

Chromium Poisoning of Cathode Materials in Solid Oxide Fuel Cells

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Chromium Poisoning of Cathode Materials in Solid Oxide Fuel Cells

by

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ABSTRACT

Intermediate temperature solid oxide fuel cells (SOFCs) operated at around 600 °C - 700 °C have recently attracted attention as high efficiency and low cost power generation systems because low cost materials such as stainless steels can be used as component materials (interconnects, manifolds, and gas supply tubes). However, when applying these metallic alloys, there arises a problem of poisoning of the cathode by chromium contamination. The degradation originates from vaporization of chromium from the surface of the alloys and the chromium vapor diffuses into the cathode and deposits at the electrochemically active sites during operation, resulting in a degradation of cathode performance.

Understanding of the chromium poisoning mechanism is important for the improvement of long-term stability of SOFC. Research efforts have been made to develop more durable cathode materials or clarify the degradation mechanism for each cathode. However, essential reaction mechanism in the chromium poisoning process has not been clearly understood yet.

The scope of this research is focused on the mechanism of chromium poisoning commonly applicable to many SOFC cathode materials, especially focusing on the influence of cathode polarization on the chromium deposition kinetics and the microscopic deposition site. This research contributes to obtain an ideal design of highly durable SOFC cathodes, necessary for the widespread commercialization of SOFC systems

In this research, we tried to clarify principle of chromium poisoning phenomena commonly applicable to many SOFC cathode materials, focusing on the influence of cathode polarization and microscopic distribution of the deposited chromium.

In chapter 4, chromium deposition kinetics and deposition profile were compared among three kinds of cathode using LSM, LSCF or LNF by changing cathode polarization. Influence of cathode polarization on the chromium deposition near the electrode reaction site was investigated.

In chapter 5, mechanism of chromium deposition on the zirconia and ceria electrolyte

surface was investigated by analyzing elemental distribution around the boundary of the zirconia surface and the deposited chromium, especially focusing on oxygen concentration near the zirconia electrolyte surface.

In chapter 6, chromium poisoning phenomena for different cathode materials, $\text{Pr}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (PrSM), $\text{Nd}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (NdSM) and $\text{Br}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$ (BSCF) were studied by regulating cathode polarization constant. Chromium deposition kinetics and deposition profile were compared and mechanism of the chromium deposition which predominantly affects the cathode performance was investigated.

固体酸化物形燃料電池における空気極材料のクロム被毒に関する研究

論文要旨

固体酸化物形燃料電池 (SOFC) は、高効率でクリーンな発電装置であり、資源の枯渇および地球温暖化問題を解決する革新的エネルギー技術として、様々な用途への実用化・大量普及が期待されている。しかし本格的な実用化・普及には、耐久性等にかかわる種々の技術課題が残されており、これらを解決していくことが重要である。SOFC の耐久性に関する技術課題の 1 つとして、空気極 (カソード) のクロム被毒・劣化現象がある。この現象は、SOFC の作動温度が高温であるため、構成材料に用いられる耐熱金属材料 (ステンレス鋼等) からクロムが微量蒸発して、カソード中に混入し長期的に劣化させるもので、クロム蒸発源を完全に除去することが困難である理由から、家庭用コージェネレーションシステム (エネファーム) が市販されている現在でも、主要な技術課題として広く認識されている。従来研究では、①一般的なカソード材料である $(\text{La}, \text{Sr})\text{MnO}_3$ (LSM) では、発電反応に伴うカソード過電圧により電極反応場にクロムが固体として析出しセル性能を低下させることが報告され、②クロムの析出機構には、酸素空孔が関与する電気化学的還元反応と、クロム析出の核となる物質の生成とその上に析出する化学的反応の 2 種類が提案され、③ $(\text{La}, \text{Sr})(\text{Co}, \text{Fe})\text{O}_3$ (LSCF) や $\text{La}(\text{Ni}, \text{Fe})\text{O}_3$ (LNF) は、クロム被毒に対して LSM よりも高い耐性を示すこと、なども報告されていた。しかし従来研究では、カソード過電圧の違いやクロム蒸気と反応性の違いなど種々の要因を含めた統一的な議論がなされておらず、クロム析出機構の詳細についても不明な点が多かった。本研究は、多くのカソード材料について共通的機構や差異を統一的に理解するため、カソード過電圧を基準としてクロム析出分布や析出速度を比較した。また析出したクロムのナノ領域における分布を詳細に観察することによって、クロム析出機構の解明に取り組んだ。その結果、カソード材料とクロム蒸気との反応性により分布に差異が生じるものの、カソード過電圧の上昇によって析出速度が増加する傾向は共通であることを明らかにした。また、カソード過電圧によって電極反応場、特に電解質 (ジルコニア等) 表面に生成する酸素空孔がクロム析出を促進する機構は共通的に予測され、この点においてカソード材料による差がないことを明らかにした。これらの成果により、クロム被毒に高い耐性を持つ SOFC カソードの設計に貢献できる。

本論文は以下の 7 章で構成される。

第1章では、SOFCの原理、特長、開発の歴史、最近の開発動向、ますます高まる今後の重要性について述べた。

第2章では、SOFCのカソード材料、電極反応の基礎、耐久性に関わる全体的な課題、クロム被毒・現象現象の位置づけ、クロム被毒に関する従来研究と課題を述べた。特に、高耐久性を示すカソード材料に開発のために、クロム被毒・劣化現象の共通機構や差異を統一的に理解することが重要であり、本研究の動機となっていることを述べた。

第3章では、本研究における実験方法を述べた。特に、カソード過電圧を基準とした材料評価方法、高分解能走査透過顕微鏡(STEM)を活用した微細構造・元素分布観察が本研究の特長であることを述べた。

第4章では、従来カソード材料であるLSM, LSCF, LNFを比較した。LNFはLSM同様にカソード過電圧上昇によって、電極反応場である電解質／カソード界面へクロム析出量が増加した。LSCFについては、初期の過電圧が200 mV以下の条件下では、カソードの表面側に析出した。300 mV以上になると、LSM, LNF同様に電解質／カソード界面へクロム析出量が増加した。カソード過電圧がクロム析出を支配し電流密度に対する相関は見られないことを明らかにした。実用面からこれら3種類を比較すると、LSCFが過電圧が最も低く(同一電流密度下)電極反応場から遠いカソード表面側からクロムが析出するため、実用上最も有利と考えられる。

第5章では、STEMを用いてナノ領域における分布を詳細に観察した。クロムの析出は、カソード材料であるLSM, LSCF, LNFの粒の上だけでなく、電解質として用いたジルコニアやセリアの表面にも顕著に観察され、カソードの電極反応場に対応していることが示唆された。カソード過電圧は、電極反応場における酸素活量低下と関連付けられるため、それに伴う酸素空孔の増加と対応すると考えられる。ジルコニアは元々電子伝導性を示さないため、ジルコニア表面に酸素空孔を生成させるためには、電子伝導性体が近傍に存在することが不可欠となるが、この役割をカソード材料から分離しジルコニア表面を薄く覆っているマンガンやニッケルが担うことが示唆された。実際に、ジルコニア表面に析出したクロムの近傍には全てこれらの元素が微量観察された。これらの元素は、セル作製時のカソード焼成工程(高温)または、カソード過電圧下で表面に広がったと考えられる。また、電子エネルギー損失分光(EELS)によって、析出クロム近傍におけるナノ領域の酸素濃度低下を確認し、酸素空孔がクロ

ム析出を促進する機構を支持するデータを得た。さらに過電圧によって、析出したクロム上にも酸素空孔が発生し、継続的に析出サイトとなることが示唆された。

第6章では、別のカソード材料として $(\text{Pr}, \text{Sr})\text{MnO}_3$ (PrSM) $(\text{Nd}, \text{Sr})\text{MnO}_3$ (NdSM), $(\text{Ba}, \text{Sr})(\text{Co}, \text{Fe})\text{O}_3$ (BSCF)を検討した。PrSM, NdSMについてはLSMと同様の結果が得られた。すなわち、カソード過電圧上昇によって電解質/カソード界面のクロム析出が促進された。ジルコニア電解質上へのクロム析出も同様の結果であり、カソード材料から分離したネオジウムやマンガンがジルコニア表面に存在し、ジルコニア表面に酸素空孔を生成させ、クロムの析出サイトを提供していることが示唆された。BSCFについては、カソード過電圧上昇によりクロム析出量は増加するものの、LSCFの場合と同様にカソード表面側に析出しやすいことも明らかにした。

第7章では本論文を総括した。

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CHAPTER 1

INTRODUCTION

1.1 Motivation

Intermediate temperature solid oxide fuel cells (SOFCs) operated at around 600 °C - 700 °C have recently attracted attention as high efficiency and low cost power generation systems because low cost materials such as stainless steels can be used as component materials (interconnects, manifolds, and gas supply tubes). However, upon applying these metallic alloys, there arises a problem of poisoning of the cathode by chromium contamination. The degradation originates from vaporization of chromium from the surface of the alloys and the chromium vapor diffuses into the cathode and deposits at the electrochemically active sites during operation, resulting in a degradation of cathode performance.

Understanding of the chromium poisoning mechanism is important for the improvement of long-term stability of SOFC. Research efforts have been made to develop more durable cathode materials or clarify the degradation mechanism for each cathode. However, essential reaction mechanism in the chromium poisoning process has not been clearly understood yet.

