed for the Cr deposition on the LSCF

cathode [Jiang, Zhang *et al.* 2006].

Figure 4.8 SEM micrographs of the LSMC ($0.0 \leq x \leq 1.0$) cathode surface under the rib of RA446 interconnect after polarized at 200 mAcm^{-2} and 900°C for 1200 min: (a) $x=0.0$, (b) $x=0.2$, (c) $x=0.4$, (d) $x=0.6$, (e) $x=0.8$, and (f) $x=1.0$.

Figure 4.9 EDS analysis on the surface of the LSMC ($0.0 \leq x \leq 1.0$) cathodes under the rib of RA446 interconnect after polarized at 200 mA cm^{-2} and 900°C for 1200 min: (a) $x=0.0$, (b) $x=0.2$, (c) $x=0.4$, (d) $x=0.6$, (e) $x=0.8$, and (f) $x=1.0$.

To determine the phase composition of the Cr depositions on the surface of LSMC ($0.0 \leq x \leq 1.0$) cathode, XRD analysis was conducted on the surface of the LSMC ($x=0.0, 0.4, 0.6$ & 1.0) cathode after 1200 min cathodic polarization at 200

mA cm^{-2} and $900\text{ }^{\circ}\text{C}$ in the presence of RA446 metallic interconnect. The result is shown in Figure 4.10 below.

Figure 4.10 XRD pattern measured on the LSMC with $x=0.0, 0.4, 0.6$ and 1.0 cathode surface after current passage at 200 mA cm^{-2} and $900\text{ }^{\circ}\text{C}$ for 1200 min.

In the XRD patterns, peaks belonging to GDC electrolyte and LSMC perovskite can be observed. On the surface of LSMC ($x=0.0$) cathode, no Cr depositions can be detected, which is consistent with the EDS analysis (Figure 4.9a). As the x value in LSMC composition increased to 1.0 (i.e., LSC), XRD peaks belonging to the SrCrO_4 phase were detected, indicating the formation of SrCrO_4 on the LSMC electrode surface. The formation of SrCrO_4 phase is in agreement with the phase composition of Cr depositions reported on the LSCF cathode surface [Jiang, Zhang *et al.* 2006; Konyshova, Penkalla *et al.* 2006]. For the LSMC cathode with $x < 1.0$, no Cr deposit peaks were shown by XRD. However, both SEM and EDS analysis

clearly indicate that Cr deposition on the surface of LSMC cathode increases as the x value in the LSMC composition increased from 0.0 to 1.0. The reason why no peaks corresponding to the SrCrO_4 phase were observed at the LSMC ($x=0.4$ & 0.6) may be explained in terms of the detecting limit of the XRD analysis. That is, the amount of the scattered chromium depositions on the electrode surface may be too small for the detection of the XRD analysis.

Figure 4.11 is the SEM micrographs of the surface of the LSMC cathodes under the channel of RA446 interconnect (location '9' in Figure 4.1) after a current passage of 200 mA cm^{-2} at 900°C for 1200 min. The magnitude of the chromium deposition on the LSMC electrode surface under channel of the interconnect is significantly smaller than that under rib of the interconnect. Nevertheless, chromium deposits on the LSMC electrode surface increased with the increase in the Co doping at the B-site of the LSMC cathode, similar to those on the electrode surface under the rib of the interconnect. The lower Cr deposition under the channel of the interconnect is most likely due to that fact that for the LSMC electrode surface under the channel, chromium species can only diffuse to the electrode surface via gaseous diffusion, while for the surface under the rib of the interconnect, both solid and gaseous diffusion and migration of Cr species can occur.

Figure 4.11 SEM micrographs of the LSMC ($0.0 \leq x \leq 1.0$) cathode surface under the channel of RA446 interconnect after polarized at 200 mA cm^{-2} and 900°C for 1200 min: (a) $x=0.0$, (b) $x=0.2$, (c) $x=0.4$, (d) $x=0.6$, (e) $x=0.8$, and (f) $x=1.0$.

4.2.5 Chromium deposition on the GDC electrolyte surface

The characteristics of the chromium deposition on the GDC electrolyte surface in contact with the LSMC electrode coatings were also examined. The LSMC cathodes were removed by a hydrochloric acid treatment. Figure 4.12 shows the SEM micrographs of the GDC electrolyte surface in contact with LSMC electrode

under the rib of RA446 interconnect (location '6' in Figure 4.1) after a current passage of 200 mA cm^{-2} at 900°C for 1200 min. Figure 4.13 is the corresponding EDS analysis of the GDC electrolyte surface in contact with LSMC cathodes with $x=0.0$ and $x=1.0$.

Figure 4.12 SEM micrographs of the GDC electrolyte surface in contact with LSMC ($0.0 \leq x \leq 1.0$) cathodes under the rib of RA446 interconnect after polarized at 200 mA cm^{-2} and 900°C for 1200 min: (a) $x=0.0$, (b) $x=0.2$, (c) $x=0.4$, (d) $x=0.6$, (e) $x=0.8$, and (f) $x=1.0$. LSMC coatings were removed by acid etching.

Figure 4.13 EDS analysis on the GDC electrolyte surface in contact with LSMC ($0.0 \leq x \leq 1.0$) cathodes under the rib of RA446 interconnect after polarized at 200 mA cm^{-2} and 900°C for 1200 min: (a) $x=0.0$, and (b) $x=1.0$.

In the case of the LSMC with $x=0$, i.e., LSM cathode, the GDC electrolyte surface under the rib of RA446 interconnect was totally covered by a layer of chromium crystals (Figure 4.12a). The corresponding EDS patterns show the strong peaks of Cr and Mn in addition of Gd and Ce of the GDC electrolyte substrate (Figure 4.13a). The grain boundary of the GDC electrolyte surface is no longer visible due to the thick Cr deposits. As the Co content at the B-site increases, the amount of chromium deposits decreases gradually. In the case of LSMC cathode with $x=0.4$ and 0.6 , the grains and grain boundaries of the GDC electrolyte surface can be clearly observed (Figure 4.12c&d), indicating the reduced chromium deposition. As the x increases to 1.0 , i.e., the LSC cathode, the GDC electrolyte surface in contact with the LSC electrode appears very clean and no chromium deposits can be seen on the GDC electrolyte (Figure 4.12f). Some convexes on the GDC electrolyte surface are due to the contacts between LSM particles and the GDC electrolyte. The corresponding EDS analysis also shows no signals from Cr deposits (Figure 4.13b). The results indicate that the chromium

deposition on the GDC electrolyte surface are also closely related to the Mn and Co ratios at the B-site of the LSMC cathodes, and it decreases significantly with the increase of the Co content at the B-site of LSMC.

Figure 4.14 is the XRD patterns of the GDC electrolyte surface after a current passage of 200 mA cm^{-2} at 900°C for 1200 min. LSMC cathodes were removed by a HCl treatment. On the electrolyte surface in contact with LSMC ($x=0.0, 0.4$ & 0.6) electrodes, XRD peaks belonging to $(\text{MnCr}_2)\text{O}_4$ spinel were detected, consistent with previous reports.[*S. P. Jiang, J. P. Zhang et al. 2001; Jiang, Zhang et al. 2005*]. On the electrolyte surface in contact with LSMC ($x=1.0$) electrode, only peaks corresponding to GDC electrolyte were detected, indicating the absence of MnCr_2O_4 depositions. Also, intensities of the XRD peaks decreased with the increase of x value of the LSMC composition, confirming the decreased chromium deposition on the electrolyte surface with the increase of the Co content in the LSMC composition.

Figure 4.14 XRD pattern on the GDC electrolyte surface in contact with LSMC with $x=0.0, 0.4, 0.6$ and 1.0 cathodes after removal of the LSMC coating.

Figure 4.15 shows the SEM micrographs of the GDC electrolyte surface in contact with LSMC electrode under the channel of RA446 interconnect (location ‘7’ in Figure 4.1) after a current passage of 200 mA cm^{-2} at 900°C for 1200 min.

Figure 4.15 SEM micrographs of the GDC electrolyte surface in contact with LSMC ($0.0 \leq x \leq 1.0$) cathodes under the channel of RA446 interconnect after polarized at 200 mA cm^{-2} and 900°C for 1200 min: (a) $x=0.0$, (b) $x=0.2$, (c) $x=0.4$, (d) $x=0.6$, (e) $x=0.8$, and (f) $x=1.0$.

Similar to that observed for the Cr deposition under the rib of the interconnect, the chromium depositions decrease with the increase in the Co content at the B-site of the cathodes, though the magnitude or the amount of the Cr deposits are smaller as compared to that under the rib of the interconnect. This again confirms the close relationship between the chromium depositions on electrolyte surface and the Mn and Co content ratios in the LSMC composition.

The results of the present study of the Cr deposition and poisoning at the LSMC cathodes clearly demonstrate a systematic change in the chromium deposition behavior as a function of the Mn and Co ratios at the LSMC composition ($0.0 \leq x \leq 1.0$). Chromium deposition increases on LSMC electrode surface and decreases on the GDC electrolyte surface, while at the same time the electrochemical activity of the LSMC cathodes increases as the B-site Co content in the LSMC composition increases. The observations can be summarized as follows:

- (1) In the absence of interconnect, the electrochemical activity and performance of the LSMC cathodes improves monotonically as the Co content, i.e., x value, increases (Figure 4.4). This can be attributed to the increase of the oxygen surface exchange coefficient and oxygen diffusion coefficient due to the substitution of B-site Mn by Co. The increase in the Co content at the B-site leads to the change from the pure electronic conductor of LSMC with $x = 0.0$ to the mixed electronic and oxygen ionic conductor of LSMC with $x = 1.0$.

- (2) In the presence of interconnect, electrochemical activity and performance of the LSMC cathodes showed different trend from that in the absence of the interconnect. Chromium poisoning effects, as measured by the increase in R_E and η , ΔR_E and $\Delta \eta$, first increased with x and reached a maximum for the LSMC composition with $x = 0.4$ (Figure 4.7). This indicates that chromium poisoning on the LSMC cathodes is most pronounced for the LSMC composition with $x = 0.4$.
- (3) Chromium deposition on the LSMC electrode surface increases significantly as B-site Mn is substituted by Co and at the same time, it decreases significantly on the GDC electrolyte surface. The significant change in the electrochemical activity of the LSMC cathodes as the results of the substitution of B-site Mn by Co affects primarily the distribution of the chromium deposition on the electrode and electrolyte surface under the conditions studied.

Figure 4.16 summarizes the chromium deposition on the LSMC electrode surface and GDC electrolyte surface and chromium poisoning on the electrochemical activity of the LSMC cathodes as a function of the B-site Co content.

Figure 4.16 Summary of the chromium poisoning effect and chromium deposition behavior on the LSMC electrode surface and GDC electrolyte surface as a function of the Co content at the B-site of the LSMC cathodes after current passage at 200 mA cm^{-2} and 900°C for 1200 min.

In the case of LSMC with $x = 0.0$ (i.e., LSM), sufficient evidences have shown that the O_2 reduction reaction could proceed via both surface and bulk path mechanism [Adler 2004]. Under low overpotential, LSM operates primarily via a

surface-mediated mechanism, while at moderate to high overpotential, LSM becomes sufficient reduced to open up a parallel bulk transport path near the three phase boundary (TPB). Lee [1995] *et al.* investigated active sites for O_2 reduction in the LSM electrode under various cathodic polarization potentials using in situ X-ray photoelectron spectroscopy (XPS). They observed a shifting of the Mn 2p peaks to the lower binding energy side as the applied potential became more cathodic. This suggests that the Mn ions in LSM are electrochemically reduced to Mn^{2+} ions under cathodic polarization, forming concomitantly oxygen vacancies. Bachhaus-Ricoult [2008] *et al.* studied the surface chemistry of the LSM cathode on the YSZ electrolyte under cathodic polarization by XPS. The results revealed the reduction in the oxidation state of manganese ions on the LSM surface from 4^+ to $3^+ - 4^+$ at low cathodic polarization and 2^+ under strong cathodic polarization. In the study, manganese was reduced to an oxidation state of +2 and enriched at the electrolyte surface. A diffusion process of manganese from the three phase boundary (TPB) to the entire electrolyte surface, closely related to the cathodic bias applied, was also observed. Similar results were also reported on the LSM cathode by Wu [2005] *et al.* The oxygen vacancies generated due to the reduction of manganese ions under cathodic polarization are considered to be responsible for the observed electrocatalytic effect on the electrode performance of LSM cathodes under cathodic polarization. As the Mn^{2+} ions due to the reduction of LSM are generally associated with TPB region, the interaction between the Mn ions and gaseous chromium species would lead to the deposition of chromium at the

electrode/electrolyte interface. On the other hand, under the cathodic electric field, Mn^{2+} ions could migrate from the LSM electrode surface to the GDC electrolyte surface and react with gaseous chromium species, forming chromium deposits and $(\text{Mn,Cr})_3\text{O}_4$. This is supported by the observations of the chromium deposits on the YSZ electrolyte surface as far as 100-200 μm from the TPB [Jiang, Zhang *et al.* 2005].

Vovk [2005] *et al.* studied the $\text{La}_{0.5}\text{Sr}_{0.5}\text{Co}_3$ perovskite oxide surfaces under electrochemical polarization using *in situ* XPS technique. Under cathodic polarization, the $\text{Sr}/(\text{La}+\text{Co})$ ratio at the oxide surface increased irreversibly by 5% while the La/Co ratio remained constant, indicating the surface enrichment of strontium. Tabata [1987] *et al.* also studied the surface chemistry of $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ and observed a considerably higher Sr/Co ratio on the surface than in the bulk, while there was no difference for the La/Co ratio on the surface and in the bulk. Thus, in the case of the Sr-containing cobaltite electrodes, gaseous chromium species would react with SrO segregated on the electrode surface, forming SrCrO_4 [Jiang, Zhang *et al.* 2006; Konysheva, Penkalla *et al.* 2006; Zhen and Jiang 2008]. Figure 4.17 shows schematically the chromium deposition process on the LSMC with $x = 0.0$ (Figure 4.17a) and $x = 1.0$ (Figure 4.17b) under SOFC operation conditions.

Figure 4.17 Schematic diagram of chromium deposition process at LSMC electrode with (a) $x = 0.0$ and (b) $x = 1.0$. The steps shown in the figure are: (1) vaporization of gaseous chromium species, (2) transportation of gaseous chromium species in the cathode, (3) transfer of Mn^{2+} ions in the cathode, (4) segregation of MnO at the electrode/electrolyte interface, (5) diffusion of MnO on the electrolyte surface, (6) formation of $(\text{Mn-Cr-O})_{\text{nuclei}}$, (7) formation of solid Cr depositions, (8) transfer of oxygen ions through Cr depositions, (9) oxygen surface diffusion process, (10) normal transfer of oxygen ion through the three phase boundary (TPB), (11) segregation of SrO on the electrode surface, (12) formation of $(\text{Sr-Cr-O})_{\text{nuclei}}$, (13) formation of SrCrO_4 depositions, (14) bulk diffusion of oxygen ions, and (15) transfer of oxygen ion across electrode/electrolyte interface.