The scope of this research is focused on the mechanism of chromium poisoning commonly applicable to many SOFC cathode materials, especially focusing on the influence of cathode polarization on the chromium deposition kinetics and the microscopic deposition site. This research contributes to obtain an ideal design of highly durable SOFC cathodes, necessary for the widespread commercialization of SOFC systems

1.2 Fuel Cells

1.2.1 Introduction

Unit of fuel cell is composed of three basic elements, namely, anode, electrolyte, and cathode as follows:

(-) fuel, anode || electrolyte || cathode, air (+)

Species of mobile ion vary among different types of fuel cells according to their electrolyte material. The mobile ion species transferring through the electrolyte

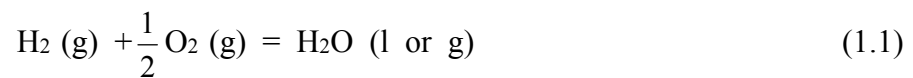
dominate the electrodes reaction and suitable electrode materials in anode and cathode. According to the phase of electrolyte, fuel cells can be divided into three systems as shown in Table 1-1.

Table 1-1: Types of fuel cell according to electrolyte phase [1]

Electrolyte phase	Mobile ion	Model materials
Aqueous solution system	H^+ OH^-	$\text{H}_2\text{SO}_{4\text{aq}}$; $\text{H}_3\text{PO}_{4\text{aq}}$; polymer membrane
Molten salt system	CO_3^{2-}	$\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3$; $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$
Solid oxide system	O^{2-}	$\text{ZrO}_2\text{-Y}_2\text{O}_3$; $\text{Ce}_2\text{O}_3\text{-Gd}_2\text{O}_3$

Driving force of ionic transport through electrolyte originates from difference in partial pressure of oxygen or hydrogen between the anode and the cathode. In other words, chemical potential gradient causes electromotive force. Acid aqueous solution system working based on the difference in hydrogen concentration is classified as hydrogen concentration cell, while molten salt system and solid oxide system working based on the difference in oxygen concentration are classified as oxygen concentration cell. (Precisely, MCFC works also on the CO_2 concentration.)

In the fuel cell utilizing hydrogen, the overall chemical reaction can be simply represented as follows:



In the case of combustion, heat corresponding to ΔH is generated by this reaction. In the case of fuel cell, electrical energy corresponding to ΔG is generated under reversible condition:

$$\Delta G = \Delta H - T \cdot \Delta S \quad (1.2)$$

where ΔG is the change in Gibbs free energy, ΔH is the change in enthalpy, T is the absolute temperature, and ΔS is the change in entropy.

For a fuel cell operated at 25°C, these parameters have the following values:

$$\Delta H = -286 \text{ (kJ mol}^{-1}\text{)}, \quad \Delta S = -164 \text{ (J K}^{-1} \text{ mol}^{-1}\text{)}$$

indicating ΔG equals to $-237 \text{ (kJ mol}^{-1}\text{)}$ can be obtained as electrical energy. Thermodynamic efficiency (eff_{th}) of fuel cell is defined as:

$$eff_{th} = \frac{\Delta G}{\Delta H} \quad (1.3)$$

The thermodynamic efficiency of hydrogen-oxygen fuel cells is thus 83% at 25°C, and higher thermodynamic efficiency than 90% can be obtained in the case of hydrocarbon fuels. The thermodynamic efficiency of hydrogen-oxygen fuel cells generally decreases with increasing temperature. On the contrary, in the case of heat engines, the thermodynamic efficiency is limited by the Carnot efficiency and it generally increases with increasing temperature. The electrical efficiency of a conventional thermal power plant is typically around 50%.

The correlation between the maximum obtainable cell potential and the change in Gibbs free energy is given by:

$$\Delta G = -n \cdot F \cdot E \quad (1.4)$$

which is defined as the Nernst equation, where n is the number of electrons involved ($n = 2$ in the case of equation (1.1)), F is the Faraday constant ($96,500 \text{ C mol}^{-1}$), and E is the theoretical cell potential. Electrochemical efficiency (eff_{el}) of a fuel cell is defined as:

$$eff_{el} = \frac{V}{E} \quad (1.5)$$

and it can be calculated by using $E = 1.23 \text{ V}$, where V is the terminal voltage of the fuel cell under electrical load conditions [2].

1.2.2 History

William Grove first invented the fuel cell as early as 1839[3], demonstrating recombination of hydrogen and oxygen to produce electric current following electrolysis. Despite its long history of 170 years since the discovery, it was not until the beginning of the 20th century that R&D started with the object of putting fuel cells to practical use. It is said that a British engineer, Francis Bacon, developed the first practical H₂/O₂ fuel cells. Considering the expensive platinum catalyst used in dilute sulphuric acid as electrolyte employed by Ludwig Mond and his assistant Charles Langer, Bacon test-produced an improved fuel cell using alkaline electrolytes and inexpensive nickel electrodes that became the basis of the later developed NASA Apollo program fuel cell.

In 1961, the National Aeronautics and Space Administration (NASA) launched a technological development plan for fuel cells as a national project, leading to development of polymer electrolyte membrane fuel cell (PEFCs), which delivered 1kW of electric power, and first practically used in a manned spacecraft, Gemini 5. Alkaline fuel cells (AFCs) were adopted subsequently for powering satellites instead of PEFCs, since at that time the performance of PEFC was not sufficiently high. In the 1960s, the tendency of using fuel cells on earth gained momentum, with the phosphoric acid fuel cells (PAFCs) developed and field-tested as a candidate for early stationary applications.

Major issues associated with the reliability or durability of fuel cells began to be recognized in the early 1990s while some fuel cell R&D programs were underway. In 1996, however, the appearance of an innovative commercial 200kW fuel system built by OSNI Co. contributed to maintain users' hope ranging over various fields. Moreover, remarkable improvement in fuel cells' performance and scalability has made them gain increasing attention as promising future energy devices for distributed power generation, mobile power, or vehicles.

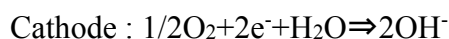
1.2.3 Types of fuel cells

At present, there are several types of fuel cells that are being developed in many fields. For example, PAFC and MCFC are targeted for distributed power generation

(co-generation, alternative emergency power source); PEFC has been commercialized as co-generation system for household and is being applied to transportation especially for automobile; AFC is applied to artificial satellite power and has been successfully applied to the spaceship and so on. SOFC has been commercialized as co-generation system for household and is also targeted for many applications such as distributed power generation, portable power sources, and auxiliary power unit for automobile application.

Alkaline Fuel cells (AFCs)

AFC was used in the mid-1960s by NASA in the manned Apollo space flights. In AFCs, the electrolyte consists of potassium hydroxide (KOH) in an aqueous (water) solution, where OH⁻ migrates from the cathode to the anode to provide water and electrons:



AFCs are operated at temperatures between 20 and 90 °C, depending on the concentration of KOH in the electrolyte. The major disadvantage of AFCs is that usage on earth is unsuitable since CO₂ in air can deteriorate the alkaline electrolytes by forming carbonate. AFCs are thus currently restricted to specialized applications (e.g. military and space applications). The advantage of AFCs is that the cathode reaction is fast in an alkaline electrolyte and there is no need to use platinum for the electrode materials.

Aqueous solution or solid polymer system--- Polymer Electrolyte Fuel Cells (PEFCs), Direct Methanol Fuel Cells (DMFCs), and Phosphoric Acid Fuel Cells (PAFCs)

PEFC (PEMFC) is composed of a proton-conducting polymer electrolyte membrane, usually an organic perfluorinated sulfonic acid polymer. The polymer membrane is coated on both sides with a thin catalyst layer composed of platinum-based catalyst supported on porous carbon black. This sandwich structure is known as a

membrane electrode assembly (MEA). Due to the low operating temperature, corrosion and failure of cell components are reduced in comparison with other high-temperature fuel cells, and start-up of operation is very quick. On the other hand, management of the water and heat in the membrane is a key issue for obtaining high performance and stability. Necessity of expensive precious metals for electro catalysts and low tolerance to impurities contained in fuels are other major PEFC disadvantages. To date, PEFCs have been demonstrated to exhibit high efficiency and R&Ds are actively underway toward transportation, mobile, and residential applications.

DMFCs are categorized as fuel cells utilizing methanol directly without reforming methanol. In most cases, the component materials of DMFCs are similar to those of PEFCs. DMFCs are targeted for high energy density mobile power applications in which conventional lithium ion battery cannot satisfy the requirements. [3].

PAFC has been developed for the purpose of distributed power generation or tactical military power [4]. In PAFC, highly-concentrated phosphoric acid (H_3PO_4) liquid, retained in a Teflon-bonded SiC matrix, is used as the electrolyte. Platinum catalyst supported by porous carbon is employed for both anode and cathode. One of the advantages of PAFC compared to PEFC is its verified durability up to several tens thousand hours and its high tolerance to impurities such as CO or H_2S . One of the disadvantages of PAFC is relatively low cell performance. PAFCs are used mainly for stationary power generation, but some have been applied in large vehicles such as city buses.

Molten salt system--- Molten carbonate fuel cells (MCFCs)

Electrolyte in molten carbonate fuel cell (MCFC) is usually a mixture of alkali carbonates, i.e., Li_2CO_3 and K_2CO_3 , impregnated in a LiAlO_2 matrix. Mobile ion in MCFC is CO_3^{2-} and its operating temperature is around 650°C , where the alkali carbonates form a highly conductive molten salt, with carbonate ions providing ionic conduction. The advantages of MCFC are that it has a higher electrical efficiency and potential flexibility to use various types of fuels and inexpensive catalysts. Nevertheless, the high operating temperature can result in corrosion and breakdown by mechanical

stresses occurred during thermal cycles.

Solid oxide system---Solid Oxide Fuel Cells (SOFCs)

SOFC employs a solid oxide electrolyte, which exhibits high oxygen ionic conductivity at high temperatures ranging from 600 to 1000°C. The most commonly-used electrolyte is yttria-stabilized zirconia (YSZ), where ionic conduction via oxygen vacancies takes place.

Advantages of SOFCs are high electrical efficiency, fuel flexibility, and ability to realize highly efficient cogeneration systems by utilizing high-temperature exhaust heat. Major disadvantages of SOFC are caused by its high operating temperature, such as mechanical or chemical incompatibility between each component. Hence, recent R&D trend is directed toward improvement of durability and reliability or lowering the operating temperature down to an intermediate temperature range of 400–600°C.

Components and reactions of each fuel cell type is summarized in Table 1-2. In this study, research is focused on SOFC and detailed overview on SOFC is described in Section 1.3.

Table 1-2: Summary of components and reactions of fuel cell types.

Fuel cell type	Operating temperature(°C)	Reactant gas		Electrolyte	Mobile ion	Applications	Advantages
		Fuel	Oxidant				Disadvantages
Alkaline (AFC)	20–90	H ₂	O ₂ , Air (without CO ₂)	KOH solution (liquid)	OH ⁻	Tactical military power Space application	High performance and low cost Multi-catalyst capability Unsuitable for on-earth use
Polymer electrolyte (PEFC)	20–100	H ₂ , CH ₃ OH	O ₂ Air	Organic perfluorinated sulfonic polymer (solid)	H ⁺	Backup power, Transportation, Portable power, Distribute power generation, Vehicle	Low temperature Quick start up Easy maintenance Difficult water management Lower tolerance to CO poison
Phosphoric Acid (PAFC)	150-200	H ₂	O ₂ Air	H ₃ PO ₄ (liquid)	H ⁺	Distributed power generation Tactical military power	Developed related technologies Higher efficiency with waste heat utilization Relatively lower electrical efficiency
Molten Carbonate (MCFC)	600-700	H ₂ CO	Air (with CO ₂)	(Li,K) ₂ CO ₃ solution (liquid)	CO ₃ ²⁻	Distributed power generation (large scale)	Multi-fuel/catalyst capability Necessity of CO ₂ recycle Slow start up Poor tolerance against thermal cycling
Solid Oxide (SOFC)	600-1000	H ₂ CO C _x H _y	Air	ZrO ₂ (Y ₂ O ₃), ZrO ₂ (Sc ₂ O ₃), CeO ₂ (Gd ₂ O ₃), La(Sr)Ga(Mg)O ₃ (Solid)	O ²⁻	Auxiliary power unit Distributed power generation Portable power	Multi-fuel/catalyst capability High efficiency with waste heat utilization Higher tolerance to impurities Poor tolerance against thermal cycling

1.3 Solid Oxide Fuel Cells (SOFCs)

1.3.1 Origin and evolution of solid oxide fuel cells

SOFCs are the most efficient fuel cell devices which can convert chemical fuels directly into electrical power. The main features of SOFCs are all solid-state construction and high-temperature operation. The combination of these features leads to a number of unique characteristics and advantages for this type of fuel cell, including flexibility in cell and stack designs, manufacturing processes, and power plant sizes [5].

Emil Baur, a Swiss scientist and his colleague H. Preis experimented on solid oxide electrolytes in the late 1930s, using such materials as zirconium, yttrium, cerium, lanthanum, and tungsten oxide. The operation of the first ceramic fuel cell at 1000°C, by Baur and Preis, was achieved in 1937 [6]. In the 1940s, O. K. Davtayan of Russia added monazite sand to a mixture of sodium carbonate, tungsten trioxide, and soda glass, in order to increase the conductivity and mechanical strength. Davtayan's design, however, also experienced unwanted chemical reactions and short life time. By the late 1950s, research into solid oxide technology began to accelerate at the Central Technical Institute in Hague, Netherlands, Consolidation Coal Company, in Pennsylvania, and General Electric, in Schenectady, New York. A 1959 discussion of fuel cells noted that problems with solid electrolytes included relatively high internal electrical resistance, melting, and short-circuiting, due to semi-conductivity. Not everybody gave up on solid oxides, however. Advantages of SOFC such as tolerance of carbon monoxide and use of a stable solid electrolyte continued to draw modest attentions. Researchers at Westinghouse, for example, experimented on a cell using zirconium oxide and calcium oxide in 1962. More recently, soaring energy prices and advances in materials technology have re-activated work on SOFCs, SOFC-micro turbine co-generation unit built by Siemens Westinghouse and Northern Research and Engineering Corporation was evaluated since April 2000. In a year of actual operating conditions, the 220 kW SOFC, running on natural gas is achieving an efficiency of 60%. Also, a world record for SOFC operation, roughly eight years, and the prototype cells have demonstrated two critical successes: the ability to withstand more than 100 thermal cycles, and voltage

degradation of less than 0.1% per thousand hours. Moreover, a 140 kW peak power SOFC cogeneration system, supplied by Siemens Westinghouse, was operated in Netherlands for over 16,600 h, becoming the longest running fuel cell system in the world. The first demonstration of the commercial prototype cells in a full scale SOFC module is equally significant.

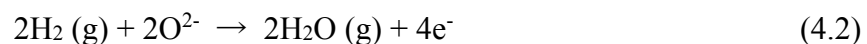
Currently, research is focused towards the development of high performance SOFCs at low temperatures (700°C or below), termed intermediate-temperature SOFC (IT-SOFC), where inexpensive stainless steels can be used as module components. Additionally, micro-SOFC is gaining increased attention owing to its high volumetric energy density [7, 8].

1.3.2 Principle of operation

Fuel cell in general converts chemical energy of the fuel directly into electrical energy without converting it to mechanical energy. Therefore, fuel cell has large potential to achieve high electrical conversion efficiency while conventional technologies are limited by the Carnot efficiency. **Figure. 1-1** shows the principle of SOFC operation. The basic unit of SOFC, i.e. cell, consists of an electrolyte sandwiched with two electrodes of anode and cathode. In the electricity generation process, oxide ion O^{2-} is generated in the cathode from oxygen in air.



Electrolyte consists of metal oxide which exhibits oxide ion conductivity at high temperatures, and normally SOFCs are operated at around 600 - 900 °C. Oxide ions generated in the cathode move to the anode and undergo the following reaction.



Not only hydrogen but also carbon mono-oxide can contribute to generate electricity in SOFC. Even when a hydrocarbon is used as fuel, hydrogen and carbon

mono-oxide can be produced by steam reforming reaction or partial oxidation reaction in the anode of the cell.

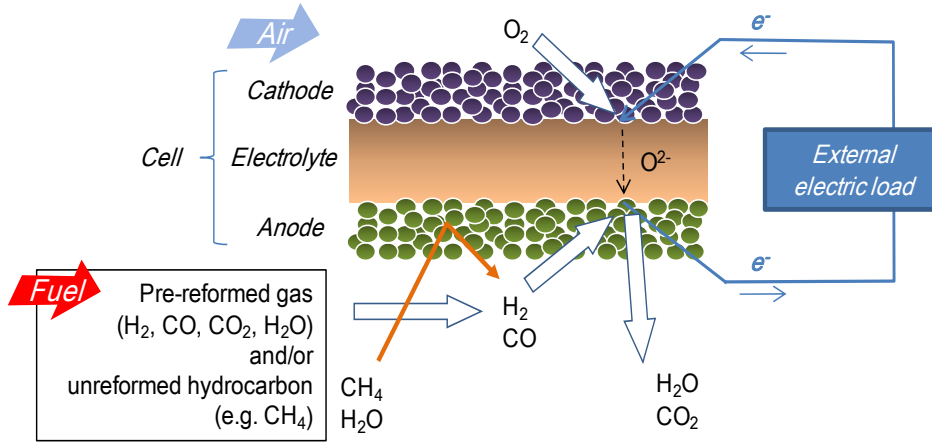


Figure 1-1. Principle of SOFC operation.

As described in section 1.2.1, theoretical value of electromotive force (EMF) can be derived from the difference in chemical potential μ . In SOFC, the difference in chemical potential of oxygen between the cathode and the anode is the driving force for the transport of oxide ions in the electrolyte:

$$\Delta G = -4EF = \mu(O_{2,a}) - \mu(O_{2,c}) \quad (1.6)$$

where E is the theoretical voltage. Chemical potential of oxygen is described as follows:

$$\mu(O_2) = \mu^\circ(O_2) + RT \ln p(O_2) \quad (1.7)$$

where $\mu^\circ(O_2)$ is the standard chemical potential,

$$E = \frac{RT}{4F} \ln \left(\frac{p(O_{2,c})}{p(O_{2,a})} \right) \quad (1.8)$$

$$p(O_2, a) = \frac{1}{K_H} \left(\frac{p(H_2O, a)}{p(H_2, a)} \right)^2, \Delta G_f^o = -RT \ln K_H \quad (1.9)$$

where K_H is the equilibrium constant of the reaction below,



and ΔG_f^o is the standard Gibbs free energy of $2H_2O$ formation.

Therefore, the correlation between the partial pressure and the theoretical voltage is given by the following equation:

$$E = -\frac{\Delta G_f^o}{4F} - \frac{RT}{2F} \ln \left(\frac{P(H_2O, a)}{P(H_2, a)}, a \right) + \frac{RT}{4F} \ln P(O_2, c) \quad (1.11)$$

For a SOFC operating at 800°C and 1 atm using 3%-humidified H_2 as a fuel and air as an oxidant, these variables have the following values and $E = 1.09$ V is obtained,

$$p(O_2, a) = 2.61 \times 10^{-18} \quad (\text{atm}), \quad p(O_2, c) = 0.21 \quad (\text{atm}),$$

$$-\Delta G_{1800}^o (H_2O) = -377.372 (\text{KJ}), \quad R = 8.314 \text{ J} \cdot (\text{mol}^{-1} \cdot \text{K}^{-1}), \quad F = 9.648 \times 10^4 (\text{C/mol})$$

Open circuit voltage (OCV) should be equal to the theoretical voltage (E) calculated above when there is no gas leakage. Cell voltage becomes lower than the OCV due to internal resistances when current flows through the circuit. The internal resistance is composed of ohmic losses of the components and resistance of electrochemical reaction at the electrodes as shown in Equation 1.12 or Equation 1.13.

$$V = E - i(R_a + R_e + R_c + R_{ae} + R_{ce}) \quad (1.12)$$

$$V = E - iR_t - (\eta_a + \eta_c) \quad (1.13)$$

where i is the current density of the cell; R_a , R_e and R_c are the ohmic resistances of anode, electrolyte, and cathode, respectively; R_{ae} and R_{ce} are the electrochemical reaction resistance of anode and cathode; η_a and η_c are the overpotentials (polarization) of anode and cathode, respectively. With increasing current density, cell voltage drops due to all kinds of resistances. Typical correlation between cell voltage and current density are shown in **Figure 1-2**.