In the $\text{La}_{1-x}\text{Sr}_x\text{Mn}_{1-y}\text{Co}_y\text{O}_{3\pm\delta}$ system oxygen surface exchange and diffusion coefficients increase with the increase of the Co substitution at the B-site of LSMC composition [De Souza and Kilner 1998; 1999]. The significant change in the oxygen exchange and trace diffusion coefficients of the LSMC series with the Co substitution can be ascribed to oxygen vacancies generated. Thus, the oxygen vacancies generated due to the Co substitution at the B-site of the LSMC composition would play an increasing role in the process of surface exchange for the O_2 reduction reaction, while at the same time, the oxygen vacancies generated due to the reduction of manganese ions in the LSMC would become less important

for the reaction. In another word, the amount of Mn^{2+} ions due to the reduction of LSM under cathodic polarization would be reduced significantly with the Co substitution. In turn, the chromium deposition due to the interaction between the Mn ions and gaseous chromium species would decrease with the increase in the Co substitution at the B-site of the LSMC composition. This explains the significant decrease in the chromium deposition at the electrode/electrolyte interface and the GDC electrolyte surface with the increase of Co content of the LSMC composition (Figure 4.12).

Thermodynamic calculations show that lanthanum strontium manganite is chemically and structurally more stable than lanthanum strontium cobaltite under SOFC operation conditions [Kawada and Yokokawa 1997; Yokokawa 2003]. As the Co ions have lower valence stability as compared to Mn ions [Yokokawa 2003], the substitution of B-site Mn ions by Co ions would increase the oxygen vacancy due to the valence change of Co cations at the B-site, and at the same time, the LSMC perovskite becomes less structurally and chemically stable. This in turn would lead to the precipitation and migration of Sr species at the A-site. Consequently, SrO segregated and migrated on the LSMC electrode surface would react with gaseous chromium species to form SrCrO_4 deposits on the electrode surface. This explains why the SrCrO_4 crystals formed on the LSMC cathode surface increases as the B-site Mn in the LSMC composition is substituted by Co (Figure 4.8). Thus, in the case of LSMC with $0.0 < x < 1.0$ chromium deposition would be the combination of the deposition processes depicted in Figure 4.17a and Figure 4.17b, respectively.

As shown in previous studies, the poisoning effect of chromium deposition can be assessed by the increase of η , $\Delta\eta$ [Matsuzaki and Yasuda 2000; S. P. Jiang, Sam Zhang *et al.* 2005; Zhen, Li *et al.* 2006]. $\Delta\eta$ for the O_2 reduction reaction on LSMC cathodes first increased from 124 mV for the LSMC with $x=0.0$ to 236 mV for the LSMC with $x=0.4$, and then continuously decreased to 73 mV for the LSMC with $x=1.0$. The chromium poisoning effects at the LSMC cathodes are most pronounced on the LSMC cathodes with $x = 0.4$. Chromium deposits at the electrode/electrolyte interface would significantly affect the charge transfer process and increase the barrier of oxygen ion transfer from the electrode to the electrolyte of the O_2 reduction reaction, while the chromium deposits on the electrode surface would be detrimental to the diffusion and transportation process of oxygen. Thus, both the chromium depositions at the interface and on the electrode surface have significant poisoning effect on the O_2 reduction reaction on the LSMC cathodes. As shown in Figure 4.16, for the LSMC with $x = 0.4$, chromium deposits on the GDC electrolyte are still significant, covering the whole electrolyte surface, and on LSMC electrode surface, the porosity appears to be very small, indicating the significant deposition of chromium on the surface. This indicates that the combined poisoning effect of chromium deposits at the interface and on the electrode surface could be the highest on the LSMC with $x=0.4$.

4.3 Summary

Chromium deposition and poisoning at the LSMC ($0.0 \leq x \leq 1.0$) cathodes were studied at 900 °C under a current passage of 200 mA cm⁻² in the presence of Fe-Cr

metallic interconnect. In the absence of metallic interconnect, the electrochemical activity and performance of the LSMC cathodes improves as the x increases, which can be attributed to the increase of the oxygen exchange coefficient and oxygen ionic conductivity due to the substitution of the B-site Mn cations by Co cations.

In the presence of interconnect, electrochemical performance of the cathodes showed a different trend from that in the absence of the interconnect. Chromium poisoning effects first increased as x increased from 0.0 to 0.4, and then decreased gradually as x increased to 1.0. The pronounced chromium poisoning effects at the LSMC ($x=0.4$) cathode is attributed to the combined poisoning effects of the chromium deposits formed both on the electrode/electrolyte interface and the electrode surface on the oxygen reduction reaction kinetics.

The results from the present study demonstrated that the enhanced electrocatalytic activity of the LSMC cathodes due to the substitution of B-site Mn by Co does not necessarily reduce the chromium deposition. Rather, the change in the LSMC composition simply changes the distribution of chromium deposition. Chromium deposition on the electrode surface increased significantly as the B-site Mn was substituted by Co and at the same time, chromium deposition on the electrolyte surface decreased considerably. The chromium deposition at the electrode/electrolyte interface and on the electrode surface is closely related to the structural and valence stability of the LSMC perovskites.

CHAPTER 5 CHROMIUM DEPOSITION AND POISONING AT LSBCF ($x=0.0-0.4$) CATHODES

Jiang [2000; 2001; 2002; 2006; 2006; 2007] et al. systematically investigated the Cr deposition process at different SOFC cathodes such as LSM, (La,Sr)(Co,Fe)O_{3-δ} (LSCF), Pt and LSM/YSZ composite and the results showed that deposition process of Cr species depends strongly on the nature of the cathode materials. Based on the observations, an alternate deposition mechanism, in which a nucleation agent (e.g, Mn²⁺ formed under electrode polarization in the case of LSM or SrO segregated on the electrode surface in the case of LSCF) interacts with gaseous Cr species, was proposed. The Cr deposition process is limited by the kinetics of the nucleation reaction and the further interaction between the nuclei and the volatile Cr species. Previous results showed that chromium depositions at the (La,Ba)(Co,Fe)O_{3-δ} (LBCF) occurred on the electrode surface, closely related to the segregated BaO on the electrode surface. The Cr deposits at the cathode appeared much less than those at the LSCF cathode, confirming that the chromium-tolerance of the cathode materials is closely related to the chemical composition of the cathode materials [Zhen and Jiang 2008]. However, the reason for the better chromium tolerance of LBCF cathode over LSCF cathode is still not very clear. In this chapter, the (La_{0.6}Sr_{0.4-x}Ba_x)(Co_{0.2}Fe_{0.8})O_{3-δ} (LSBCF, 0.0≤ x ≤0.4) cathodes are taken as a system for a systematic study on the effect of electrode

composition on the chromium deposition and poisoning effects.

5.1 Experimental

The chromia-forming alloy interconnect used in this study was the commercially available RA446 interconnect and GDC was used as the electrolyte. The details in the fabrication of the testing cell can be found in Chapter 3. The polarization behaviors of the LSBCF ($x=0.0-0.4$) were carried out under a constant current passage of 200 mA cm^{-2} at 900°C . The electrode potential (E_{cathode}) was measured against the Pt air reference electrode. Current passage was interrupted from time to time for the EIS measurements at the open circuit condition. The EIS test was investigated in the frequency range of 0.1 Hz to 100 kHz with a signal amplitude of 10 mV. SEM and EDS were used to examine the chromium deposition at the LSBCF ($x=0.0-0.4$) cathodes.

5.2 Results and discussion

5.2.1 XRD pattern and chemical stability of LBSCF materials

Figure 5.1 gives the XRD pattern of the LSBCF ($0.0 \leq x \leq 0.4$) powders prepared by GNP method after heated at 1100°C for 6 h. All the major peaks in the XRD pattern belong to the perovskite structure, indicating that the perovskite phase has been formed as the primary phase in the LSBCF powders within the composition range studied. However, the peaks have a tendency to broaden and split with the increase in Sr content. Therefore, the prepared LSBCF ($0.0 \leq x \leq 0.4$) powders were used as the cathode materials in this study.

To avoid the influence of reactions between cathode and electrolyte materials on the electrochemical characterizations, chemical compatibility between the LSBCF and GDC electrolyte was studied. The LSBCF ($x=0.0, 0.2, 0.4$) and GDC powders with a weight ratio of 1:1 were mechanically mixed and calcined at 1100 °C for 6 h before XRD characterization. Figure 5.2 shows the XRD patterns of the mixed powders. The XRD patterns show that peaks of the mixture are just a combination of peaks belonging to the LSBCF and GDC materials, indicating good chemical compatibility between GDC and LSBCF materials at 1100 °C. Therefore, GDC was adopted as the electrolyte materials in this study.

Figure 5.1 XRD patterns of LSBCF ($0.0 \leq x \leq 0.4$) powders after calcined at 1100 °C for 6 h.

Figure 5.2 XRD patterns of powder mixtures (a) GDC + LSCF, (b) GDC+LSBCF($x=0.2$) and (c) GDC+LBCF after calcined at 1100 °C for 6h.

5.2.2 Electrochemical behavior of LSBCF cathodes in the absence of the interconnect

Figure 5.3 shows the electrochemical behavior of the LSBCF ($x = 0.0, 0.2, 0.4$) cathodes as a function of cathodic current passage at 200 mA cm^{-2} , 900°C in the absence of Fe-Cr metallic interconnect. As shown in the figure, R_Ω of the LSBCF cathodes decreased during the cathodic current passage, which could be attributed to the improved contact between the cathode and the electrolyte. R_E for the LSBCF with $x = 0.0$ (i.e., LSCF) cathode is $\sim 0.05 \text{ } \Omega \text{ cm}^2$ and remains almost unchanged with the cathodic polarization. Similar electrochemical behavior for the O_2 reduction reaction was also observed on LSBCF with $x = 0.2$ and LSBCF with $x = 0.4$ (i.e., LBCF). R_E is $\sim 0.02-0.03 \text{ } \Omega \text{ cm}^2$ for the reaction on the LBCF cathode and the change in R_E is negligible with the cathodic current passage (Figure 5.3e). Also, the overpotential (η) of the LSBCF cathodes for the O_2 reduction reaction is very low ($< 10 \text{ mV}$) and there is essentially no increase in η during the cathodic polarization. The stable R_E and η values show the typical characteristics of a mixed ionic and electronic conducting perovskite cathode such as the LSCF electrode [Zhen, Li et al. 2006]. This indicates that the cathodic current passage has little effect on the electrocatalytic activities of LSBCF electrodes for the O_2 reduction reaction. The similarity in the electrochemical behavior indicates that LSBCF in the present study is also a mixed ionic and electronic conducting oxide and has similar electrochemical activities for the O_2 reduction reaction at the electrode and electrolyte interface in the absence of Fe-Cr interconnect.

Figure 5.3 Initial impedance and polarization curves of (a,b) LSCF, (c,d) LSBCF ($x=0.2$) and (e,f) LBCF cathodes as a function of cathodic current passage time at 200 mA cm^{-2} and 900°C in the absence and of Fe-Cr alloy interconnect.

5.2.3 Electrochemical behavior of LSBCF cathodes in the presence of interconnect

Figure 5.4 shows the impedance curves of the LSBCF ($0.0 \leq x \leq 0.4$) cathodes measured under the open circuit condition at 900°C in the presence of Fe-Cr metallic interconnect as a function of cathodic polarization time. Different from

those in the absence of Fe-Cr alloy interconnect, R_{Ω} of the cathodes generally increased with the current passage time. R_{Ω} is also higher than that in the absence of Fe-Cr interconnect, indicating the additional contact resistance of the metallic interconnect. The corresponding polarization curves of the LSBCF cathodes in the presence of the Fe-Cr metallic interconnect are shown in Figure 5.5. In contrast to those in the absence of Fe-Cr alloy interconnect, R_E and η of the LSBCF cathodes in the presence of Fe-Cr metallic interconnect increased significantly with the current passage time, indicating the chromium poisoning on the O_2 reduction reaction. The polarization potential, E_{Cathode} , increases with the cathodic polarization time, showing the typical characteristics of the polarization behavior for the reaction in the presence of Fe-Cr alloy [Jiang 2002; Zhen, Li et al. 2006].

However, the magnitude in the increase of R_E , E_{Cathode} and η for the reaction in the presence of the Fe-Cr metallic interconnect is related to the cathodic polarization time and to the composition of LSBCF materials. In the initial stages of the polarization, the change in R_E and η is more or less the same for the reaction at the LSBCF cathodes. For example, after polarized for 15 min, R_E and η increased from $0.11 \Omega \text{ cm}^2$ and 22.6 mV to $0.113 \Omega \text{ cm}^2$ and 23.0 mV for the O_2 reduction reaction on the LSBCF cathode with $x = 0.0$ (i.e., $\Delta R_E = 0.003 \Omega \text{ cm}^2$ and $\Delta \eta = 0.4$ mV). For the reaction on LSBCF with $x = 0.2$, the corresponding ΔR_E and $\Delta \eta$ are $0.0004 \Omega \text{ cm}^2$ and 2.8 mV, respectively. Such negligible ΔR_E and $\Delta \eta$ values were also found for the reaction on LSBCF with $x = 0.4$. The significant changes in R_E and η , i.e., the ΔR_E and $\Delta \eta$ for the O_2 reduction on the LSBCF cathodes only start to

increase after the extended cathodic current passage. For the reaction on LSBCF with $x = 0.0$, η was increased by nearly 100 mV ($\Delta\eta = 100$ mV) while in the case of LSBCF with $x = 0.4$ it increased by 45 mV ($\Delta\eta = 45$ mV) at the end of the polarization test, as compared to the initial η values. The lower $\Delta\eta$ indicates better chromium tolerance of the LSBCF cathode with $x = 0.4$ in comparison to the LSBCF cathode with $x = 0.0$, consistent with the previous report [Yongda Zhen, A. I. Y. Tok et al. 2008].

Figure 5.4 Impedance curves of LSBCF cathodes (a) $x=0$, (b) $x=0.1$, (c) $x=0.2$, (d) $x=0.3$ and (e) $x=0.4$ measured as a function of cathodic current passage time at 200 mA cm^{-2} and 900°C in the presence of Fe-Cr metallic interconnect.

Figure 5.5 Electrochemical behaviors of LSBCF cathodes (a) $x=0.0$, (b) $x=0.1$, (c) $x=0.2$, (d) $x=0.3$ and (e) $x=0.4$ at 900 °C for 1200 min in the presence of the Fe-Cr metallic interconnect.

5.2.4 Cr deposition at LSBCF cathodes

Figure 5.6 shows the SEM micrographs of the surface of the LSBCF ($0.0 \leq x \leq 0.4$) cathodes after the cathodic polarization at 200 mA cm^{-2} and 900 °C for 1200 min in the presence of a Fe-Cr metallic interconnect. For the purpose of comparison, a SEM micrograph of a LBCF cathode before the test is shown in Figure 5.6f.

Figure 5.6 SEM micrographs of LSBCF cathode surface with (a) $x = 0.0$, (b) $x = 0.1$, (c) $x = 0.2$, (d) $x = 0.3$ and (e) $x = 0.4$ under the rib of the Fe-Cr metallic interconnect after the polarization test at 200 mA cm^{-2} and 900°C for 1200 min. SEM micrograph of a LSBCF cathode with $x = 0.4$ before the test is shown in (f).

The SEM micrographs were taken under the rib of the interconnect. Similar deposition morphology was also observed on the electrode surface under the channel of the interconnect. The corresponding EDS analysis of the LSBCF electrode surface is given in Figure 5.7. The surface of the LSBCF cathode with $x =$

0.0 (i.e., LSCF) was almost completely covered by a layer of Cr deposits (Figure 5.6a) and the deposition of Cr on the LSBCF electrode surface decreased with the increase of Ba content. As x increased to 0.4 (LBCF), Cr deposits were not observed and the surface morphology of the LBCF is very similar to that of the original LBCF in the absence of the Fe-Cr alloy (Figure 5.6e&f).