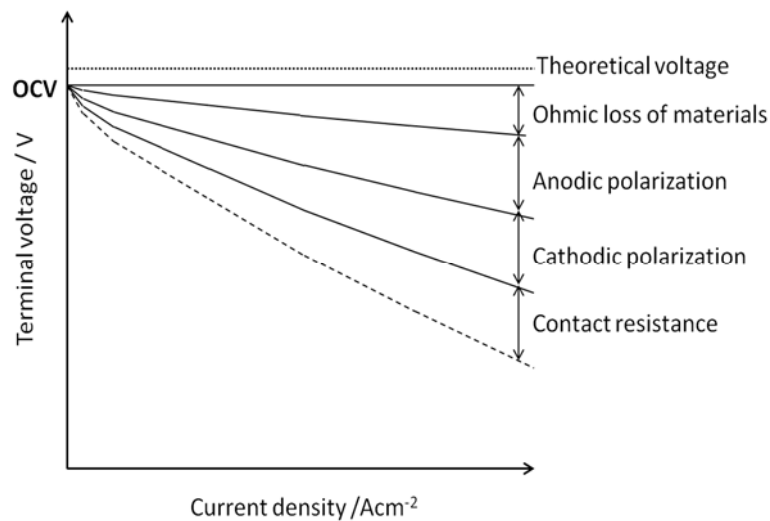


Figure 1-2. Typical correlation between cell/stack terminal voltage and current density.

1.3.3 Component materials and structure of cell and stack

Table 1-3 shows requirements for component materials of cell and interconnector and the typical materials. Electrolyte is required to be gas-tight to suppress leak of fuel and oxidant. Both electrodes need to be porous to provide electrode reaction sites. Interconnector plays a role of electrically connecting anode of one cell and cathode of the adjoining cell, and it must also separate the fuel in the anode from the oxidant in the cathode. Each component material must be heat resistant and durable in the atmosphere it is exposed during SOFC operation. That is, cathode side becomes highly oxidative atmosphere and anode side becomes highly reductive atmosphere.

To fabricate a cell, powders of these component materials are used as starting materials. They are formed into desired shapes by the general ceramic processing such

as extrusion, slip casting, pressing, tape casting, printing and dip coating. After the formation, these "green" ceramics undergo heat-treatments called firing or sintering. Sintering at high temperature above 1300 °C is normally required to obtain a dense and gas tight electrolyte layer.

Table 1-3: Requirements and typical materials used for cell and interconnector.

		Requirements	Typical materials
Cell	Electrolyte	Gas tight, Ionically conductive	Y ₂ O ₃ -stabilized ZrO ₂ (YSZ), Sc ₂ O ₃ -stabilized ZrO ₂ (ScSZ), Gd ₂ O ₃ doped CeO ₂ (GDC), (La,Sr)(Ga,Mg)O ₃ (LSGM))
	Anode	Porous, Electrochemically active, Electronically conductive	NiO-YSZ, NiO-ScSZ, NiO-GDC
	Cathode	Porous, Electrochemically active, Electronically conductive	(La,Sr)MnO ₃ , (La,Sr)(Fe,Co)O ₃
Interconnector		Gas tight, Electronically conductive	(La,Sr)CrO ₃ , (La,Ca)CrO ₃ , (Sr,La)TiO ₃ , Stainless steel

(I) Electrolyte

Specific material are used as an electrolyte when they show ionic transport number near the unity, and then the theoretical voltage determined by the oxygen potential difference can be obtained. Current technology employs several ceramic materials as the state-of-the-art SOFC components. Although a variety of oxide combinations has been used for solid non-porous electrolytes, the most common to date has been the stabilised zirconia with conductivity by oxygen ions (O²⁻), especially yttria-stabilised zirconia (Y₂O₃—stabilized ZrO₂ or YSZ, (ZrO₂)_{0.92}(Y₂O₃)_{0.08} for example) in which a small amount of Y₂O₃ is added to the zirconia during manufacturing. This choice is mainly due to availability and cost (70% of the world's supply of zirconia comes from

Australia). YSZ exhibits purely oxygen ionic conduction (with very low electronic conductivity) at 1000 °C and $p(\text{O}_2) > 10^{-25}$ atm. The crystalline array of ZrO_2 has two oxide ions to every zirconium ion. But in Y_2O_3 there are only 1.5 oxide ions to every yttrium ion. This results in oxygen vacancy formation in the crystal structure where oxide ions are missing. Oxide ions from the cathode thus leap from a hole to a neighboring hole in the oxygen sub-lattice until they reach the anode. The most commonly used stabilizing dopants are CaO , MgO , Y_2O_3 , Sc_2O_3 and certain rare earth oxides such as Nd_2O_3 , Sm_2O_3 , Yb_2O_3 . Other oxide based ceramic electrolytes that can be used in SOFCs include doped cerium oxide electrolyte, such as cerium oxide doped with gadolinium (GDC) while they exhibit electronic conduction at 800°C and $p(\text{O}_2) < 10^{-10}$ atm, thus resulting in a lower OCV. Besides, cerium oxide doped with samarium (SDC), cerium oxide doped with yttria (YDC), cerium doped with calcia (CDC), lanthanum gallate ceramic that include lanthanum, strontium, gallium, and magnesium (LSGM), bismuth yttrium oxide (BYO), barium cerate, and strontium cerate are being developed [9].

(II) Anode

Metals can be used as SOFC anode materials because of the reducing conditions in the presence of the fuel gas. Moreover, these metals must be non-oxidized since the composition of the fuel changes during the operation of the cell. SOFC anodes are fabricated from composite powder mixtures with nickel oxide NiO (the nickel oxide subsequently being reduced to nickel metal prior to operation), electrolyte material (YSZ, GDC, or SDC) and which serves to inhibit sintering of the metal particles and to provide a thermal expansion coefficient comparable to those of the other cell materials. NiO/YSZ anode material is suitable for applications with YSZ electrolyte material. NiO/SDC and NiO/GDC anode materials are best used with ceria-based electrolyte materials. The anode structure is fabricated with a porosity of 30–50% to ensure mass transport of reactant and product gases.

(III) Cathode

Because of the high operating temperature of SOFCs, only noble metals or electronic conducting oxide can be used as cathode materials. Noble metals are unsuitable for practical applications because of their cost and insufficient long term stability. Several complex oxides have been proposed and tested. The choice of the electrode material depends on the target application, the specific ceramic electrolyte material, the desired operating temperature range, the electrochemical cell design, and the specific ceramic fabrication methods. Perovskite-type lanthanum strontium manganite, $\text{La}(\text{Sr})\text{MnO}_3$ (LSM) and lanthanum calcium manganite, $\text{La}(\text{Ca})\text{MnO}_3$ (LCM) offer an excellent thermal expansion matching with the zirconia-based electrolytes and provide good performance at operating temperatures above 800°C . For applications requiring lower temperature operation ($600\text{--}800^\circ\text{C}$), a range of alternative perovskite-structured ceramic electrode materials are available. These include: lanthanum strontium ferrite (LSF), lanthanum strontium cobaltite (LSC), lanthanum strontium cobaltite ferrite (LSCF), lanthanum strontium manganite ferrite (LSMF), samarium strontium cobaltite (SSC), lanthanum calcium cobaltite ferrite (LCCF), praseodymium strontium manganite (PSM), $(\text{PrSr})\text{MnO}_3$, and praseodymium strontium manganite ferrite (PSMF) etc.

For even better electrode performance, some companies offer a line of composite electrode powders, with electrolyte materials (YSZ, SDC, or GDC) mixed with the perovskite electrode materials (LSM, LSF, or PSMF). The incorporation of electrolyte material into the cathode material has been shown to improve electrode performance at lower temperatures by increasing the number of active sites available for electrochemical reactions. Similar to the anode, the cathode has a porous structure that must permit rapid mass transport of reactant and product gases.

1.3.4 Component materials for SOFCs

The configurations in SOFC single cells can be classified into two broad categories: self-supporting and external-supporting. In the self-supporting configuration, one of the cell components (often the thickest layer) acts as the cell structural support. Thus, single

cells can be designed as electrolyte-supported, anode-supported, or cathode-supported. In the external-supporting configuration, the single cell is configured as thin layers on the interconnect or a porous substrate. Various cell configurations for SOFCs are schematically shown in **Figure1-3**. The key features of each configuration are summarized in **Table 1-4**.

The main function of the electrode is to bring about reaction between the reactant (fuel or oxygen) and the electrolyte, without itself being consumed or corroded. It must also offer the contacts of the three phases, i.e., the gaseous fuel, the solid electrolyte, and the electrode itself. The anode, used as the negative electrode of the fuel cell, disperses the hydrogen gas equally over its whole surface and conducts the electrons that are freed from hydrogen molecule, to be used as a useful power in the external circuit. The cathode, the positive electrode of the fuel cell, distributes the oxygen fed to it onto its surface and conducts the electrons back from the external circuit where they can recombine with oxygen ions, passed across the electrolyte, and hydrogen to form water. The electrolyte determines the operating temperature of the fuel cell and is used to prevent the two electrodes to come into electronic contact by blocking the electrons. It also allows the flow of charged ions from one electrode to the other to maintain the overall electrical charge balance. It can either be an oxygen ion conductor or a hydrogen ion (proton) conductor, the major difference between the two types is the side in the fuel cell on which the water is produced: the oxidant side in proton-conducting fuel cells and the fuel side in oxygen-ion-conducting ones.