Figure 5.7 EDS patterns of LSBCF cathode surface with (a) $x = 0.0$, (b) $x = 0.1$, (c) $x = 0.2$, (d) $x = 0.3$ and (e) $x = 0.4$ after the polarization test as shown in Figure 5.6.

The EDS analysis indicates the presence of Cr on the surface of LSBCF cathodes after the cathodic polarization test under 200 mA cm^{-2} at 900°C for 1200 min (Figure 5.7). However, the intensity of Cr decreased significantly with the increase of Ba content in the LSBCF cathode. As the K_α X-ray peak of Cr overlaps with L_β peak for La, the decrease in the $\text{La}_{L\alpha}/\text{La}_{L\beta}$ atomic ratio as compared to that for pure LSCF and LBCF is an indication of chromium deposition. For pure LBCF without Cr contamination, the $\text{La}_{L\alpha}/\text{La}_{L\beta}$ atomic ratio is 5.21, close to 5.29 for LSCF. For the purpose of comparison an average value of 5.25 is taken as the $\text{La}_{L\alpha}/\text{La}_{L\beta}$ atomic ratio for the LSBCF cathodes without Cr deposition. Thus, the intensity of Cr on the surface of LSBCF cathode can be semi-quantitatively represented by the $\text{La}_{L\alpha}/\text{La}_{L\beta}$ atomic ratio. In the case of LSBCF cathodes with $x = 0.0$ (i.e., LSCF) the $\text{La}_{L\alpha}/\text{La}_{L\beta}$ atomic ratio is 0.07 (Figure 5.7a), substantially lower than 5.29 for pure LSCF without Cr deposition. This indicates very high Cr deposits on the electrode surface, consistent with the observed complete coverage of the Cr deposits on the LSCF electrode surface (Figure 5.6a). The $\text{La}_{L\alpha}/\text{La}_{L\beta}$ atomic ratio started to increase with the Ba content in LSBCF. With $x = 0.1$, the $\text{La}_{L\alpha}/\text{La}_{L\beta}$ atomic ratio is 0.53 (Figure 5.7b), significantly higher than 0.07 for LSBCF with $x = 0.0$. When x increased to 0.4 (i.e., LBCF), the $\text{La}_{L\alpha}/\text{La}_{L\beta}$ atomic ratio increased to 2.83 (Figure 5.7e), much higher than that for the LSBCF with $x=0.0$ in the presence of the interconnect. The results indicate that Cr deposition on the surface of LSBCF cathode depends strongly on the Ba content in the cathode.

To determine the phase composition of the chromium deposits, XRD was

performed on the surface of LSBCF with $x=0.0$ (i.e., LSCF) and LSBCF with $x=0.4$ (i.e., LBCF) after a cathodic current passage of 200 mA cm^{-2} for 2400 min in the presence of the Fe-Cr alloy interconnect at 900°C . The XRD patterns are given in Figure 5.8. The peaks corresponding to LSCF, LBCF and GDC were generated by the cathode and electrolyte of the samples. As shown in Figure 5.8a, XRD peaks belonging to SrCrO_4 were detected, indicating that SrCrO_4 is the primary phase of the chromium deposits formed during the cathodic current passage at 900°C in the presence of the Fe-Cr alloy on the surface of LSCF cathode. Similarly, BaCrO_4 is the main phase of the Cr deposits on the surface of the LBCF cathode (Figure 5.8b). Some of the unidentified peaks may belong to the Cr_2O_3 phase. The XRD together with the EDS results indicate that the chromium deposits formed at the LSBCF ($0.0 \leq x \leq 0.4$) cathodes would mainly consist of $(\text{Sr}, \text{Ba})\text{CrO}_4$ phase and the Sr and Ba ratio in the Cr deposits may be related to the composition of LSBCF electrodes.

Figure 5.8 XRD patterns of the surface of (a) LSBCF with $x=0.0$ and (b) LSBCF with $x=0.4$ cathodes after a cathodic current passage of 200 mA cm^{-2} for 2400 min in the presence of the Fe-Cr alloy interconnect at 900°C .

Figure 5.9 shows the SEM micrographs of the cross-section of the *LSBCF* cathodes ($0.0 \leq x \leq 0.4$) after the cathodic polarization test at 200 mA cm^{-2} and 900°C for 1200 min. The corresponding EDS analysis of the cross-section areas of the cathodes is given in Figure 5.10.

Figure 5.9 SEM micrographs of the cross sections of *LSBCF* cathodes with (a) $x = 0.0$, (b) $x = 0.1$, (c) $x = 0.2$, (d) $x = 0.3$ and (e) $x = 0.4$ after the polarization test at 200 mA cm^{-2} and 900°C for 1200 min in the presence of a Fe-Cr alloy interconnect.

In contrast to the Cr deposition observed on the electrode surface (Figure 5.6), the differences in the microstructure of the cross-section (i.e., inside the bulk) of the

LSBCF electrodes are not significant. There is no formation of large Cr deposits, indicating that the Cr deposition inside the LSBCF cathode is significantly slower than that on the electrode surface. However, the EDS analysis indicates the presence of Cr inside the electrodes (Figure 5.10). The $La_{L\alpha}/La_{L\beta}$ atomic ratios for the LSBCF cathodes with $x = 0.0$, 0.2 and 0.4 are 4.45, 4.47 and 4.45, respectively, and are smaller than the ratio 5.25 for the LSBCF cathodes in the absence of the interconnect.

Figure 5.10 EDS patterns of the cross-section areas of the LSBCF cathodes with (a) $x = 0.0$, (b) $x = 0.2$, and (c) $x = 0.4$ after the polarization test as shown in Figure 5.8.

The $\text{La}_{\text{La}\alpha}/\text{La}_{\text{La}\beta}$ atomic ratios measured from the cross-section of the LSBCF cathodes do not change significantly with the Sr and Ba contents and are also significantly higher than that measured on the surface of the LSBCF cathode (see Figure 5.7). This indicates that the chromium deposition in the bulk of the LSBCF ($0.0 \leq x \leq 0.4$) cathodes does not depend on the LSBCF composition and is much lower than that on the surface of the LSBCF cathodes under the conditions of the present study.

In the absence of Fe-Cr interconnect, the electrochemical activity of LSBCF ($0.0 \leq x \leq 0.4$) cathodes for the O_2 reduction reaction is very close. The LSBCF cathodes are characterized by very low R_E and η values and the change in R_E and η (i.e., ΔR_E and $\Delta \eta$) with the cathodic current passage is negligible, showing typical electrochemical behavior associated with a mixed ionic and electronic conducting perovskite cathode such as LSCF [Jiang 2002]. This indicates that the oxygen activities at the LSBCF cathode and GDC electrolyte interface are similar for the O_2 reduction on the LSBCF electrodes in the composition range studied here.

In the presence of Fe-Cr interconnect, there is a significant change in the electrochemical behavior for the O_2 reduction reaction on the LSBCF electrodes. The increase in the R_E , E_{Cathode} , and η of the LSBCF cathode for the reaction indicates the poisoning effects of the chromium on the O_2 reduction reaction, showing typical characteristics of the polarization behavior for the reaction in the presence of Fe-Cr alloy [Jiang 2002; Zhen, Li et al. 2006]. However, the magnitude

in the increase of R_E , E_{Cathode} and η for the reaction in the presence of the Fe-Cr metallic interconnect is related to the Ba content in LSBCF. For the reaction on LSBCF with $x = 0.1$, R_E and η increased from $0.09 \Omega \text{ cm}^2$ and 14 mV at the beginning of the test to $0.48 \Omega \text{ cm}^2$ and 161 mV at the end of the polarization test. The increase in R_E and η (i.e., ΔR_E and $\Delta \eta$) is $0.39 \Omega \text{ cm}^2$ and 147 mV, respectively. When the Ba content increases to 0.3, the corresponding ΔR_E and $\Delta \eta$ are $0.27 \Omega \text{ cm}^2$ and 65 mV, respectively, significantly smaller than those of LSBCF with $x = 0.1$. The difference in the increase of the electrode polarization resistance and overpotential shows that the chromium poisoning on the electrocatalytic activity of the LSBCF cathodes is related to the Ba content in the LSBCF despite the fact the LSBCF cathodes have a very close electrocatalytic activity for the O_2 reduction reaction in the absence of Fe-Cr alloy.

The most significant results in the present study are the remarkable differences between the Cr depositions on the LSBCF electrodes and the electrochemical activities of the LSBCF cathodes for the O_2 reduction in the absence and presence of the Fe-Cr interconnect. Figure 5.11 summarizes the electrochemical behavior of LSBCF electrodes in the absence and presence of Fe-Cr interconnect and the Cr deposition as a function of x values (i.e., the Ba content) in the LSBCF cathodes.

Figure 5.11 Summary of electrochemical behavior and chromium deposition at the LSBCF electrodes in the absence and presence of a Fe-Cr interconnect as a function of Ba content (i.e., x value in LSBCF). (a) ΔR_E and $\Delta\eta$ of the LSBCF electrode in the absence of a Fe-Cr interconnect after cathodic current passage of 200 mA cm^{-2} at 900°C for 15 and 240 min; (b) ΔR_E and $\Delta\eta$ of the LSBCF electrode in the presence of a Fe-Cr interconnect after cathodic current passage of 200 mA cm^{-2} at 900°C for 15 and 1200 min; and (c) $\text{La}_{L\alpha}/\text{La}_{L\beta}$ atomic ratios measured on the surface and in the bulk of the LSBCF electrodes after cathodic current passage of 200 mA cm^{-2} at 900°C for 1200 min.

In the figure, Cr deposition is semi-quantitatively represented by the change of the $\text{La}_{\text{L}\alpha}/\text{La}_{\text{L}\beta}$ atomic ratios of the LSBCF cathode, while the electrochemical activities are represented by the changes in R_{E} and η , i.e., ΔR_{E} and $\Delta\eta$ as a function of cathodic polarization time in the absence and presence of Fe-Cr interconnect as discussed above. When $\text{La}_{\text{L}\alpha}/\text{La}_{\text{L}\beta}$ atomic ratio is 5.25, chromium deposition is zero for pure LSBCF cathode. The lower the $\text{La}_{\text{L}\alpha}/\text{La}_{\text{L}\beta}$ atomic ratio, the higher amount of chromium deposited on the LSBCF electrodes, as shown by the arrow in Figure 5.11c. The early stage electrochemical activities of the LSBCF cathodes for the reaction in the presence of the Fe-Cr interconnect is represented by the ΔR_{E} and $\Delta\eta$ measured after cathodic current passage for 15 min.

As shown, there are negligible changes in ΔR_{E} and $\Delta\eta$ for the O_2 reduction on the LSBCF cathodes ($0.0 \leq x \leq 0.4$) in the absence of Fe-Cr interconnect and in the early stages of the presence of Fe-Cr interconnect (Figure 5.11a&b). This indicates the similar electrochemical activities or oxygen potential gradients for the O_2 reduction reaction at the LSBCF cathode and GDC electrolyte interface. The significant change in ΔR_{E} and $\Delta\eta$ for the reaction on the LSBCF electrodes at the end of the cathodic polarization test is clearly related to the Cr deposition on the cathode surface (Figure 5.11c). The Cr deposition on the electrode surface (see Figure 5.6) has significant effect on the electrochemical activity of the LSBCF electrode for the O_2 reduction reaction. Cr deposits on the electrode surface blocks the transport of oxygen to the porous LSBCF electrodes while the gaseous chromium species strongly inhibit the dissociation and diffusion of oxygen species

on the surface of LSBCF, similar to that for the reaction on LSCF cathode [Jiang 2001; Jiang, Zhang *et al.* 2006]. The reason for the maximum $\Delta\eta$ and ΔR_E occurred at the LSBCF with $x = 0.1$ is not completely understood at this stage. One of the explanations could be attributed to the combined poisoning effect of the solid Cr deposits to block the transportation of oxygen and the gaseous Cr species to inhibit the dissociation and diffusion of oxygen on the electrode surface. Chromium poisoning of SOFC cathode occurs significantly by the surface diffusion of chromium from the chromia-forming interconnect to the cathode [Tucker, Kurokawa *et al.* 2006]. This indicates that the poisoning effect of gaseous chromium species may also be related to the Sr and Ba content in the LSBCF cathodes. As the Ba content increases, Cr deposition at the LSBCF electrode surface decreases significantly as indicated by the increase of the $\text{La}_{L\alpha}/\text{La}_{L\beta}$ atomic ratio (Figure 5.11c). The reduction in the Cr deposition results in the decrease of the blocking effect of solid Cr deposits on the transport and diffusion of oxygen, leading to the decrease in the ΔR_E and $\Delta\eta$.

The results in this study show again that there is no direct correlation between the electrochemical activity (i.e., the overpotential and the electrode polarization resistance) of the cathode and the magnitude and characteristics of the Cr deposition (i.e., the change of the $\text{La}_{L\alpha}/\text{La}_{L\beta}$ atomic ratios of the cathode). The significant differences in the Cr deposition observed on LSBCF electrodes as a function of Ba content cannot be explained based on the oxygen or electrochemical activities nor on the oxygen potential gradient as proposed in the literature

[Taniguchi, Kadowaki *et al.* 1995; Hilpert, Das *et al.* 1996; Badwal, Deller *et al.* 1997; H. Yokokawa, T. Horita *et al.* 2006]. Recent results show that Sr and Ba may have very different affinities to chromium species [Zhen and Jiang 2008]. It is known that Sr segregation occurs on the surface of perovskite oxides such as LSM and LSCF [Matsuzaki and Yasuda 2001; Viitanen, V. Welzenis *et al.* 2002]. In the case of LSBCF, segregation of BaO could also occur particularly for high Ba content as the ionic radius of Ba²⁺ is 1.61 Å, significantly larger than 1.16 Å of La³⁺ [Shannon 1976]. The segregated SrO and BaO would react with gaseous chromium species, forming SrCrO₄ and BaCrO₄ on the electrode surface of LSBCF, as shown in Figure 5.8.

Azad [1992] *et al* studied the standard Gibbs energies of formation of MCrO₄ (M = Ca, Sr and Ba) chromates from EMF measurements. The standard Gibbs Energy of formation ($\Delta G_f^\ominus$) of CaCrO₄, SrCrO₄ and BaCrO₄ are given in the following equations:

$$\Delta G_f^\ominus(\text{CaCrO}_4) = -1356.6 + 0.31641T (\pm 0.63) \text{ kJ mol}^{-1} \quad (788-1070\text{K}) \quad (5.1)$$

$$\Delta G_f^\ominus(\text{SrCrO}_4) = -1359.1 + 0.32998T (\pm 0.30) \text{ kJ mol}^{-1} \quad (851-1116\text{K}) \quad (5.2)$$

$$\Delta G_f^\ominus(\text{BaCrO}_4) = -1323.7 + 0.31159T (\pm 0.34) \text{ kJ mol}^{-1} \quad (850-1168\text{K}) \quad (5.3)$$

Figure 5.12 provides the standard Gibbs Free Energy ($\Delta G_f^\ominus$) of the three kinds of chromium oxides as a function of the temperature. The results indicate that there is a systematic trend in the thermodynamic stability of these alkaline earth metal chromates; the stability decreases as one goes down the group from Ca, Sr to Ba in

the temperature range close to the present study. The relatively low stability of BaCrO_4 in comparison with that of SrCrO_4 appears to be supported by the observation that the deposition of Cr species has little effect on the microstructure and morphology of the LSBCF electrodes with $x = 0.4$ (Figure 5.6e). This also indicates that formation and the grain growth of Cr deposits such as BaCrO_4 between the gaseous chromium species and Cr-Ba-O nuclei (or segregated BaO) would be kinetically a very slow process. Work is needed to fundamentally understand the interaction between the volatile Cr species and segregated strontium and barium in LSBCF under SOFC operation conditions. Nevertheless, the results in the present study show that the resistance and tolerance towards Cr deposition and Cr poisoning increase with the Ba content in the LSBCF electrodes.

Figure 5.12 Standard Gibbs Free Energy (ΔG_f^θ) of chromium oxides as a function of temperature [Azad, Sudha et al. 1992].

5.3 Summary

Chromium deposition and poisoning effects at stoichiometric LSBCF ($0.0 \leq x \leq 0.4$) electrodes were studied in the absence and presence of a Fe-Cr alloy interconnect at 900 °C. The electrochemical (i.e., the oxygen) activities of the LSBCF electrodes towards the O₂ reduction reactions in the absence of a Fe-Cr interconnect and at early stages in the presence of a Fe-Cr interconnect are very close. However, the chromium deposition changed significantly at the LSBCF cathodes as x varied from 0.0 to 0.4. At $x = 0.0$ (i.e., LSCF), the Cr deposition was the most significant, completely covering the surface of the electrode after it was polarized at 200 mA cm⁻² for 1200 min. As the Sr content in LSBCF cathodes decreased (i.e., Ba content increases), the Cr deposits on the electrode surface were reduced significantly. The results provide clear evidence that the significant difference in the Cr deposition is closely related to the Sr and Ba content and not related to the electrochemical activities of the LSBCF cathodes. The results of the present study also indicate that the high tolerance of LSBCF cathode with $x = 0.4$ towards chromium deposition and poisoning may be because of the low stability of BaCrO₄ deposits formed on the electrode surface.

CHAPTER 6 SUPPRESSION OF CHROMIUM POISONING AT LSM CATHODE WITH NOVEL Ni-Mo-Cr INTERCONNECT

Chromium deposition and poisoning effects of different interconnect materials on the electrochemical performance of LSM cathode have been extensively studied [Taniguchi, Kadowaki *et al.* 1995; Fujita, Ogasawara *et al.* 2004; Jiang, Zhang *et al.* 2005; Jiang, Zhen *et al.* 2006; Konyshcheva, Penkalla *et al.* 2006]. Despite the discrepancies in the chromium deposition mechanism, a clear consensus exists that the chromium gaseous phases vaporized from the chromia-forming alloy metallic interconnect are the source of the serious chromium deposition and poisoning effects. Studies on the chromium volatility of commercial Fe-Cr alloys such as RA600, RA446 and Crofer22APU indicated that both composition (e.g., $(\text{Mn,Cr})_3\text{O}_4$ layer) and the microstructure of the oxide have significant effect on the chromium volatility of the interconnect [Jiang, Zhen *et al.* 2006]. Therefore, it is an effective approach to suppress the chromium vaporization of the interconnect materials by modification of the composition and microstructure of the oxide scale. Recently, Ni-Mo-Cr alloys with compatible thermal expansion coefficient with other cell components and low oxidation rate under the SOFC working conditions were developed. The alloy was characterized by the formation of a Cr-free NiMn_2O_4 layer on top of inner Cr_2O_3 layer, indicating the potentially low

chromium vaporization of the oxide scale of the alloy [Hua, Pu et al. 2009]. In this study, chromium deposition and poisoning effects of the Ni-Mo-Cr materials on the electrochemical performance of the standard LSM cathode is investigated.

6.1 Experimental

The chromium-containing alloy interconnect used in this study was the commercially available RA446 interconnect and the novel Ni-Mo-Cr interconnect. The composition of the two kinds of interconnect materials is listed in Table 6.1 below. Details on the fabrication of the LSM testing cell can be found in Chapter 3. The polarization behaviors of the LSM were carried out under a constant current passage of 200 mA cm^{-2} at 900°C . The electrode potential (E_{cathode}) was measured against the Pt air reference electrode. Current passage was interrupted from time to time for the EIS measurements at the open circuit condition. The EIS test was carried out in the frequency range of 0.1 Hz to 100 kHz with a signal amplitude of 10 mV. SEM and EDS were used to examine the chromium deposition at the LSM cathode.

Table 6.1 Chemical composition of Ni-Mo-Cr and RA446 alloys (in weight percent).

Alloy	Mo	Cr	W	Co	Ti	Mn	Y	La	C	S	Si	Ni	Fe
Ni-Mo-Cr	20.76	12.24	4.12	3.02	1.18	0.98	0.005	0.012	0.004	0.002	0.033	bal	
RA446	-	24	-	-	-	07	-	-	0.05	-	0.5	-	bal

The LSM cathode after the current passage treatment in contact with RA446 and Ni-Mo-Cr alloy interconnect was examined in detail. Figure 6.1 illustrates the different parts of LSM electrode and YSZ electrolyte examined for the chromium deposition characterizations, including (1) LSM electrode/YSZ electrolyte interface region near the edge of LSM electrode, (2) YSZ electrolyte surface under rib of interconnect, (3) YSZ electrolyte surface under channel of interconnect, (4) LSM electrode surface in contact with interconnect, and (5) YSZ electrolyte surface not in contact with LSM electrode and interconnect. For the characterization of chromium depositions on the electrolyte surface, the LSM cathode was removed by 20 % HCl acid, followed by washing with de-ionized water

1. Electrode/ electrolyte interface region;
2. Electrolyte surface under rib of interconnect;
3. Electrolyte surface under channel of interconnect;
4. Electrode surface in contact with interconnect;
5. Electrolyte surface not in contact with interconnect;
6. Interconnect; 7. Electrode; 8. Electrolyte;
9. Rib of interconnect; 10. Channel of interconnect.

Figure 6.1 Different examination areas of LSM electrode and YSZ electrolyte for chromium deposition characterization.

6.2 Results and discussion

6.2.1 Electrochemical behavior

Figure 6.2 shows the XRD pattern of the LSM cathode materials prepared by the GNP method after calcined at 1000 °C for 6h. All the peaks in the pattern can be attributed to the perovskite structure of LSM and no impurity phase was detected, confirming the single phase structure of the thus prepared LSM powders.

Figure 6.2 XRD pattern of LSM powders prepared by GNP method after calcined at 1000 °C for 6h.

Figure 6.3 shows the electrochemical behavior of LSM cathode under a current density of 200 mA cm⁻² at 900 °C during the 240 min polarization test in the absence of interconnect. During the test, the ohmic resistance (R_{Ω}) is almost constant and the small decrease in R_{Ω} can be attributed to the improved contact between the electrolyte and the cathode. In the first 30 min, the polarization resistance (R_E) decreased quickly from 3.52 Ω cm² to 0.31 Ω cm² and then decrease in R_E is rather moderate. The electrode overpotential (η) also decreased from 90

mV to 54 mV with the current passage. The rapid decrease in the electrode polarization resistance and overpotential implies the activation effect of cathodic current passage on the oxygen reduction reactions of the LSM cathode [Jiang 2006].

Figure 6.3 Electrochemical behavior of the LSM cathode under a current density of 200 mA cm^{-2} at 900 °C during 240 min test in the absence of metallic interconnects: (a) impedance curves measured at open circuit, and (b) polarization curves.

Figure 6.4 presents the electrochemical behaviors of the LSM cathode under a current density of 200 mA cm^{-2} at 900 °C during the 1200 min polarization test in the presence of RA 446 and Ni-Mo-Cr interconnect. For the O_2 reduction on LSM cathode in the presence of RA446 and Ni-Mo-Cr interconnects, R_e calculated from EIS measured at the open circuit conditions decreased with the current passage time (Figure 6.4a and c), similar to that observed at LSM cathode in the absence of interconnect. Some fluctuation of R_Ω was also observed during the polarization test. However, the electrode potential (E_{cathode}) and η for the reaction on LSM cathode in the presence of Ni-Mo-Cr and RA446 behave very differently. In the presence of RA446 interconnect, the polarization curves show typical Cr poisoning effect on

the O_2 reduction on LSM cathode (see Figure 6.4b); E_{cathode} increases rapidly initially and reaches a plateau where the increase in E_{cathode} is much slower [Jiang, Zhang et al. 1999; Jiang, Zhang et al. 2005]. η increased from the initial value of 464 mV to 651 mV at the end of the polarization test.

Figure 6.4 Electrochemical behaviors of LSM cathode as a function of polarization at a current density of 200 mA cm^{-2} and 900°C in the presence of RA 446 and Ni-Mo-Cr interconnect; (a and c) impedance curves measured at open circuit, and (b and d) polarization curves.

In contrast to the polarization behavior in the presence of RA446 interconnect, E_{cathode} decreased significantly for the O_2 reduction on the LSM cathode in the presence of Ni-Mo-Cr interconnect (Figure 6.4d), similar to that in the absence of metallic interconnect (Figure 6.3b). η also decreased significantly from 529 mV to 111 mV for the reaction on the LSM/Ni-Mo-Cr interconnect system. This is probably the first reported observation of the significant decrease of the

polarization potential and overpotential for the O₂ reduction reaction on LSM cathode in the presence of a metallic interconnect, showing that the Ni-Mo-Cr interconnect has little chromium poisoning effects on the LSM cathodes.

6.2.2 Chromium deposition

Figure 6.5 shows SEM micrographs of chromium depositions on YSZ electrolyte surface not in contact with LSM cathode after 1200 min current passage of 200 mA cm⁻² in the presence of RA446 and Ni-Mo-Cr interconnect. Figure 6.6 provides the corresponding EDS analyses on some selected YSZ electrolyte surface. According to the SEM image in Figure 6.5a, the surface of the YSZ electrolyte, near the electrode/electrolyte interface indicated as location '1' in Figure 6.1, was completely covered by a layer of small particles after 1200 min current passage in the presence of RA 446 interconnect. The grain boundaries of the YSZ electrolyte could still be seen underneath the small deposits. The small particle deposits were confirmed to contain Cr and Mn by the EDS analysis (Figure 6.6a), indicating the formation of (Cr, Mn)₃O₄ spinel. As the distance from the electrode edge increased, chromium depositions on the surface of YSZ electrolyte decrease significantly (Figure 6.5a, b, c & d). Nevertheless, the deposition of small particles is still clearly visible on the YSZ electrolyte surface. On the YSZ electrolyte surface at a location 100 μm from the electrode edge, only Cr can be detected (Figure 6.6b), indicating the formation of Cr₂O₃. The Cr deposits can occur on the YSZ electrolyte surface as far as 6 mm (i.e., the edge of the YSZ electrolyte disc, location '5' in Figure 6.1) from the edge of the LSM cathode (Figure 6.5d). In comparison, the YSZ

electrolyte surface without contact with LSM electrode after 1200 min current passage in the presence of Ni-Mo-Cr interconnect appeared much cleaner with very little chromium depositions (Figure 6.5e, f, g & h). A few large particles on the YSZ electrolyte surface near the LSM electrode edge are LSM particles (Figure 6.5e); EDS analyses cannot detect the presence of Cr on the YSZ electrolyte near the edge of the LSM and at location 100 μm from the LSM electrode edge (Figure 6.6c & d). It indicates that chromium depositions on the YSZ electrolyte surface not in contact with LSM particles are negligible and below the detection limit of EDS analysis.

As discussed, the deposition of chromium species on the YSZ electrolyte surface not in direct contact with LSM and the interconnect is primarily governed by the flux and concentration of manganese and gaseous chromium species on the YSZ electrolyte surface [Jiang, Zhang *et al.* 2000; Jiang, Zhang *et al.* 2001]. Under the conditions of present study, the significant differences observed for the Cr deposition on the YSZ electrolyte surface not in contact with LSM electrode are clearly related to the difference in the RA446 and Ni-Mo-Cr metallic interconnects as other conditions of LSM cathode, YSZ electrolyte, temperature, air flow and current passage time are identical in both cases. Therefore, the magnitude of the chromium depositions on the YSZ electrolyte surface not in contact with LSM can be taken as a direct indicator of the chromium vaporization rate of the interconnect materials used. Evidently, the much clearer YSZ electrolyte surface (Figure 6.5) indicates that chromium vaporization rate of Ni-Mo-Cr interconnect is very low as compared to that of the conventional RA446 Fe-Cr alloys.

Figure 6.5 SEM micrographs of chromium depositions on the electrolyte surface not in contact with LSM cathode after 1200 min current passage of 200mA cm^{-2} in the presence of RA446 and Ni-Mo-Cr interconnect; (a & e) near the edge of the LSM cathode; (b & f) $\sim 100\text{ }\mu\text{m}$ from the edge; (c & g) $\sim 1\text{ mm}$ from the edge; (d & h) $\sim 6\text{ mm}$ from the edge of the electrode (at the edge of YSZ electrolyte pellets). SEM micrograph of the electrolyte surface before the test is shown in (i).

Figure 6.6 EDS patterns on the electrolyte surface not in contact with LSM cathode after 1200 min current passage at locations shown in Figure 6.5: (a & c) YSZ electrolyte surface near the edge of the LSM electrode coating, and (b & d) YSZ electrolyte surface at ~ 100 μm from the LSM electrode.

Figure 6.7 is the SEM micrographs of YSZ electrolyte surface under the channel of RA446 and Ni-Mo-Cr interconnect (location ‘3’ in Figure 6.1) after removal of the LSM electrode. The corresponding EDS analyses on the YSZ electrolyte surface are given in Figure 6.8. Under the channel of RA 446 interconnect, the YSZ electrolyte surface is totally covered by a layer of deposit (Figure 6.7a), which is confirmed to be $(\text{Cr}, \text{Mn})_3\text{O}_4$ spinel phase by the EDS analysis (see Figure 6.8a). Moreover, the deposits seem to be formed layer by layer with a special orientation on each YSZ grain surface as indicated by the arrows. During the test, air first enters the interconnect (Figure 3.1) through the top hole at the center of the channel and then diffuses in different directions in the channel,

which is responsible for the different orientation of the Cr deposits. On the YSZ electrolyte surface but away from the electrode center region under RA446 interconnect, there are also significant Cr deposits, as shown by the EDS analysis (Figure 6.8b), but the deposits show no particular orientation (Figure 6.7b). The reason could be related to differences in the air flow as the air flow rate at the edge of LSM electrode would be much smaller than that in the center of the electrode. The kinetics of the Cr deposition process depends strongly on the air flow [Jiang, Zhang *et al.* 2001] and orientation formation of Cr deposits indicates the influence of the air flow on the formation and growth of the Cr deposits. The circles with diameter of $\sim 1\mu\text{m}$ are the contact rings between LSM particles and YSZ grain surface (Figure 6.7b), formed during the cathode sintering stage [Jiang and Wang 2005].

Figure 6.7 SEM micrographs of YSZ electrolyte surface in contact with LSM electrode under the channel of RA 446 and Ni-Mo-Cr interconnect; (a & c) center of the LSM electrode, (b & d) edge of the electrode. LSM electrode was removed by HCl etching.

In contrast, the YSZ electrolyte surfaces under the channels of Ni-Mo-Cr interconnect near the center (Figure 6.7c) and edge (Figure 6.7d) of the LSM electrode surface are much clearer. The scattered white particles were $(\text{Cr, Mn})_3\text{O}_4$ deposits according to the EDS analysis shown in Figure 6.8c. The contact rings between the LSM particles and electrolyte can be easily identified and no chromium depositions can be detected (Figure 6.8d). This indicates that chromium deposition on the YSZ electrolyte surface in contact with LSM cathode under the channel of Ni-Mo-Cr metallic interconnect is substantially smaller than that on the YSZ electrolyte surface under the channel of RA446 interconnect.