Each component of the SOFC serves several functions and must therefore meet certain requirements such as: proper stability (chemical, phase, morphological, and dimensional); proper conductivity; chemical compatibility with other components; similar thermal expansion to avoid cracking during the cell operation; dense electrolyte to prevent gas mixing; porous anode and cathode to allow gas transport to the reaction sites; compatibility at higher temperatures at which the ceramic structures are fabricated; and low cost.

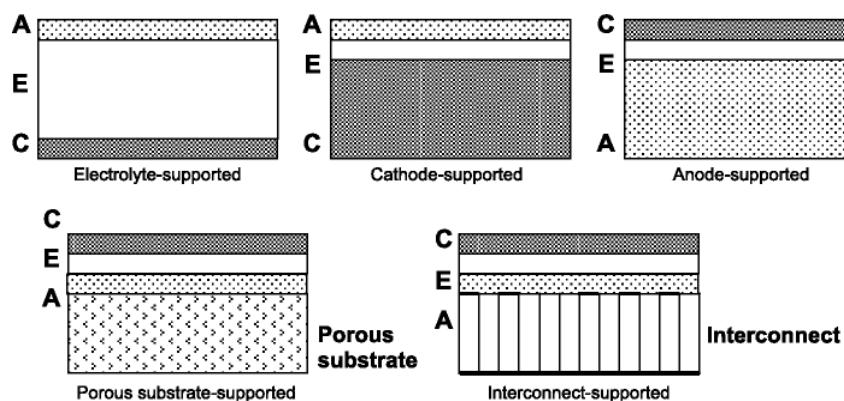


Figure 1-3. SOFC single cell configurations.

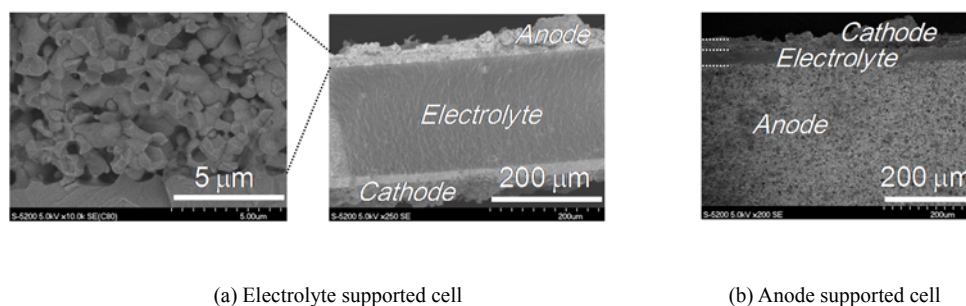


Figure 1-4. Cross-sectional SEM images of an electrolyte supported cell and an anode supported cell.

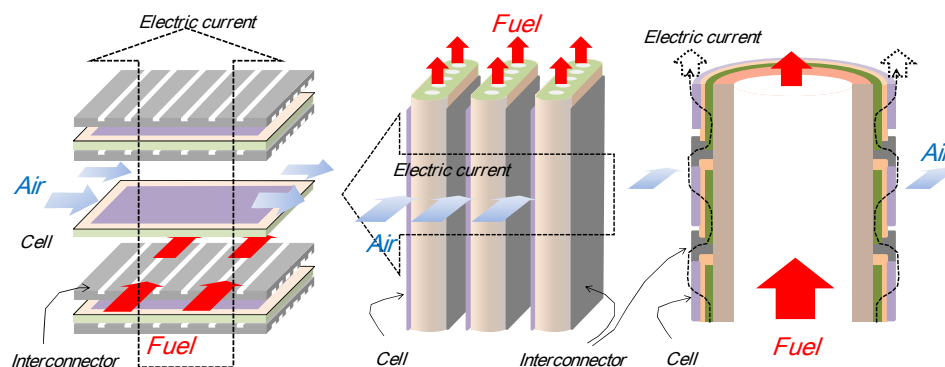
Table 1-4: Features of single cell configurations. [10]

Cell configuration	Advantage	Disadvantage
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Self-supporting Electrolyte-supported	- Relatively strong structural support from dense electrolyte - Less susceptible to failure due to anode re-oxidation (Ni/YSZ) anode and cathode reduction (LSM)	- Higher resistance due to low electrolyte conductivity - Higher operating temperatures required to minimize electrolyte ohmic losses
Anode-supported	- Lower operating temperature via use of thin electrolytes	- Potential anode re-oxidation - Mass transport limitation due to thick anodes
Cathode-supporting	- No-oxidation issues but potential cathode reduction - Lower operating temperature via use of thin electrolyte	- Lower conductivity - Mass transport limitation due to thick cathode
External-supporting Interconnect-supported	- Thin cell components for lower operating temperature - Stronger structures from metallic interconnects	- Interconnect oxidation - Flow field design limitation due to cell support requirement
Porous substrate	- Thin cell components for lower operating temperature - Potential for use of non-cell material for support to improve properties	- Increase complexity due to the addition of new materials - Potential electrical shorts-circuiting with porous metallic substrate due to uneven surface

1.3.5 Stack design

SOFC single cell can be configured into various shapes depending on the specific stack design, including tubular, flat-plate or planar, bell-and-spigot, banded, and corrugated structures. The two most common designs of SOFCs are shown in **Figure1-4**, namely, planar and tubular. It turned out that there were several problems with planar stacks as they were made larger to generate increased power, including sealing around the edges and thermal expansion mismatch which caused cracking. Consequently, tubular designs have had greater success in recent years.



(a) Anode supported planar (b) Anode supported flat tubular (c) Segmented-in-series tubular

Figure 1-5. Structures of SOFC stack [11].

1.4 Recent status of development

Large scale SOFC systems are being developed aiming to realize electric power plant and distributed power generation system with high electric conversion efficiency. Mitsubishi Heavy Industries (JP) has developed 200 kW class micro gas turbine hybrid system, and a maximum efficiency of 52.1%-LHV and maximum gross power of 229 kW-AC was achieved with natural gas as the fuel. Their ultimate goals are electric efficiency of 70% or more by large-scale power generation system integrated with SOFC, gas turbine and steam turbine [12]. Rolls-Royce Fuel Cell Systems (GB), now called LG Fuel cell systems, is designing a stationary 1 MW SOFC power generation system based on their segmented-in-series cell stack named Integrated-Planar SOFC technology [13, 14]. FuelCell Energy (US) is developing SOFC power plants, currently utilizing SOFC stacks developed by Versa Power Systems (CA). Their ultimate goal is to develop Multi-MW SOFC power plants suitable for integration with coal gasifiers and capable of capturing >90% of carbon in coal syngas [15].

Small scale SOFC of 1 -2 kW class are now being developed all over the world, aiming for early commercialization of residensital combined heat and power systems. Natural gas is generally used as the fuel and high overall efficiency is obtained by utilizing both electricity and heat. In Japan, demonstrative research project was carried out in FY2007-2013, in which Kyocera (JP), Tokyo gas (JP), and TOTO (JP) were the

manufacturers of SOFC stacks. More than 200 systems had been installed by FY2010 at actual sites of residences. A long-term operation over 25,000 hours was demonstrated, and technical potential of over 40,000 hours is being confirmed. Reduction of primary energy by 16% and reduction of CO₂ by 34% was demonstrated for the average customers [16]. Ceramic Fuel Cells (AU) manufactured their residential system called BlueGen which can deliver initial electrical efficiency of 60%-LHV at 1.5 kW-AC, and 55% efficiency after 1 year operation [17, 18]. Hexis Ltd. (CH) operated 1 kW class system for 28,000 hours [20]. Acumentrics (US) [19] and Ceres Power (GB) also developed residential SOFC systems [21].

General issues for the SOFC systems to be solved before becoming widely used are durability against long-term operations and thermal cycling, product reliability and cost reduction. Further enhancement of electrical efficiency, fuel flexibility, and durability against thermal cycling are also necessary for this technology to expand in application. From the view point of cell and stack, further improvement of mechanical stability and chemical stability of component materials are required in the future.

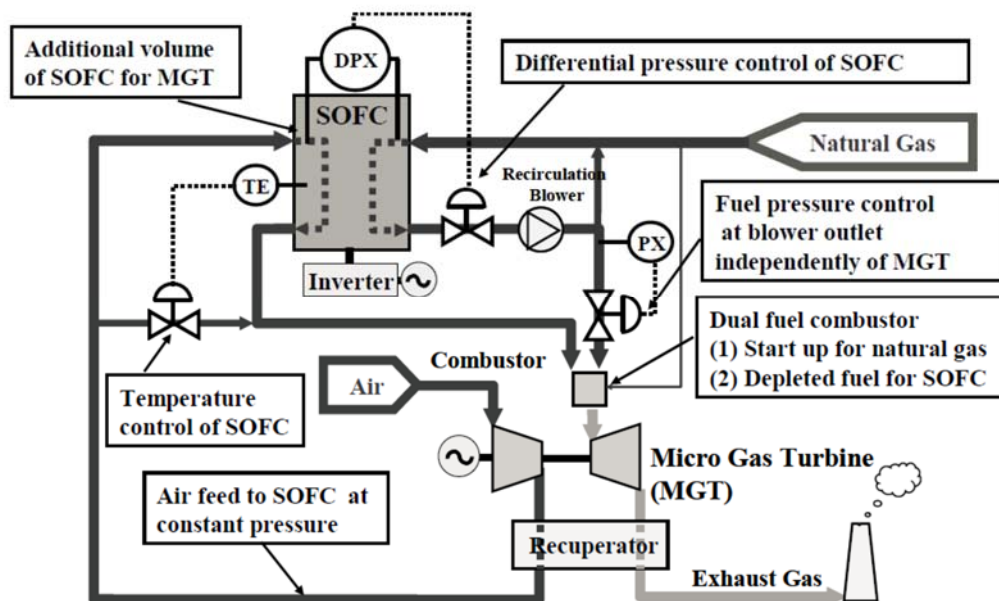


Figure 1-6. Flow diagram of 200 kW-class SOFC-micro gas turbine combined system developed by Mitsubishi Heavy Industries [12].