Figure 6.8 EDS pattern at different locations on the YSZ electrolyte surface after removal of LSM cathode under the channel of RA 446 and Ni-Mo-Cr interconnect shown in Figure 6.7; (a & c) near the center of the LSM electrode, and (b & d) near the edge of the LSM electrode. Arrows in (a) show the orientation of the deposits.

Figure 6.9 shows the SEM micrographs and the corresponding EDS analysis on

YSZ electrolyte surface in contact with LSM cathode under the rib of RA446 and Ni-Mo-Cr interconnect (location '2' in Figure 6.1) after 1200 min current passage. LSM cathode coating was removed by HCl treatment.

Figure 6.9 SEM micrographs and EDS patterns on YSZ electrolyte surface in contact with LSM cathode under the rib of RA 446 and Ni-Mo-Cr interconnect after 1200 min polarization test. (a & b) RA446, and (c & d) Ni-Mo-Cr. LSM electrode coating was removed by HCl treatment.

Chromium depositions on YSZ electrolyte surface in contact with LSM cathode occur under the rib of RA446 and Ni-Mo-Cr interconnect (Figure 6.9a and c). The deposits are characterized by cubic crystals and contain both Mn and Cr as shown by the EDS analysis (Figure 6.9b & d), indicating the formation of $(\text{Cr,Mn})_3\text{O}_4$ crystals. Nevertheless, the amount of Cr deposits on the YSZ electrolyte surface

under the rib of RA446 appears to be significant in comparison with that under the rib of Ni-Mo-Cr interconnect. The significant growth and densely packed Cr crystals on the YSZ surface under the rib of the metallic interconnect, in contrast to that on the YSZ surface under the channel, indicate that chromium depositions on the LSM/YSZ system are significantly affected by the air flow and the flow field of the interconnect. Solid state diffusion process of Cr species could also contribute to the significant deposition and growth of Cr species on the YSZ electrolyte surface [Tucker, Kurokawa *et al.* 2006].

Figure 6.10 shows SEM images on the LSM cathode surface at the center and near the edge of the cathode before and after 1200 min current passage of 200 mA cm⁻² at 900°C in the presence of RA 446 and Ni-Mo-Cr interconnects. Figure 6.11 is the corresponding EDS analyses. The LSM electrode surface before the test appears very clean and takes on the interconnected porous structure (Figure 6.10e). The peak intensity ratio of La_{Lα}: Mn_{Kα}: La_{Lβ} = 5.45: 4.46: 1.00 was measured on the LSM electrode surface before test (Figure 6.11e). On the LSM surface center after 1200 min current passage in the presence of both RA 446 and Ni-Mo-Cr interconnects, no obvious chromium deposits can be observed (Figure 6.10a & b). However, EDS analysis revealed the existence of chromium species and the La_{Lα}/La_{Lβ} is 4.24 for the LSM cathode in the presence of RA 446 interconnect (Figure 6.11a), lower than La_{Lα}/La_{Lβ} ratio of 5.45 on the LSM electrode surface before the test. The decreased La_{Lα}/La_{Lβ} value is attributed to the overlapping of Cr_{Kα} peak with La_{Lβ} peak, therefore increasing the relative intensity of the La_{Lβ}

peak [Tucker, Kurokawa et al. 2006]. On the other hand, $La_{L\alpha}/La_{L\beta}$ is 5.38 for LSM in the presence of Ni-Mo-Cr interconnect (Figure 6.11b), close to 5.45 for LSM surface before the test.

Figure 6.10 SEM micrographs of LSM electrode surface at the center and near the edge of the electrode after 1200 min current passage of 200 mA cm^{-2} in the presence of RA446 and Ni-Mo-Cr interconnect: (a & b) LSM cathode surface near the center of the electrode, and (c & d) LSM cathode surface near the edge of the electrode. The LSM electrode before the test is shown in (e).

Figure 6.11 EDS patterns on the LSM electrode surface at the center and near the edge of the electrode after 1200 min current passage of 200 mA cm⁻² in the presence of RA446 and Ni-Mo-Cr interconnect as shown in Fig 6.10: (a & b) LSM cathode surface near the center of the electrode, and (c & f) LSM cathode surface near the edge of the electrode. The EDS pattern of the LSM electrode before the test is shown in (e).

In contrast, chromium depositions on the LSM electrode surface near the edge of the electrode seem very obvious. The LSM electrode surface near the edge after 1200 min current passage in the presence of RA 446 interconnect was covered by layer of small white particles, which most likely consists of both (Cr,Mn)₃O₄ and

Cr_2O_3 according to the EDS analysis shown in Figure 6.11c. The LSM electrode surface near the edge after 1200 min current passage in the presence of Ni-Mo-Cr interconnect is also covered by deposited crystals (Figure 6.10d), which was also confirmed to be $(\text{Cr,Mn})_3\text{O}_4$ and Cr_2O_3 chromium deposits. The difference between the chromium depositions on the LSM surface near the edge in the presence of RA 446 and Ni-Mo-Cr interconnect can be ascribed to the different concentration of Cr. The $\text{La}_{\text{L}\alpha}/\text{La}_{\text{L}\beta}$ value for the electrode at this location with RA 446 interconnect is 0.36, compared with 1.26 for the electrode with Ni-Mo-Cr interconnect, indicating the much more serious chromium depositions on the LSM electrode surface near interface with RA 446 interconnect. The $\text{Mn}_{\text{K}\alpha}/\text{La}_{\text{L}\beta}$ value for the electrode near interface with RA 446 interconnect is 0.51, compared with that of 6.46 for the electrode with Ni-Mo-Cr interconnect, also illustrating the higher content of Cr in chromium depositions on LSM 90 electrode surface in the presence of RA446 interconnect. Therefore, a conclusion can be drawn that chromium depositions on the LSM 90 electrode surface primarily happened on the electrode surface near electrode/electrolyte interface and they are more serious on the electrode surface after current passage in the presence of RA 446 interconnect.

6.2.3 Phase compositions of oxide layer on the Ni-Mo-Cr interconnect

Electrochemical tests, in combination with chromium deposition characterizations, clearly indicated that chromium deposition and poisoning effects of the Ni-Mo-Cr interconnect materials are much less significant than the

conventional RA446 Fe-Cr interconnect. It can be attributed to the much lower vaporization of gaseous chromium from the Ni-Mo-Cr interconnect under SOFC operation conditions. Figure 6.12 is the XRD patterns of the Ni-Mo-Cr interconnect after oxidized at 750 °C for different periods. As can be seen, signals from MoNi_3 , Cr_2O_3 and a spinel phase (probably NiMn_2O_4), were detected in the XRD pattern in addition to the signals from the matrix. Figure 6.13 shows the SEM micrograph and the corresponding EDX line scan profile at a polished cross-section of the Ni-Mo-Cr interconnect after oxidized at 750 °C for 1000h in air. The interconnect after oxidation was primarily composed of three layers (Figure 6.13a). The EDS line scan profile (Figure 6.13b), together with the XRD pattern, confirmed that the middle layer is composed of MoNi_3 intermetallic compound, and the oxide scales formed on the surface of the interconnect consist two layers. A Cr-free NiMn_2O_4 spinel layer was formed on top of the Cr_2O_3 layer formed outside the intermetallic compound layer. The formation of the Cr-free NiMn_2O_4 inhibited the diffusion of Cr element to the oxide scale surface of the interconnect, thereby greatly reducing the vaporization of the gaseous chromium species. Another important reason for the lower vaporization of gaseous chromium from the Ni-Mo-Cr interconnect can be attributed to the lower Cr content compared with that in the RA 446 Fe-Cr interconnect, as listed in Table 6.1. The Cr content in the Ni-Mo-Cr interconnect materials is nearly half that in the RA 446 Fe-Cr interconnect. As a result, the chromium deposition and poisoning effects of the Ni-Mo-Cr interconnect are much less significant than the conventional RA446 Fe-Cr interconnect materials.

Figure 6.12 XRD patterns of Ni-Mo-Cr interconnect after heat treatment at 750 °C in air for different periods.

Figure 6.13 SEM micrograph and corresponding EDX line scan profile at the cross-section of the Ni-Mo-Cr interconnect after heat treatment at 750 °C in air for 1000h.

The newly developed Ni-Mo-Cr interconnect materials possess a TEC value of $13.92 \times 10^{-6} \text{ K}^{-1}$ between 35 and 800°C, which is compatible with that of the other cell components ($10\text{-}13 \times 10^{-6} \text{ K}^{-1}$). After 250 h oxidation, the oxidation rate of the materials decreased and the oxide layer formed on the surface has good thermal cyclicability. It possesses an ASR of $4.48 \text{ m}\Omega \text{ cm}^2$, which can satisfy the requirement for the interconnect materials [Hua, Pu et al. 2009]. Under the SOFC operation conditions, the Ni-Mo-Cr interconnect also shows much less significant chromium poisoning effects on the cathode performance than RA 446 Fe-Cr interconnect and other kinds of interconnect materials. Therefore, the Ni-Mo-Cr materials can be regarded as a promising kind of interconnect materials for IT-SOFCs.

6.3 Summary

In this chapter, chromium deposition and poisoning effects of a new kind of chromia-forming metallic interconnect materials were investigated. The electrochemical test showed that η for the LSM cathode in the presence of the Ni-Mo-Cr interconnect decreased from 529 to 111 mV as the current passage, compared with an increase of 97 mV for the LSM cathode in the presence of RA 446 interconnect. The decrease in η for the LSM cathode in the presence of metallic interconnect materials is observed for the first time, clearly indicating the much less significant chromium poisoning effects of the Ni-Mo-Cr interconnect on the cathode performance than RA 446 and other kinds of metallic interconnect materials. The chromium deposition characterization showed that the chromium

depositions at LSM 90 cathode in the presence of Ni-Mo-Cr interconnect were much less than those at the cathode in the presence of RA 446 interconnect, which can be attributed to the low Cr content and the formation of the Cr-free NiMn_2O_4 layer formed on top of the Ni-Mo-Cr interconnect, which inhibited the diffusion of Cr element and reduced the vaporization of gaseous chromium species. The Ni-Mo-Cr interconnect can be regarded as a promising kind of interconnect materials with little chromium poisoning effects for IT-SOFC.

CHAPTER 7 CHROMIUM DEPOSITION AND POISONING AT LSM CATHODE IN DRY AND HUMIDIFIED AIR

Opila [2006] et al. studied the volatility of $\text{CrO}_2(\text{OH})_2$ at 600 °C by transpiration experiments and found that the volatility of $\text{CrO}_2(\text{OH})_2$ obeys power law dependencies of 1 and 3/4 for water vapor and oxygen, respectively. Gindorf [2001; 2005] et al. investigated the Cr vaporizations from Cr_2O_3 powders at 850 °C in air with different humidities by transpiration experiment and found that the Cr vaporization increased significantly as the humidity in air increased from 0.0007 bar to 0.3 bar. Therefore, the humidity in air has a significant influence on the Cr vaporization, and the Cr deposition and poisoning at the cathodes under SOFCs operation conditions would be dependent on the humidity of the air on the cathode side. Ishihara [2005] et al investigated the effects of water addition on the performance of La-doped $\text{BaCoO}_{3-\delta}$ (LBC) and $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ (SSC) cathodes on LaGaO_3 -based oxide electrolyte and found that the overpotential of LBC and SSC cathodes decreased by the addition of H_2O to oxygen. The positive effect of a humidified oxidant was attributed to the enhanced dissociation of oxygen. However, there is little information on the influence of humidity in air on the Cr deposition and poisoning at the cathodes of SOFCs. Thus, the effect of humidity in air on the Cr deposition and poisoning at the standard LSM cathode is investigated

in this study.

7.1 Experimental

The chromia-forming alloy interconnect used in this study was the commercially available RA446 interconnect. Air (industrial grade, H₂O content < 3 ppm) passing through a molecular sieve was used as the dry air. Humidified air with ~3% water was achieved by passing the dry air through a water bubbler at room temperature. The air flow rate was 100 ml min⁻¹. Details on the fabrication of the testing cell can be found in Chapter 3.

The polarization behaviors of the LSM cathode were carried out under a constant current passage of 200 mA cm⁻² at 900 °C. The electrode potential (E_{cathode}) was measured against the Pt air reference electrode. Current passage was interrupted from time to time for the EIS measurements at the open circuit condition. The EIS test was carried out in the frequency range of 0.1 Hz to 100 kHz with a signal amplitude of 10 mV. SEM and XRD were used to examine the morphology and composition of the Cr deposits on the electrolyte in contact with the LSM cathodes under the Fe-Cr metallic interconnect. To reveal the Cr deposition on the surface of the electrolyte, LSM cathodes after polarization test were removed by the HCl acid etching at room temperature.

7.2 Results and discussion

7.2.1 Electrochemical behavior

Figure 7.1 shows the impedance and polarization curves of the LSM cathode as a function of a cathodic current passage time at 200 mA cm^{-2} and 900°C in the absence of RA446 metallic interconnect in dry and humidified air. In the absence of metallic interconnect, LSM cathode showed a similar electrochemical behavior towards the oxygen reduction reaction in dry and humidified air. The size of the impedance arc, i.e., the polarization resistance (R_E), for the O_2 reduction reaction decreases significantly with the current passage time in both dry and humidified air (Figure 7.1a & b), similar to activation effects observed at LSM cathode in previous studies. The magnitude in the reduction in R_E is also similar for the reaction on the LSM cathode in dry and humidified air; R_E decreased from $1.16 \Omega \text{ cm}^2$ to $0.13 \Omega \text{ cm}^2$ for the reaction in dry air while it decreased from $1.06 \Omega \text{ cm}^2$ to $0.17 \Omega \text{ cm}^2$ for the reaction in humidified air after polarized for 240 minutes. The polarization curves for the O_2 reduction on LSM cathodes are also similar in dry and humidified air (Figure 7.1c & d). Both E_{Cathode} and η decrease significantly with the cathodic current passage, similar to the polarization resistance. Initial η value was 221 mV and decreased to 60 mV after polarized at 200 mA cm^{-2} for 240 minutes for the O_2 reduction on the LSM cathode in dry air. In the case of humidified air, it decreased from 241 to 62 mV under identical test conditions in humidified air. Both impedance and polarization behavior for the O_2 reduction reaction on LSM cathodes is very similar under cathodic polarization in dry and humidified air in the

absence of Fe-Cr metallic interconnector. This is different from that observed by Ishihara et al for the reaction on LBC and SSC cathode [Ishihara, Fukui et al. 2005] where the η of LBC and SSC cathodes decreased with the addition of H₂O in oxygen. The results in the present study show that the dehumidification in air does not have any significant influence on the electrochemical activity of the LSM. The similarity in the magnitude in the reduction in the R_E and η of the LSM cathode as a function of the cathodic current passage time indicates that the activation effect of the cathodic polarization on the electrocatalytic activity of LSM cathodes is not affected by the humidity in air.

Figure 7.1 Impedance and polarization curves of the O₂ reduction reaction on LSM cathodes as a function of a current passage time at 200 mA cm⁻² and 900 °C in the absence of Fe-Cr metallic interconnect in (a,c) dry and (b,d) humidified air. Impedance curves were measured under open circuit.

Figure 7.2 shows the electrochemical behavior of the LSM cathode at 900 °C under a current passage of 200 mA cm⁻² in the presence of RA446 metallic interconnect in dry and humidified air. The impedance curves were measured in open circuit.

Figure 7.2 Impedance and polarization curves of the O₂ reduction reaction on LSM cathodes as a function of a current passage time at 200 mA cm⁻² and 900 °C in the presence of Fe-Cr metallic interconnect in (a,c) dry and (b,d) humidified air. Impedance curves were measured under open circuit condition.

In the presence of the Fe-Cr metallic interconnect, R_Ω fluctuated during the polarization test (Figure 7.2a & b), which could be attributed to the formation of the oxide layers on the surface of the metallic interconnect. The LSM electrode shows typical polarization behavior for the reaction in the presence of Fe-Cr metallic interconnect [Jiang, Zhang *et al.* 2005], a rapid increase in E_{Cathode} initially,

followed by a region where the increase in $E_{Cathode}$ is much slower. However, the increase in $E_{Cathode}$ for the reaction in humidified air is significantly higher than that in dry air. For example, for the reaction after polarized for 120 min, the change in $E_{Cathode}$ is 577 mV for the reaction in humidified air, significantly higher than 408 mV for the reaction in dry air. The change in η for the reaction in humidified air is also significantly higher than that in dry air. For the reaction in dry air, the initial η was 413 mV and increased to 647 mV after polarized at 200 mA cm^{-2} for 1200 min. The increase in η , $\Delta\eta$, is 234 mV. For the reaction in humidified air, the $\Delta\eta$ value after polarized at 200 mA cm^{-2} for 1200 min is 566 mV. This indicates that the Cr poisoning effect on the O_2 reduction reaction is reduced and slowed down in dry air.

Figure 7.3 is the plots of R_E and η values of the O_2 reduction reaction on the LSM cathode in the absence and presence of RA446 metallic interconnect, measured in dry and humidified air and at 900°C . The data were taken from Figure 7.1 and 7.2. In the absence of metallic interconnect, the changes in the R_E and η values for the reaction on the LSM cathode in dry and wet air at 900°C are almost identical (Figure 7.3a), showing that the difference in the electrocatalytic activity of LSM cathode for the O_2 reduction reaction is negligible. Low level of humidity in air has little effect on the electrochemical performance of the LSM cathode. However, the differences in the changes in the R_E and η for the reaction on the LSM cathode in dry and humidified air in the presence of the metallic interconnect are substantial (Figure 7.3b). The increase in R_E and η for the reaction in humidified air is significantly higher than that in dry air. The much larger values

of ΔR_E and $\Delta \eta$ for the LSM cathode operated in humidified air clearly indicated the much more serious Cr poisoning effect of the Fe-Cr metallic interconnect on the electrochemical performance of the LSM cathode in humidified air. The significant difference in the Cr poisoning effects at LSM cathode in dry and humidified air can be ascribed to the different vaporization kinetics of gaseous Cr species from the metallic interconnect in dry and humidified air.

Figure 7.3 Plots of η and R_E of the O_2 reduction reaction on LSM cathode as a function of current passage time at 200 mA cm^{-2} and 900°C in dry and humidified air in the (a) absence and (b) presence of a Fe-Cr metallic interconnect.

7.2.2 Chromium deposition

Previous studies showed that Cr deposition at the LSM cathode primarily occurs on the electrolyte surface in contact with the electrode coating at the early stage of the polarization [Jiang, Zhang *et al.* 1999; Jiang, Zhang *et al.* 2002]. Figure 7.4 shows the SEM micrographs of the YSZ electrolyte surface in contact with the LSM electrode after 1200 min current passage at 900°C in the presence of RA446 metallic interconnect. The LSM coating was removed by HCl acid treatment. The electrolyte surface in contact with the electrode coating under the rib and channel of the interconnect can be easily identified. The YSZ electrolyte surface under the rib of the interconnect looks brighter and whiter in color, as compared to the surface under the channels of the interconnect due to the significant deposition of Cr particles under the rib of the interconnect.

Figure 7.4 SEM micrographs of YSZ electrolyte surface in contact with the LSM cathode after 1200 min current passage at 200 mA cm⁻² and 900 °C in the presence of a Fe-Cr metallic interconnect, showing the regions under the rib and channels of the interconnect. LSM cathode was removed by HCl etching.

Figure 7.5 is the SEM micrographs with different magnifications of the YSZ electrolyte surface in contact with a LSM electrode under the rib of the interconnect after 1200 min current passage at 900 °C in dry and humidified air. The corresponding EDS analysis is shown in Figure 7.5e and f.

Figure 7.5 SEM micrographs of the YSZ electrolyte surface in contact with LSM electrode under the rib of the interconnect after 1200 min current passage at 200 mA cm⁻² and 900 °C in (a,c) dry and (b,d) humidified air. The EDS analysis of the deposits in dry and humidified air is shown in (e) and (f), respectively.

The Cr deposition on the YSZ electrolyte surface is significant, as indicated by the formation of the large number and thick layers of Cr deposits on the electrolyte surface. The deposits are characterized by facets of spinel crystals and contain Cr and Mn, indicating the formation of $(\text{Cr,Mn})_3\text{O}_4$ spinel phases. The differences in the amounts of Cr deposits on the YSZ electrolyte surface after polarization in dry and humidified air are significant. There are much more and thicker Cr deposits on the electrolyte surface in humidified air as compared to that under dry air (Figure 7.5c & d). This is also supported by the much higher relative intensity ratio of Cr/Zr at Cr deposits on electrolyte surface formed in humidified air than that in dry air (Figure 7.5e & f). Cr deposition on the electrolyte surface in contact with LSM electrode under the rib of the interconnect after current passage is much more serious in humidified air as compared to that in dry air.

Figure 7.6 is the corresponding SEM micrographs and EDS analysis of the YSZ electrolyte surface in contact with LSM electrode under the channel of the interconnect after 1200 min current passage at 900 °C in dry and humidified air. After the removal of LSM electrode coating, the electrolyte surface was also covered by a layer of Cr deposits (Figure 7.6a & b). The deposits also contain Cr as well as Mn, as confirmed by the EDS analysis (Figure 7.6e & f). Similar to that under the rib of the interconnect, clear differences can also be seen between the Cr deposition on electrolyte surface after the current passage in dry and humidified air. On the electrolyte surface in dry air, the Cr deposition appears to be much less than that in humidified air. The grain boundaries and contact rings between the LSM

particles and YSZ electrolyte on the electrolyte surface are clearly visible in the case of dry air (Figure 7.6a&c). On the other hand, the grain boundaries of the electrolyte surface after the current passage in humidified air are hardly visible due to the complete coverage by a layer of Cr spinel crystals (Figure 7.6 & d). Furthermore, the deposition of Cr on the electrolyte surface after current passage in dry and humidified air is random, occurring around the contact rings between the LSM particles and electrolyte and as well as on the areas between the contact rings, indicating that the Cr deposition is not closely related to the electrocatalytic activity of the LSM cathode for the O₂ reduction reaction at the three phase boundaries at the electrode/electrolyte interface, in agreement with the previous studies [Jiang, Zhang *et al.* 2000; Jiang, Zhang *et al.* 2001]. The results indicate that Cr deposition on the electrolyte surface in contact with LSM electrode under the channel of interconnect after current passage is much more serious in humidified air as compared to that in dry air, similar to the Cr deposition under the rib of the interconnect. The humidity in air will lead to high Cr poisoning and high Cr deposition for the O₂ reduction reaction at LSM cathodes. Thus, for SOFCs using Fe-Cr metallic interconnect, the humidity in air or oxygen on the cathode side should be kept as low as possible in order to minimize the impact of the water on the Cr deposition and Cr poisoning effect. De-humidification or drying of the inlet air in SOFCs would be an economic and effective method to minimize the vaporization of Cr species, particularly the Cr oxyhydroxides, thereby alleviating the chromium deposition and poisoning effects at cathode for SOFCs.

Figure 7.6 SEM micrographs of the electrolyte surface in contact with LSM electrode particles under the channels of the interconnect after 1200 min current passage at 900 °C in dry (a&c)and humidified (b&d) air together with the corresponding EDS analysis (e & f).

7.3. Summary

Cr deposition and poisoning effect at the LSM cathode in dry and humidified air under a current passage at 900 °C were investigated in detail. In the absence of the Fe-Cr metallic interconnect, the LSM cathode showed very similar

electrochemical performance in both dry and humidified air. However, in the presence of the metallic interconnect, LSM cathode behaved very differently for the O_2 reduction reaction in dry and humidified air. The effect of Cr poisoning in humidified air for the oxygen reduction reaction at the LSM cathode is significant as compared to that in dry air. Similarly, Cr deposition at the LSM cathode is also significantly accelerated in humidified air as compared to that in dry air under identical experimental conditions. The high Cr poisoning and high Cr deposition in the case of humidified air is most likely related to the high concentration of the $CrO_2(OH)_2$ gaseous species formed in humidified air. Therefore, the humidity in air has a significant adverse effect on the Cr deposition and poisoning effect and dehumidification comprises an economic and effective method to decrease the Cr deposition and poisoning effect at LSM cathode for SOFCs.

CHAPTER 8 DEVELOPMENT OF CHROMIUM-TOLERANT CATHODE FOR SOFCs

Studies on the Cr deposition processes at different cathodes of SOFCs showed that the deposition process of Cr species depends strongly on the nature of the cathode materials, i.e., the electrode composition [Jiang, Zhang *et al.* 2000; Jiang, Zhang *et al.* 2001; Jiang, Zhang *et al.* 2002; Jiang, Zhang *et al.* 2006; Jiang, Zhen *et al.* 2006; Zhen, Tok *et al.* 2007]. The study in chapter 4 showed that chromium deposition and poisoning at the cobaltite cathodes could be greatly reduced by increasing the Ba content and decreasing the Sr content at the A-site of the perovskite structure. The $\text{Ba}(\text{Co}_{0.7}\text{Fe}_{0.3-x}\text{Nb}_x)\text{O}_{3\pm\delta}$ (BCFN, $x=0.08$) materials have an oxygen permeation flux of $25.77 \text{ ml min}^{-1} \text{ cm}^{-2}$ at 875°C , several times that of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) materials [Cheng, Zhao *et al.* 2008]. Su [2009] *et al.* studied the performance of the BCFN ($0.0 \leq x \leq 0.12$) as novel cathode for IT-SOFCs and found that it has good polarization performance between $600\text{-}800^\circ\text{C}$. However, the maximum power density of the cell with the BCFN cathode is only $\sim 200 \text{ mW cm}^{-2}$ at 600°C , which may be ascribed to the large ohmic resistance caused by the low conductivity below 20 S cm^{-1} between $100\text{-}900^\circ\text{C}$ [Cheng, Zhao *et al.* 2008; Zhu, Liu *et al.* 2009]. In this chapter, a new kind of $(\text{La}_{0.24}\text{Sr}_{0.16}\text{Ba}_{0.6})(\text{Co}_{0.5}\text{Fe}_{0.44}\text{Nb}_{0.06})\text{O}_{3\pm\delta}$ (LSBCFN40) cathode, derived from the

mixture of LSCF and BCFN powders, is prepared and characterized as chromium-tolerant cathode for IT-SOFCs.

8.1 Experimental

LSBCFN materials were prepared by the direct calcinations of the mixture of LSCF and BCFN powders at high temperature. The phase composition and properties of the materials, including the conductivity and electrocatalytic activity at different temperatures, were characterized. Chromium-tolerance of the LSBCFN cathode was studied at 900 °C, compared with that of the two original BCFN and LSCF materials. The chromia-forming alloy interconnect used in this study was the commercially available RA446 interconnect. The performance of the anode-supported cell with NiO-GDC anode, GDC thin film electrolyte, and LSBCFN40 cathode, was investigated using the two-electrode method. Detailed information of the preparation of the materials, sample for conductivity test, half-cell and full-cell can be found in chapter 3. For half-cell test, the electrode potential (E_{cathode}) was measured against the Pt air reference electrode. Current passage was interrupted from time to time for the EIS measurements at the open circuit condition. For full-cell test, the cell voltage (V) was measured between the anode and cathode. EIS test was carried out in the frequency range of 0.1 Hz to 100 kHz with a signal amplitude of 10 mV. SEM and EDS were used to examine the chromium deposition at different cathodes.

8.2 Results and discussion

8.2.1 XRD pattern of synthesized powders

Despite the good polarization performance of BCFN cathode, its electronic conductivity needs to be further improved to meet the requirements. Cheng [2008] et. al. reported a conductivity of below 20 S cm^{-1} between 100 and 900 °C for BCFN. LSCF has high electrical conductivity during the operation temperature of SOFCs. Sehlin [1995; 1995] et al. reported that $(\text{La}_{0.6}\text{Sr}_{0.4})(\text{Co}_{0.2}\text{Fe}_{0.8})\text{O}_{3-\delta}$ (LSCF) materials has an electrical conductivity of $\sim 280 \text{ S cm}^{-1}$ at 800 °C and $\sim 210 \text{ S cm}^{-1}$ at 900 °C. Therefore, it is expected that the conductivity of BCFN materials can be improved by mixing with LSCF materials to form BCFN-LSCF composite materials.

BCFN and LSCF materials, mixed at different weight ratio, were calcined at 1050 °C and 1100 °C for 4h to study the compatibility of these two oxides at the sintering temperature of the cathodes. Figure 8.1 shows the XRD pattern of the mixed LSCF and BCFN powders after calcinations at 1050 °C and 1100 °C. The results show that the XRD peaks belonging to LSCF and BCFN disappear and peaks of a new perovskite structure appear at 2θ angles between the original LSCF and BCFN perovskites, indicating the strong reaction between LSCF and BCFN and the formation of a single-phased perovskite. There are some broadened and bifurcated peaks in the XRD pattern of the mixture after calcinations at 1050 °C, but no such phenomena occur for the mixture after calcinations at 1100 °C. This

indicates that a single-phased perovskite structure is formed after the calcinations of the LSCF and BCFN mixture at 1100 °C for 4h. The newly formed materials are named LSBCFN oxides followed by the corresponding weight percent of LSCF materials in the mixture. For example, the $(\text{La}_{0.36}\text{Sr}_{0.24}\text{Ba}_{0.4})(\text{Co}_{0.4}\text{Fe}_{0.56}\text{Nb}_{0.04})\text{O}_{3\pm\delta}$ materials prepared by the calcination of LSCF and BCFN mixture at a weight ratio of 60:40 are nominated as LSBCFN60.

Figure 8.1 XRD pattern of LSBCFN materials after calcination at (a) 1050 °C and (b) 1100 °C for 4h.

Table 8.1 gives the (110) peak position and lattice parameter of LSCF, BCFN, and LSBCFN powders calcined at 1100 °C for 4h. The (110) peak gradually shifts

from the higher diffraction angle to the lower diffraction angle as the content of LSCF in the mixture for LSBCFN preparation decreases and the content of BCFN in the mixture increases, indicating the increase in the lattice parameter as the composition changes from LSCF to LSBCFN and finally to BCFN. LSCF has a unit parameter of 3.884 Å, and a unit volume of 58.6 Å³, which increases to 3.904 Å and 59.5 Å³ for the LSBCFN 60 materials. The lattice parameters increase to 3.986 Å and 63.3 Å³ for the LSBCFN30 materials. For the BCFN materials, the lattice parameters are 4.086 Å and 68.2 Å³, respectively. The specific reason for the increase remains unclear because a lot of factors, such as the change in the structure defects and size difference of the metal ions, can influence the lattice parameters of the perovskites.