Figure. 1-7. Appearances of installation sites of residential SOFC combined heat and power systems under demonstrative research project in Japan [16].

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CHAPTER 2

CATHODE MATERIALS AND DEGRADATION OF SOFC

2.1 Cathode Materials of SOFC

2.1.1 Working principle

Electrochemical reaction occurring at the SOFC cathode is the reduction of oxygen as follows:



The reaction takes place in the vicinity of the three phase boundary (TPB, similar to the anode functional layer) among electronic conductor (cathode), an ionic conductor (electrolyte), and oxygen gas (air). Further, the TPB is electrochemically active only if electrons, oxygen vacancies or ions, and oxygen gas can transport to or away from the boundary. The required simultaneous transport of oxygen ions and electrons implies that a mixed conductor, a material conductive of both oxygen ions and electrons, would be a better cathode than a pure electronic conductor.

Therefore, cathode materials for SOFC have to satisfy various requirements including high electrical conductivity, high catalytic activity for oxygen reduction, and compatibility with other cell components. Cathode materials can be divided into two typical types: pure electronic conductor and mixed ionic-electronic conductor (MIEC), including single-phase mixed conductor and composite of ionic and electronic phases. Oxygen diffusion and reaction path is different in the two types of cathode materials as shown in **Figure 2-1**, in which $La_xSr_{1-x}MnO_3$ (LSM) perovskite is selected as a typical cathode material because of its high thermal and chemical stability. Its functional layer is a mixture of LSM and the electrolyte material, YSZ. As described in **Figure 2-1(a)**, the three phase boundary area, where oxygen gas, electrons, and an ion conducting phase are present, is marked with small grey circles. A different approach is shown in **Figure 2-1(b)** and **(c)**. The three phase area has been increased (grey area on the surface of the particles in the sketch) when the cathode material exhibits both electronic and ionic conductivities [1].

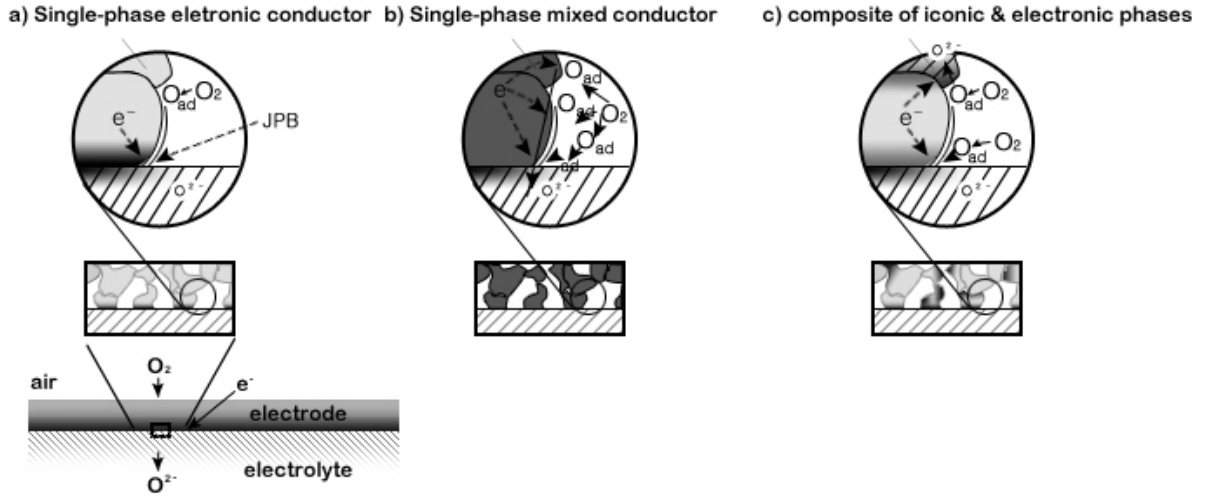
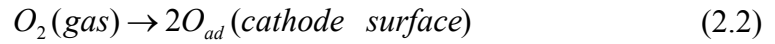


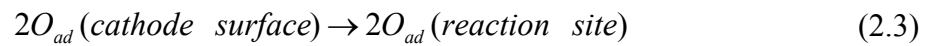
Figure 2-1. SOFC cathode material (a) Single-phase electronic conductor; (b) Single-phase mixed conductor; (c) Composite of ionic and electronic phases [2].

Although reaction paths may be different for various cathode materials, reaction step has been considered as follows:

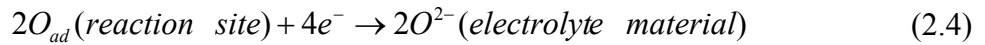
Step 1: Oxygen molecule adsorption and dissociation into oxygen atom O_{ad} ,



Step 2: Surface diffusion of adsorbed oxygen atom O_{ad} ,

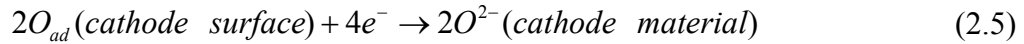


Step 3: Reaction between adsorbed oxygen O_{ad} and electron at the reaction sites (at TPB),



For the single-phase electronic conductor, reaction sites for (2.3) and (2.4) are limited to the TPB, while for the single-phase mixed conductor and composite of ionic and electronic phases, the following step way also occurs:

Step 4: Reaction between adsorbed oxygen O_{ad} and electron in cathode.



which implies that the reaction is not limited to the TPB but is extended to the whole cathode surfaces. Since TPB length determines the oxygen reduction rate and thus the performance of the cathode can be improved by this way [3].

The basic structure of typical cathode materials is the perovskite structure. The crystal structure of perovskite, ABO_3 , is shown in **Figure 2-2**. This oxide consists of three elements, namely the large cation A^{n+} , the small cation $B^{(6-n)+}$, and the oxide ions O^{2-} , where n is the positive charge on the A ions. Cation $B^{(6-n)+}$ 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 tolerance of cations and anions in this structure is described by the Goldschmidt tolerance factor defined as follows:

$$t = (r_A + r_O) / [2^{1/2}(r_B + r_O)] \quad (2.6)$$

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 [5] for specific coordination numbers. When the tolerance factor is near the unity, the structure is the ideal cubic one. In other cases, orthorhombic or rhombohedral distortion appears.

Various properties of cathode materials directly relating to their perovskite structure may be summarized as follows:

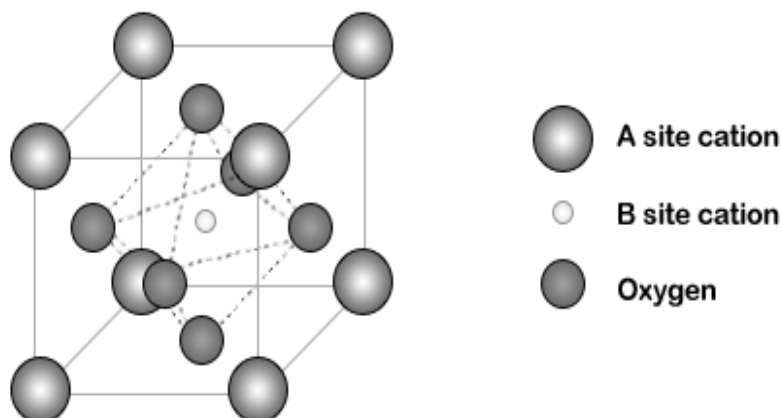


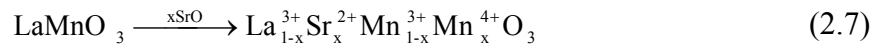
Figure 2-2. Perovskite lattice structure [4]

(I) Physical and physicochemical properties

Crystal structure of cathode materials is sensitive to various environmental conditions. For example, the crystallographic transformation temperature of LSM strongly depends on the oxygen nonstoichiometry, and hence on the mean manganese valence. Undoped stoichiometric LaMnO_3 shows orthorhombic structure at 25 °C and rhombohedral above 600 °C [6]. 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. This eventually decreases the transformation temperature. Although the cubic structure does not appear in pure LaMnO_3 , it appears around 1000 °C in $(\text{La}_{0.7}\text{Sr}_{0.3})\text{MnO}_3$. The most interesting features of LaMnO_3 -based perovskites are their oxygen nonstoichiometry and related defect structure [7-11], that is, in addition to the oxygen deficient region, the ‘Oxygen-excess’ region appears [7]. Sometimes, the ‘Oxygen-excess’ can be discussed together with the A-site deficiency in the structure, because there is an expectation that the metal vacancies can be easily formed on the A sites compared to the B sites. While for the other cathode materials, such property has not been observed.

(II) Electrical conductivity

LaMnO₃-based perovskites exhibit intrinsic p-type conductivity due to the changes in the Mn valence state. The electrical conductivity of these materials is higher than 10 S cm⁻¹ at 700 °C. The electrical conductivity is enhanced by replacing La³⁺ with lower valence cations (such as Ca²⁺ and Sr²⁺) or doping with other cations (Mg²⁺, Co³⁺, etc.) for the application as a cathode material [9-12]. In particular, LaMnO₃ doped with calcium and strontium has been examined to improve its electrical conductivity because such doped materials have high electrical conductivity as well as thermal expansion and chemical properties compatible with other SOFC component materials. When a La³⁺ ion is replaced by a Sr²⁺ ion, an electric hole is formed on the Mn³⁺ site to maintain the electron neutrality and this leads to an increase in electrical conductivity:



For La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} the electronic conductivity is about 280 S/cm at 800 °C, which is higher than that of LSM material.