Table 8.1 (110) peak position and lattice parameter of the BCFN, LSCF, and LSBCFN materials calcined at 1100 °C for 4h.

Composition	Position of (110) peak	Structure	a,b,c (Å)	α (°)	V (Å ³)
LSCF	32.560	Cubic	3.884	90	58.6
LSBCFN60	32.399	Cubic	3.904	90	59.5
LSBCFN50	32.259	Cubic	3.920	90	60.2
LSBCFN40	32.080	Cubic	3.945	90	61.4
LSBCFN30	31.720	Cubic	3.986	90	63.3
BCFN	30.940	Cubic	4.086	90	68.2

In this study, the LSBCFN oxide was also prepared through the solid state

reaction method, in which the corresponding metal oxides were mechanically mixed and calcined at 1100 °C for 4h. Figure 8.2 shows the XRD patterns of LSBCFN40 materials prepared by the solid state reaction method and direct calcinations of LSCF and BCFN mixture at 1100 °C for 4h. It can be observed the main cubic structure also formed in the LSBCFN40 materials prepared by the solid state reaction method. However, small peaks which do not belong to the cubic structure also appear in the pattern of LSBCFN40 oxides prepared by the solid state reaction method, indicating the existence of impurities. Therefore, LSBCFN powders prepared by the direct calcinations of LSCF and BCFN mixture at 1100 °C for 4h are adopted in this study.

Figure 8.2 XRD patterns of LSBCFN40 powders prepared by the solid state reaction method and direct calcinations of LSCF and BCFN mixture at 1100 °C for 4h.

8.2.2 Chemical compatibility with YSZ and GDC electrolyte materials

Chemical compatibility of LSBCFN pervoskites with YSZ and GDC electrolyte is also studied at 1100 °C. The LSBCFN cathodes are sintered at 1050 °C for 2h in this study. Figure 8.3 gives the XRD patterns of the mixture of LSBCFN40 and electrolyte powders after heating at 1100 °C for 4h.

Figure 8.3 XRD pattern of mixture of LSBCFN40 and electrolyte powders after heating at 1100 °C for 4h: (a) LSBCFN40+YSZ, and (b) LSBCFN40+GDC.

In the XRD pattern of the mixture of LSBCFN40 and YSZ (Figure 8.3a), new peaks appear in the XRD pattern of the mixture of LSBCFN40 and YSZ materials,

indicating partial reactions between the LSBCFN40 and YSZ materials at the temperature studied. The reaction product has been confirmed to be $\text{YBa}_3\text{Fe}_2\text{O}_{7.5}$ oxide with the cubic structure according to the XRD analysis. Therefore, YSZ is not suitable to be used as electrolyte for the LSBCFN cathode at temperature above 1100 °C due to their poor chemical compatibility. Meanwhile, peaks in XRD pattern of the LSBCFN40 and GDC mixture (Figure 8.3b) are just a simple combination of peaks belonging to LSBCFN40 and GDC materials, indicating good chemical compatibility between the LSBCFN and GDC electrolyte. In this study, GDC is adopted as electrolyte for the evaluation of LSBCFN cathode.

8.2.3 Electrochemical performance of LSBCFN cathode

Figure 8.4 shows the polarization resistance (R_E) of the LSBCFN cathodes as a function of the temperature. It can be observed that the LSBCFN cathodes have smaller R_E values than both the LSCF and BCFN cathodes above 650 °C, indicating the improved electrochemical performance of LSBCFN cathode materials. The LSBCFN40 cathodes possess the smallest R_E value among all the cathodes in the temperature range studied. Figure 8.5 shows the impedance curves of the LSCF, BCFN and LSBCFN40 cathodes without correction in ohmic resistance (R_Ω) at 600, 700, and 800 °C, respectively. It can be observed that the new LSBCFN40 cathode has R_E values of 0.02, 0.05 and 0.23 $\Omega \text{ cm}^2$ at 800, 700, and 600 °C respectively. The R_E values of the LSBCFN40 cathode are smaller than those of 0.05, 0.11 and 0.38 $\Omega \text{ cm}^2$ for BCFN cathode, and 0.05, 0.18 and 0.97 $\Omega \text{ cm}^2$ for LSCF cathode at 800, 700, and 600 °C respectively.

Figure 8.4 Polarization resistance (R_E) of LSBCFN cathodes as a function of temperature.

Figure 8.5 Impedance curves of the LSCF, BCFN and LSBCFN40 materials without correction in ohmic resistance (R_Ω) at 600 , 700 , and 800 °C.

Another interesting observation is that the BCFN cathode on GDC electrolyte has a much larger R_{Ω} value than the LSCF and BCFN cathodes on GDC electrolyte. Figure 8.6 compares the R_{Ω} values of the three cathodes on GDC electrolyte measured at different temperatures. R_{Ω} of BCFN cathode at 600 °C is 6.64 $\Omega \text{ cm}^2$, more than two times higher than R_{Ω} of 2.43 and 2.73 $\Omega \text{ cm}^2$ observed for LSCF and LSBCFN40 cathodes. As the cathodes were prepared on GDC electrolyte discs with more or less the same thickness, the significant difference in R_{Ω} of the BCFN, LSCF and LSBCFN40 cathodes is most likely due to the difference in the conductivities of the cathode materials. To support this view, conductivities of BCFN, LSCF and LSBCFN40 materials were characterized at different temperatures and the results are shown in Figure 8.7. For the mixed ionic and electronic conductors, the electronic conductivity is always at least one order of magnitude higher than the ionic conductivity. Therefore, the measured conductivity can be referred to the electronic conductivity. It can be seen that the conductivity of LSBCFN40 is 124 S cm^{-1} at 600 °C and 93 S cm^{-1} at 700 °C, significantly higher than the values of 11 S cm^{-1} at 600 °C and 13 S cm^{-1} at 700 °C for BCFN. Cheng [Cheng, Zhao et al. 2008] et. al. studied the conduction behavior and found that electron holes act as charge carriers in BCFN. The introduction of Nb ions into the B-site results in the partial reduction of $(\text{Co,Fe})^{4+}$ to $(\text{Co,Fe})^{3+}$ and hence decrease the concentration of electron holes for charge compensation. It explains why BCFN has such a low conductivity. As a result, it is reasonable to attribute the large R_{Ω} to the low conductivity of the BCFN, which also explains why

the cell with BCFN cathodes has very low power densities despite the good polarization performance.

Conductivities BCFN, LSBCFN40 and LSCF oxides show different temperature dependence behaviors (Figure 8.7b). The conductivity of LSBCFN40 increases with the increase of temperature, showing the characteristics of metallic conductors. For LSCF, the conductivity first increases with temperature, attains a maximum value at ~ 650 °C and then decreases as the temperature further increases, which is in agreement with the previous studies [Tai, Nasrallah *et al.* 1995; Tai, Nasrallah *et al.* 1995]. It clearly indicates that the conduction behavior of LSCF changes from a semi-conductor behavior at low temperature, observing the hopping mechanism, to a semi-metallic behavior at high temperature, observing the band-model conduction mechanism [Mizusaki, Matsuura *et al.* 1989]. The activation energy calculated for LSCF in the low temperature range is 0.07 eV. For BCFN, the conductivity shows the characteristics of semi-conductors and increases in the temperature range studied. A turning point is observed for BCFN at 550 °C (Figure 8.7b). The activation energy at 400-550 °C is 0.33 eV and it is 0.22 eV at 550-900 °C. The change in the activation energy may be attributed to the weak defect association at high temperature, which has influence on the hopping of small polarons and thus changes the activation energy [Cheng, Zhao *et al.* 2008].

Figure 8.6 Comparison of R_{Ω} values of LSCF, BCFN, and LSBCFN40 cathodes on GDC electrolyte at different temperature.

Figure 8.7 Conductivities of LSCF, BCFN and LSBCFN40 materials as a function of temperature: (a) $\sigma \sim T$, and (b) $\log(\sigma T) \sim 1000/T$.

In the cathode of SOFCs, the oxygen reduction reactions happened according to the equation below:

where $V_o^{\bullet\bullet}$ is the oxygen vacancy, e^- is the electrons and $O_o^{\times}$ is the normal oxygen ions in the lattice structure. The oxygen reduction reactions happen at the places where oxygen vacancy, oxygen and electrons are present; therefore, the transportation kinetics of them should influence the performance of the reactions. After the enhancement of the conductivity of the cathode materials, the cathode reaction kinetics becomes faster, which should be responsible for the improved electrochemical performance of the novel LSBCFN40 cathode materials.

Figure 8.8 shows the temperature dependence of polarization resistance (R_E) of LSCF, BCFN and LSBCFN40 cathodes in together with the activation energy calculated from the Arrhenius plot. A linear relationship between $\log(R_E)$ and $1000/T$ is clearly observed during the temperature range studied. The activation energy for the LSBCFN40 cathode calculated from the plot is 106 kJ mol^{-1} , compared with those of 112 kJ mol^{-1} for LSCF cathode and 90 kJ mol^{-1} for the BCFN cathode. The activation energy of LSCF, BCFN and LSBCFN40 cathodes is similar, but the electrode polarization resistance of the oxygen reduction reactions is significantly smaller as compared to the reaction at LSCF and BCFN cathodes. Therefore, LSBCFN40 is more suitable than LSCF and BCFN to be used as cathode of IT-SOFCs considering the polarization resistance.

Figure 8.8 Temperature dependence of polarization resistance (R_E) of LSCF, BCFN and LSBCFN40 cathodes.

Figure 8.9 gives the impedance and polarization curves of the LSCF, BCFN and LSBCFN40 cathodes as a function of cathodic current passage time at 200 mA cm⁻² and 900 °C in the absence of the Fe-Cr metallic interconnect. Impedance curves were measured at the open circuit condition. The ohmic resistance (R_Ω) decreased gradually during the test, which can be attributed to the improved contact between the cathode and the electrolyte. In the absence of Fe-Cr metallic interconnect, all the cathodes maintained nearly constant overpotential (η) and electrode polarization resistance (R_E) values during the current passage, showing typical characteristics of mixed oxygen ionic and electronic conductors for the O₂ reduction reactions. The LSBCFN40 cathode kept a R_E value of $\sim 0.006 \Omega \text{ cm}^2$, smaller than that of $\sim 0.05 \Omega \text{ cm}^2$ for both the LSCF and BCFN cathodes. It also confirms the better electrochemical catalytic activity of the LSBCFN40 cathode

than the LSCF and BCFN cathodes. η values for the LSCF, BCFN, and LSBCFN40 cathodes are about 8, 6, and 2 mV during the current passage (Figure 8.9 b, d & f). The constant R_E and η values of the cathodes during the current passage indicates the good stability of the LSCF, BCFN, and LSBCFN40 cathodes at 900 °C in the absence of the Fe-Cr metallic interconnect.

Figure 8.9 Impedance and polarization curves of the LSCF, BCFN and LSBCFN40 cathodes as a function of cathodic current passage time at 200mA cm^{-2} and 900 °C in the absence of the Fe-Cr metallic interconnect: (a,b) LSCF, (c,d) BCFN, and (e,f) LSBCFN. Impedance curves were measured at the open circuit condition.

Figure 8.10 shows I - V and EIS curves of the anode supported cell with NiO-GDC as anode, GDC thin film as electrolyte, and LSBCFN40 materials as cathode operated at different temperature using H_2 as the fuel. Figure 8.11 provides the cross-section SEM image of the full cell after the I - V test.

Figure 8.10 Performance of the anode supported cell with NiO-GDC anode, GDC thin film electrolyte, and LSBCFN40 cathode operated at different temperatures using H_2 as the fuel: (a) I - V curve, and (b) EIS spectroscopy.

Figure 8.11 Cross-section SEM image of the cell after the I - V test: (a) cell, (b) electrolyte layer, and (c) cathode layer.

The cell displays attractive performance with its maximum powder densities attaining 530 mW cm^{-2} at 600°C , 390 mW cm^{-2} at 550°C , and 215 mW cm^{-2} at 500°C . The polarization resistances of the cell are $0.22 \Omega \text{ cm}^{-2}$ at 600°C , $0.63 \Omega \text{ cm}^{-2}$ at

550 °C, and $1.62 \Omega \text{ cm}^{-2}$ at 500 °C. The maximum power density of the cell is much higher than that of 202 mW cm^{-2} at 600 °C for the cell with $\text{BaCo}_{0.7}\text{Fe}_{0.2}\text{Nb}_{0.1}\text{O}_{3-\delta}$ as the cathode reported by Zhu [2009] et. al.. It can be observed that the large polarization resistance at the low temperature range becomes the limiting factor governing the cell performance, which can be improved by further optimization the electrode microstructure and materials preparation process. It can be seen that a dense GDC electrolyte layer of $\sim 8 \mu\text{m}$ in thickness is successfully prepared and the LSBCFN40 cathode materials is well attached to the electrolyte film, indicating good adherence of the cathode materials to the GDC electrolyte (Figure 8.11).

8.2.4 Chromium-tolerance of LSBCFN40 cathode

Chromium poisoning effects and depositions at the LSBCFN40 cathode materials are also investigated to ensure good long-term stability of the cathodes under the SOFC working conditions in the presence of Fe-Cr metallic interconnect. Figure 8.12 gives the impedance and polarization curves of the LSCF, BCFN, and LSBCFN40 cathodes of the LSCF, BCFN and LSBCFN40 cathodes as a function of cathodic current passage time at 200 mA cm^{-2} and 900 °C in the presence of the Fe-Cr metallic interconnect. Impedance curves were measured under the open circuit condition.

Figure 8.12 Impedance and polarization curves of the LSCF, BCFN and LSBCFN40 cathodes as a function of cathodic current passage time at 200mA cm^{-2} and 900°C in the presence of the Fe-Cr metallic interconnect: (a,b) LSCF, (c,d) BCFN, and (e,f) LSBCFN40. Impedance curves were measured at the open circuit condition.

In the presence of Fe-Cr interconnect (Figure 8.12 a, c, & d), some fluctuations happened in R_Ω , which can be attributed to the formation and detachment of the chromium oxides formed on the interconnect surface. In contrast to the nearly constant R_E and η values in the absence of the interconnect, R_E and η measured in

the presence of RA446 interconnect increased with the cathodic polarization time for the LSCF, BCFN and LSBCFN40 cathodes, clearly indicating the chromium poisoning effects of the Fe-Cr metallic interconnect on the electrochemical activity of the cathodes. For the LSCF cathode, R_E increased from $0.11 \Omega \text{ cm}^2$ to $0.42 \Omega \text{ cm}^2$ and η increased from 23 mV to 122 mV during the 1200 min current passage. In the case of the BCFN cathode, R_E increased from $0.14 \Omega \text{ cm}^2$ to $0.19 \Omega \text{ cm}^2$ while η increased from 14 mV to 40 mV at the end of the test. For the LSBCFN40 cathode, R_E increased from $0.04 \Omega \text{ cm}^2$ to $0.07 \Omega \text{ cm}^2$ while η increased from 18 mV to 22 mV during the test.

As shown previously, the increase in η and R_E in the presence of the metallic interconnect can be taken as an effective criterion to evaluate the chromium poisoning effects. Larger increase in η and R_E means more serious chromium poisoning effects caused by the chromium depositions at the cathodes. The increase in η for LSCF, BCFN, and LSBCFN40 cathodes are 99, 26, and 4 mV respectively under the current passage of 200 mA cm^{-2} while the increase in R_E for the cathode are 0.31, 0.16, and $0.03 \Omega \text{ cm}^2$. The increase in η and R_E for the O_2 reduction in the presence of the Fe-Cr metallic interconnect on LSBCFN cathode is negligible, indicating that the LSBCFN40 cathodes has high chromium-tolerance towards Cr poisoning, as compared with the LSCF and BCFN cathodes.

Figure 8.13 shows the SEM image of the LSCF, BCFN, and LSBCFN40 cathodes before and after current passage of 200 mA cm^{-2} at 900°C in the presence

of the Fe-Cr metallic interconnect. The corresponding EDS analysis on the surface of the cathodes is provided in Figure 8.14.

Figure 8.13 Surface SEM image of the LSCF, BCFN, and LSBCFN40 cathodes before and after the 1200 min current passage of 200 mA cm^{-2} in the presence of the Fe-Cr metallic interconnect: (a) & (b) LSCF cathode, (c) & (d) BCFN cathode, and (e) & (f) LSBCFN40 cathode.

Figure 8.14 EDS analysis on the surface of the the LSCF, BCFN, and LSBCFN40 cathodes before and after the 1200 min current passage of 200 mA cm^{-2} in the presence of the Fe-Cr metallic interconnect: (a) & (b) LSCF cathode, (c) & (d) BCFN cathode, and (e) & (f) LSBCFN40 cathode.

It can be clearly observed that chromium depositions on the electrode surface decrease significantly as the electrode changes from LSCF electrode (Figure 8.13b) to LSBCFN40 electrode (Figure 8.13f), which explains why LSBCFN40 cathode shows much better chromium-tolerance than LSCF and BCFN cathode during the 1200 min current passage. For the LSCF electrode, the porous structure almost

disappears and the electrode surface is completely covered by a layer of large crystals, which is primarily composed of Sr and Cr element according to the EDS analysis (Figure 8.14b). The phase composition of the large crystals has been confirmed to be SrCrO_4 by XRD analysis in previous studies [Jiang, Zhang *et al.* 2006]. Cr depositions can also be observed on the surface of the BCFN cathode after the 1200 min current passage in the presence of the Fe-Cr metallic interconnect (Figure 8.13d). The electrode particles cannot be separated because they are covered by the chromium depositions according to the EDS analysis (Figure 8.14d); however, the porous structure still exists, indicating the decreased Cr depositions on the surface of BCFN cathode. For the LSBCFN40 cathode, there is no significant change in the cathode porous structure before and after the current passage in the presence of the interconnect (Figure 8.13e & f). Only can some scattered crystals be observed on the surface of the LSBCFN40 electrode surface and they are confirmed to be Cr depositions according to the EDS analysis (Figure 8.14f).

Therefore, the better stability of the LSBCFN40 cathode over LSCF and BCFN cathode during current passage in the presence of the Fe-Cr metallic interconnect can be attributed to the decreased chromium depositions at the electrode, indicating the enhanced chromium-tolerance of the LSBCFN40 cathode. To evaluate the long-term stability of LSBCFN40 cathode, the impedance and polarization curves of the LSBCFN40 cathode under a current passage of 200 mA

cm^{-2} at $900\text{ }^{\circ}\text{C}$ in the presence of the Fe-Cr metallic interconnect were measured for 100 h and the results are shown in Figure 8.15.

Figure 8.15 Impedance curves (a) and polarization curves (b) of the LSBCFN40 cathode under a current passage of 200 mA cm^{-2} at $900\text{ }^{\circ}\text{C}$ for 100h in the presence of the Fe-Cr metallic interconnect.

During the 100h current passage, R_E for the LSBCFN40 cathode increased from the initial value of $0.03\text{ }\Omega \text{ cm}^2$ to $0.12\text{ }\Omega \text{ cm}^2$ at the end and η increased gradually from 6 mV to 23 mV. The increase in R_E is $0.09\text{ }\Omega \text{ cm}^2$, which is even smaller than the increase in R_E of the LSCF and BCFN cathodes during the 20h current passage at $900\text{ }^{\circ}\text{C}$ in the presence of the interconnect. The increase in

overpotential (η) of the LSBCFN40 cathode materials was 17 mV during the 100h current passage, even smaller than the increase of 99 mV for LSCF cathode and 26 mV for BCFN cathode during the 20h test in the presence of the interconnect materials. The comparison clearly confirms the high chromium-tolerance of the LSBCFN40 cathode. Indeed, the LSBCFN40 cathode possesses the best chromium-tolerance among all the cathode materials have been studied so far, including the LSM, LSCF, LBCF, BCFN and LNF cathodes [Jiang, Zhang *et al.* 1999; Zhen and Jiang 2008]. In conclusion, LSBCFN40 materials can be used as the cathode for IT-SOFCs considering its good electrochemical performance and chromium-tolerance in the presence of the Fe-Cr metallic interconnect.

Figure 8.16 shows the surface SEM micrographs and the corresponding EDS analysis of the LSBCFN40 cathode after 100h long term stability test under a current passage of 200 mA cm^{-2} at 900°C in the presence of the Fe-Cr metallic interconnect. After the long-term stability test, chromium depositions can be clearly observed on the surface of the LSBCFN40 cathode (Figure 8.17a&b) and appear more serious than the chromium depositions at the LSBCF40 cathode during the previous 20h test (Figure 8.14f). However, the porous structure of the cathode can still be observed. The EDS analysis (Figure 8.17c) shows that the chromium depositions on the LSBCFN40 cathode surface are primarily composed of Ba, Sr, Cr and O, in agreement with the study on cobaltite cathodes in chapter 5. It confirms that the chromium deposition at the LSBCFN40 cathode is also closely

related to the A-site Sr and Ba dopant, which can react with the gaseous chromium species to form solid chromium depositions.

Figure 8.16 Surface SEM micrographs (a&b) and corresponding EDS analysis (c) of the LSBCFN40 cathode after 100h long term stability test under a current passage of 200 mA cm^{-2} at 900 °C in the presence of the Fe-Cr metallic interconnect.

8.3 Summary

A new LSBCFN40 cathode with high electrochemical performance and high chromium-tolerance was successfully developed by direct calcinations of the mixture of 40 wt. % LSCF and 60 wt. % BCFN oxides at 1100 °C in this study. The LSBCFN40 materials had a high conductivity of $\sim 124 \text{ S cm}^{-1}$ at 600 °C, compared with that of only $\sim 11 \text{ S cm}^{-1}$ for the BCFN cathode. The polarization resistance for the LSBCFN40 cathode was $0.02 \text{ } \Omega \text{ cm}^2$ at 800 °C, $0.05 \text{ } \Omega \text{ cm}^2$ at 700 °C and $0.23 \text{ } \Omega \text{ cm}^2$ at 600 °C, much smaller than those of the widely used LSCF cathodes, illustrating the high electrochemical catalytic activity of the LSBCFN40 cathode towards the oxygen reduction reactions. The anode-supported cell with LSBCFN40 as the cathode showed maximum power densities of 530 mW cm^{-2} at 600 °C, 390 mW cm^{-2} at 550 °C, and 215 mW cm^{-2} at 500 °C, indicating the potential application of LSBCFN40 materials as cathode materials for IT-SOFCs. The improved cell performance could be attributed to the increase in the conductivity of cathode materials, which effectively reduces the power density loss resulted by the ohmic resistance. The LSBCFN40 cathode materials also showed the best chromium-tolerance among all the cathode material studied so far and the increase in polarization resistance and overpotential during the 1200 min current passage at 900 °C in the presence of the Fe-Cr metallic interconnect is negligible. Chromium deposition characterization showed that the chromium deposition at the LSBCFN40 cathode was much less than those at the LSCF and BCFN cathode, which explains the high chromium-tolerance of LSBCFN40 cathode. The 100 h

long-term stability test at 900 °C in the presence of the Fe-Cr metallic interconnect confirmed that the LSBCFN40 cathode materials can be used as the cathode materials with high stability under the SOFC operating conditions.

CHAPTER 9 CONCLUSIONS AND RECOMMENDATIONS

9.1 Conclusions

The objective of this project was to fundamentally study the mechanism of chromium deposition and poisoning at cathodes of SOFCs and to develop chromium-tolerant cathodes. Based on the results of this project, the following conclusions have been obtained:

1. The $(\text{La}_{0.8}\text{Sr}_{0.2})_{0.95}(\text{Mn}_{1-x}\text{Co}_x)\text{O}_{3\pm\delta}$ (LSMC, $0.0 \leq x \leq 1.0$) cathodes showed improved electrocatalytic activity towards the oxygen reduction reaction as the B-site Mn was substituted by Co, which could be ascribed to the faster cathode reaction kinetics caused by the transformation of the cathode materials from pure electronic conductors, i.e., LSM ($x=0.0$), to mixed electronic and oxygen ionic conductors, i.e., LSC ($x=1.0$). However, the chromium deposition at the LSMC cathodes was closely related to the structure and valence instability of Mn and Sr ions, in the perovskite structure rather than the electrocatalytic activity of the cathodes. The chromium deposition on the electrolyte surface in contact with the electrode was caused by the segregation of MnO, which reacted with the gaseous chromium species to form the $(\text{Cr}, \text{Mn})_3\text{O}_4$ deposits while the chromium deposition on the electrode surface was primarily related to the segregation of SrO, which reacts with the gaseous chromium species to

form the SrCrO_4 deposits, confirming the chemical deposition mechanism at the LSMC cathode again.

2. Although the electrocatalytic activity of the $(\text{La}_{0.6}\text{Sr}_{0.4-x}\text{Ba}_x)(\text{Co}_{0.2}\text{Fe}_{0.8})\text{O}_{3-\delta}$ (LSBCF, $0.0 \leq x \leq 0.4$) cathodes is very close, the chromium deposition at the LSBCF cathodes significantly reduces as the Sr ions at the A-site are substituted by the Ba ions, indicating that the chromium deposition at the LSBCF cathodes are closely related to the contents of Sr and Ba ions at the A-site. The improved chromium-tolerance of the LSBCF cathode with high Ba and low Sr contents was most likely due to the lower thermodynamic stability of BaCrO_4 over SrCrO_4 . It also provided a strategy for the development of chromium-tolerant cathodes based on the cobaltite pervoskites.
3. The chromium deposition and poisoning effects at the LSM cathode could be effectively suppressed by using the Ni-Mo-Cr metallic interconnect. The decreased chromium deposition and poisoning effects could be attributed to the decrease in the vaporization kinetics of the gaseous chromium species from the Cr-free NiMn_2O_4 covered metallic interconnect.
4. The humidity of air, which had no significant influence on the electrocatalytic activity of the LSM cathode towards the oxygen reduction reactions, had a significant influence on the chromium deposition and poisoning effects at the LSM cathode. The water vapor in the air stream accelerated the chromium deposition and poisoning and should be kept as low as possible for SOFC

systems based on metallic interconnect.

5. A novel $(\text{La}_{0.24}\text{Sr}_{0.16}\text{Ba}_{0.6})(\text{Co}_{0.5}\text{Fe}_{0.44}\text{Nb}_{0.06})\text{O}_{3\pm\delta}$ (LSBCFN40) cathode was developed by the direct calcination of the mixture of LSCF and BCFN powders at 1100 °C for 6h. The new LSBCFN 40 cathode showed much better electrocatalytic activity towards the oxygen reduction reactions as compared with the constituent LSCF and BCFN cathodes. The cell composed of the Ni-GDC anode, GDC electrolyte and the LSBCFN40 cathode, achieved a maximum power density of about 530 mW cm⁻² at 600 °C, 390 mW cm⁻² at 550 °C, and 215 mW cm⁻² at 500 °C, indicating the potential application of the LSBCFN40 material as cathode materials for IT-SOFCs. The LSBCFN 40 cathode also showed excellent tolerance towards the chromium deposition and poisoning. During the long-term test in the presence of the metallic interconnect, the increases in polarization resistance and overpotential for the LSBCFN 40 cathode were only about 0.09 Ω cm² and 17 mV under a current passage of 200 mA cm⁻² at 900 °C for 100h, indicating the promising potential of using the LSBCFN40 cathode as the chromium-tolerant cathode for SOFCs.

9.2 Major achievements

1. The detailed and systematic study of chromium deposition and poisoning at LSMC and LSBCF cathode systems clearly demonstrated that the variation in the electrochemical activity of the cathodes did not necessarily lead to the increase or decrease in the chromium deposition. Rather, the chromium

deposition was closely related to the chemical affinity and stability of the specific species or ions which could induce the chromium deposition and grain growth on the cathode/electrolyte systems. In the case of LSMC system it was the segregation of manganese and strontium species from the perovskites, which significantly depended on the B-site Co/Mn ratio and in the case of LSBCF system, segregation of strontium depended strongly on the A-site Sr/Ba ratio and was the primary reason for the poor chromium-tolerance of the LSCF and LSBCF cathodes with high Sr content. The study provided solid evidence for the chemical nature of chromium deposition at SOFC cathodes.

2. The study also showed that the chromium deposition and poisoning could be minimized by developing new metallic alloys with low chromium vaporization and by reducing the humidity level in the air stream under the practical SOFC working conditions.
3. A new chromium-tolerant LSBCFN40 cathode was developed based on the direct calcination of the mixture of LSCF and BCFN powders at 1100 °C. The resulted single-phased LSBCFN cathode had high electrocatalytic activity towards the oxygen reduction reactions and excellent chromium-tolerance.

9.3 Recommendations

1. Investigation on the influence of cathode microstructure on the chromium deposition and poisoning effects at multi-layer functional graded cathode materials in the presence of metallic interconnect.

The multi-layer graded composite cathodes, i.e., graded LSM-YSZ [Antunes, Golec *et al.* ; Song, Lee *et al.* ; Simonet, Kapelski *et al.* 2007; Sun, Piao *et al.* 2008], LSM-YSZ-LSC [Hart, Brandon *et al.* 2002] or LSCF-LSM [Jin, Liu *et al.* 2008] cathodes have been widely used in SOFCs due to their possibility of joining dissimilar incompatible materials with different desired properties. Previous studies have primarily focused on the chromium deposition and poisoning effects at pure-phased cathode materials. However, the microstructure also has great influence on the electrochemical performance as well as chromium poisoning effects of the cathodes. Therefore, the study on the chromium deposition and poisoning effects at the widely used functional graded cathodes is highly recommended.

2. Further improvement of the chromium-tolerance of the LSBCFN cathode by reducing the Sr content at the A-site.

Previous studies have confirmed that the chromium-tolerance of the cobaltite cathodes can be improved by substituting the Sr ions with the Ba ions at the A-site. In this project, the LSBCFN40 cathode showed the best chromium-tolerance among all the cathodes studied previously, but its chromium tolerance can still be further improved by decreasing the Sr content at the A-site. Therefore, this part of work is highly recommended in the future work.

3. Study of the chromium deposition and poisoning effects at infiltrated cobaltite

cathodes.

Previous studies have shown that the performance of the LSM and LSCF cathode can be greatly improved by infiltrating an amount of PdO or GDC particles into the porous structure of the cathodes [*Liang, Chen et al. 2008; Chen, Liang et al. 2009; Vohs and Gorte 2009*]. Previous research works of the chromium deposition and poisoning effects at cobaltite cathodes have indicated that chromium deposition was caused by the reaction between the gaseous chromium species and the segregated SrO or BaO on the surface. Therefore, infiltrated PdO or GDC particles at a high loading can act as a barrier between the gaseous chromium species and the segregated SrO or BaO, reducing the chromium deposition at the cobaltite cathodes. This part of work is recommended in the future research.

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