(III) Thermal expansion

To minimize stresses during cell fabrication and cell operation, thermal expansion of the cathode should be matched with other SOFC component materials, especially electrolyte and interconnect. The thermal expansion coefficient (TEC) of undoped LaMnO₃ is $11.2 \pm 0.3 \times 10^{-6} \text{ K}^{-1}$ in the temperature range of 35-1000°C. In the slightly A-site deficient LaMnO₃ (La_{0.99}MnO₃), the TEC values are lower than those in the stoichiometric composition. This is due to a crystal structure change caused by the A-site deficiency. With Sr doping in La_{0.99}MnO₃, the TEC values increase with increasing Sr concentration, while for La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} the value is $15.1 \pm 0.3 \times 10^{-6} \text{ K}^{-1}$ (20–800 °C) [13].

(IV) Surface reaction rate and oxide ionic conductivity

Oxygen incorporation is a very important process for perovskite cathode materials because the oxygen stoichiometry can change during cell operation and also on thermal cycling. The oxygen incorporation rate and the oxygen flux through the materials can be characterized in terms of two parameters: the oxygen diffusion coefficient and the oxygen surface exchange coefficient. The $^{16}\text{O}/^{18}\text{O}$ isotope exchange technique provides very meaningful data on these parameters [14-15]. The oxygen diffusion coefficients for LaMnO_3 -based perovskites are scattered over one or two orders of magnitude, and the values range in the orders of 10^{-13} to $10^{-11} \text{ cm}^2 \text{ S}^{-1}$ at 1000°C at $p(\text{O}_2)=1\text{atm}$. These values for diffusivity are low compared with the values required for mixed conducting oxide cathodes. This implies that when doped LaMnO_3 is used as a cathode, oxygen will be transported through the gaseous phase or on the surface of the LaMnO_3 to the major electrochemical reaction sites at the electrolyte/ cathode / gas, so called, three-phase boundary. Such (but slow) oxygen diffusion inside the lanthanum manganite was confirmed with ^{18}O labeling and SIMS analysis [16]. LaCoO_3 -based oxides exhibit higher oxide ionic diffusivity with the ionic conductivity around $2 \times 10^{-3} \text{ S/cm}$, and larger surface exchange coefficients than the LaMnO_3 -based ones [14, 15].

2.1.2 Developmental status of cathode material

As described in Section 1.3.2, cathode losses dominate the performance in many SOFC designs, the development of better SOFC cathodes remains a very important research topic. An excellent review of SOFC cathode materials has been published by Singhal et al. [17]. In the earliest stages of SOFC development, platinum was used as a cathode material since other appropriate materials were not available. However, platinum is too expensive and its use in cost-effective commercial SOFCs for power generation is not practical. Less expensive perovskites [18] also possess the required properties and have consequently attracted strong interest. In 1969, LaCoO_3 was tested by Tedmon et al. [19] and its initial performance in cells was satisfactory. However, severe degradation occurred with increasing time of operation due to reactions with yttria-stabilized zirconia (YSZ) electrolyte. Investigations on cathodes then moved to

lanthanum manganite (LaMnO_3)-based materials. Although degradation of lanthanum manganite cathodes was not so severe, some potential reactions with YSZ, particularly at higher cell fabrication temperatures, were recognized [20].

Success of the seal-less tubular cells with electrolyte fabricated using electrochemical vapor deposition method [21] stimulated investigations of fabricating SOFC components by a more cost-effective slurry/sintering process [22]. To utilize this process successfully, any chemical interactions between the cathode and the YSZ electrolyte had to be avoided during cell fabrication without sacrificing cathode performance. For this purpose, the reactivity of lanthanum manganites with YSZ was investigated using thermodynamic considerations [23], and to avoid $\text{La}_2\text{Zr}_2\text{O}_7$ formation, A-site (La)-deficient LaMnO_3 was proposed for the cathode. Its use inhibited $\text{La}_2\text{Zr}_2\text{O}_7$ formation and resulted in better cathode performance, as confirmed by Dokiya et al. [24] on test cells and by Ipponmatsu et al. [25] on tubular cells in a 1KW system. Aizawa et al. [26] also used the A-site deficient lanthanum manganite cathode to fabricate tubular cells by a wet slurry/ sintering process and achieved about the same cell performance as cells fabricated by using electrochemical vapor deposition for the YSZ electrolyte [21].

While high-temperature operation brings about problems such as cell performance degradation and durability, further works have been done to decrease operating temperature. For intermediate temperature SOFCs, a composite cathode consisting of strontium-doped lanthanum manganite (LSM) and YSZ has shown good performance [27]. Besides, MIEC cathode material, $(\text{La,Sr})(\text{Co,Fe})\text{O}_3$ (LSCF) based cathode has been developed [28]. $(\text{La,Sr})(\text{Co,Fe})\text{O}_{3-\delta}$ materials (LSCF) exhibit mixed conductivity: for $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ the electronic conductivity is about 280 S/cm at 800 °C while the ionic conductivity is around 2×10^{-3} S/cm. Moreover, the surface exchange kinetics is faster compared to the LSM. A disadvantage is the large thermal expansion coefficient: the expansion coefficient of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ ($\alpha = 15.1 \times 10^{-6} \text{ K}^{-1}$ (20–800 °C)) is much larger than that of YSZ ($\alpha = 10.8 \times 10^{-6} \text{ K}^{-1}$). It was pointed out by Ullmann et al. that there is a clear correlation between (high) ionic conductivity and (high) thermal expansion coefficient [29]. For that reason there always has to be a

compromise between ionic conductivity and unacceptable high thermal expansion. A further disadvantage is the low chemical stability compared to LSM. On one hand, LSCF allows the oxygen ions to move easily among lattice sites. On the other hand, Sr ions can diffuse too. Direct contact between LSCF and YSZ electrolyte leads to the formation of insulating SrZrO_3 at the LSCF–YSZ interface after sintering the cathode at temperatures above 1000 °C. Significant effort has been done for trying to take advantage of the excellent cathode properties of LSCF. One method for doing this is to insert a buffer layer, such as doped ceria, between the YSZ and the cathode. The ceria layer is essentially part of the electrolyte and prevents direct contact between the YSZ and the cathode material. The approach has been shown to provide excellent cathode performance and can suppress the formation of SrZrO_3 [30]. However, it requires an additional processing step and the mechanical properties of these electrodes tend to be poor, further develop should be done to solve this issue. Besides the two typical cathode materials, more efforts have been done to develop cathode materials as described in Section 1.3.3.

2.2 Degradation of SOFC

Improvement of long-term durability is one of the major issues towards commercialization of SOFCs. Various degradation mechanisms, however, may appear such as chemical instability between different component materials and poisoning of electrode materials especially during a long-range operation at high temperatures. These degradations come from several sources as follows:

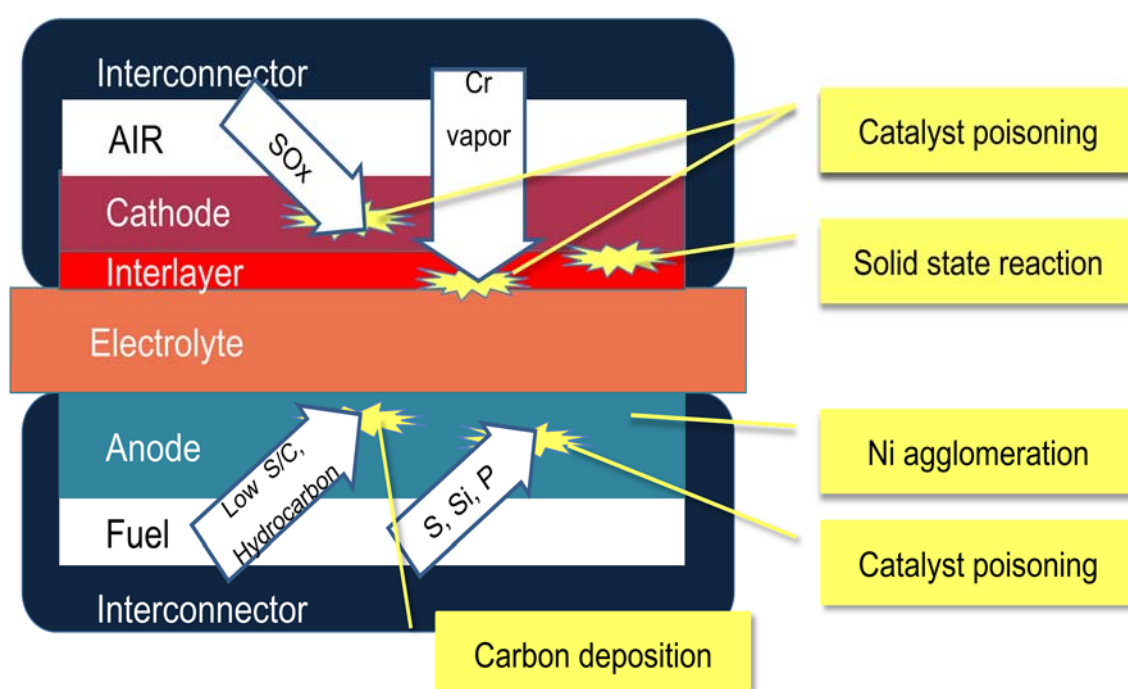


Figure 2-3. Fundamental processes affecting durability of SOFC.

1) Fuel contamination

One overwhelming advantage of SOFC (and MCFC) over the other types of fuel cells lies in the possibility of internal reforming, which means that it is possible to use practical hydrocarbon fuels ((e.g., natural gas, liquefied petroleum gas (LPG), kerosene, coal-derived syngas, biogas, alcohol, gasoline etc.) Yet problem arises consequently: minor constituents involved in these fuels can cause fatal degradation of cell performance or affect overall SOFC system durability. Sasaki et al. have detected anode

performance degradation by such impurities as H_2S etc. [31] and K. Haga has described in detail the chemical degradation phenomena of Ni-based anode materials [32].

2) Air contamination

Air is the most practical and economical oxidant to feed the fuel cell stack. However, air pollutants, such as nitrogen oxides (NO_x , including NO and NO_2), sulfur oxides (SO_x , including SO_2 and SO_3), carbon dioxide (CO_2), ozone and other organic chemical species (such as benzoic compounds) contaminate the fuel cell, resulting in possible performance degradation of SOFC cathodes in a long-term operation.

Air pollution is a major issue in an increasing number of megacities around the world, and new policies to address urban air pollution are likely to be enacted in many developing countries irrespective of the participation of these countries in any explicit future climate policies. M.E. Schlesinger et al. have reported relationship between the air pollution and climate [33]. Urban air pollution has a significant impact on the chemistry of the atmosphere and thus potentially on regional and global climate. The emissions of gases and microscopic particles (aerosols) that are important in air pollution and climate are often highly correlated because of shared generating processes. Most important among these processes is combustion of fossil fuels and bio-mass which produces carbon dioxide (CO_2), carbon monoxide (CO), nitrogen oxides (NO_x), volatile organic compounds (VOCs), black carbon (BC) aerosols, and sulfur oxides (SO_x , consisting of some sulfate aerosols, but mostly SO_2 gas which subsequently forms white sulfate aerosols). In addition, the atmospheric lifecycles of common air pollutants such as CO, NO_x , and VOCs, and of the climatically important methane (CH_4) and sulfate aerosols, both involve the fast photochemistry of the hydroxyl free radical (OH). Hydroxyl radicals are the dominant “cleansing” chemical in the atmosphere, annually removing about 3.7 gigatonnes (1GT = 10^{15} g) of reactive trace gases from the atmosphere; while the environmental impact of each gas is different, this amount is similar to the total mass of carbon removed annually from the atmosphere by the land and ocean combined.

Among the human activities, the major sources of air contaminants are the automotive vehicle exhaust and industrial manufacturing processes. For example, the NO_x level in the Vancouver BC can be as high as 100 ppb and in a battlefield, the SO_x could be as high as 0.5 ppm. As for CO_2 , it increases drastically every year and reaches 400 ppm, which brings about the severe influence on global climate.

Table 2-1 provides a list of contaminants presented in the operational environment of SOFCs. It is necessary to clarify the influence of these trace impurities and to propose the strategies in impurity-tolerant SOFC materials.

3) Contamination from system components

In addition to the fuel contamination and air contamination mentioned above, some trace amounts of system components can also cause fuel cell degradation, for example, inlet/outlet manifold, thermal insulating materials, metallic gas supply pipes, sealing gasket and so on. It is well known that typical stainless steel (e.g. SUS 430) contains Cr and also a small amount of S, P. They may cause cathode degradation [34]. Chromium poisoning is briefly overviewed in 2.3 and dealt with in this study in detail. Furthermore, several impurities such as Na and Si in cells were detected after several thousand-hour operations in real SOFC stacks, whose sources are considered to be system components exposed at high temperatures for long periods of time [31, 35].

Table 2-1: Major contaminants identified in the operation of SOFCs.

Impurity Source	Typical contaminant	Typical concentration
Air ➤ combustion of fossil fuels and bio-mass ➤ automotive vehicle exhaust ➤ industrial manufacturing processes ➤ atmospheric lifecycles of air pollution ➤ Others	● NO_x(NO, NO₂) ● SO_x(SO₂, SO₃) ● NH₃ ● O₃ ● CO_x (CO, CO₂) ● NaCl ● Water vapor	ca. 100 ppb~ ca. 0.5 ppm~ ca. 10 ppm ca. 0.5 ppm~ ca. 360 ppmv~ ca. 800 nmol m ⁻³ ca. 3% (25 °C)
Fuel [31] ➤ Coal derived syngas ➤ Various hydrocarbon fuels ➤ City gas ➤ LPG ➤ Biogas ➤ Bio-ethanol ➤ Others	● Sulfides ● Hydrogen chloride ● Ammonia	ca. 10 ppb ~100 ppm ca. 10 ppb ~100 ppm ca. 10 ppm
Components ➤ Sealing gasket ➤ Interconnect ➤ Others	Si, B, Mg, Na, Cr, S, P	

2.3 Chromium Poisoning of SOFC Cathodes

2.3.1 Preceding studies

Among several degradation factors in solid oxide fuel cells (SOFCs), chromium poisoning of cathodes has been one of the major technological concerns [37-38]. The degradation originates from a vaporization of chromium from the surface of metallic components such as interconnects, manifolds and gas supply tubes. The chromium vapor deposits at the electrochemically active sites during operation, resulting in a degradation of cathode performance. In the case of cathodes consisting of lanthanum strontium manganite (LSM), the chromium vapor deposits at the electrochemically active sites during operation, resulting in a degradation of cathode performance [35, 39-40] (as shows **Figure 2-4**). It was revealed that cathode polarization (overpotential) affects the chromium poisoning kinetics for the cathode consisting of LSM, by which it was concluded that the decrease in oxygen activity in the cathode accompanied by the electrode reaction could be the driving force of the deposition of chromium [34].

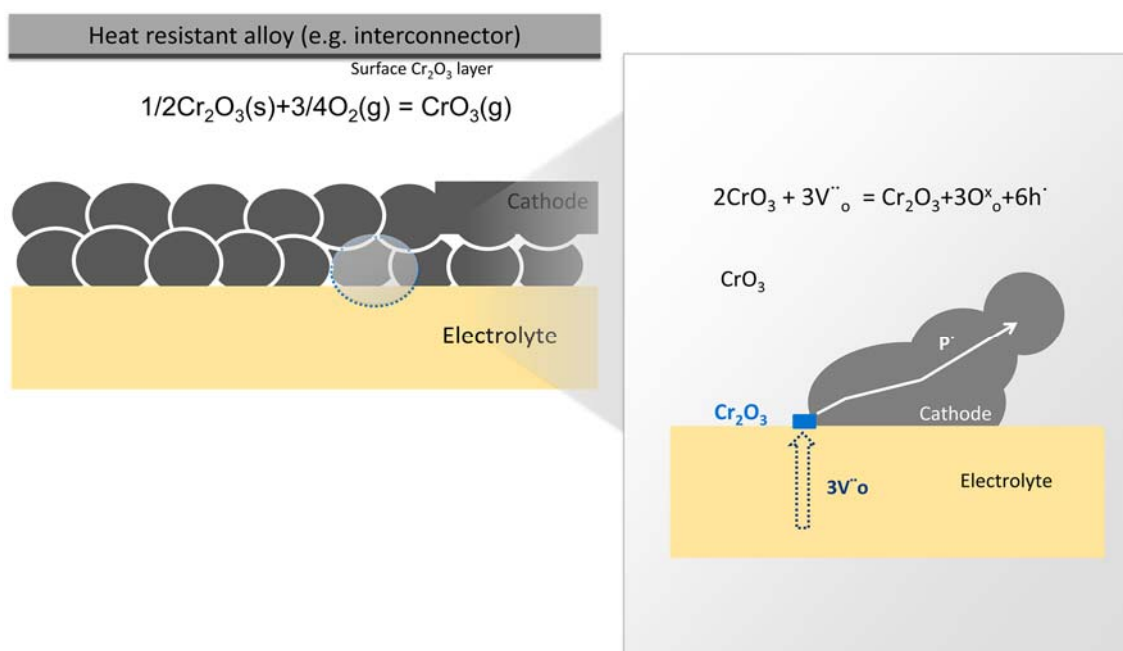


Figure 2-4. Chromium poisoning phenomena.

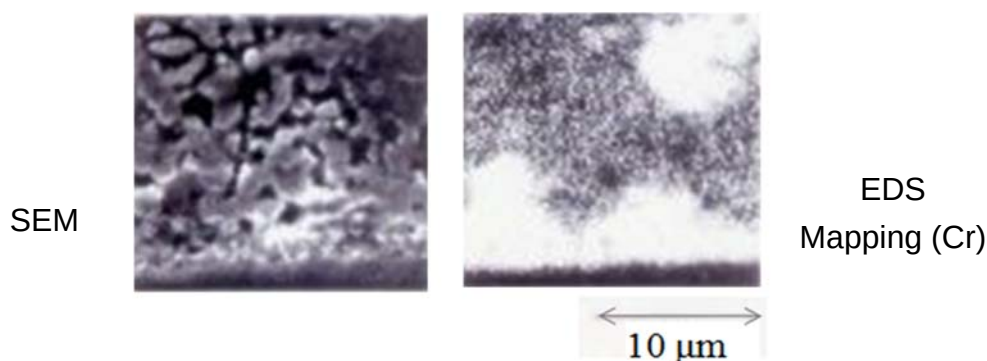
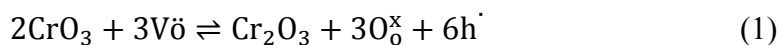


Figure 2-5. Chromium deposition near the cathode/electrolyte interface. [34, 53, 55-56, 59]

Two types of reactions have been considered for the chromium deposition process, one is (i) electrochemical deposition and the other is (ii) chemical dissociation reaction.

(i) Electrochemical deposition

Mechanism of the electrochemical deposition is considered as follows [60].



Cathode polarization has relationship with concentration of oxygen vacancy, therefore with increasing cathode polarization, the electrochemical chromium deposition should be enhanced. The electrochemical chromium deposition i.e. electrochemical reduction of volatile chromium species has been reported to take place at the triple phase boundary (TPB) .

(ii) Chemical dissociation reaction

The chemical dissociation reaction, which is a non-electrochemical process, has been considered to be caused by local low oxygen partial pressure near active sites (TPB) [34, 39, 48], which may be an indirect effect of the cathodic polarization [49]. Chemical deposition of chromium (ii) has been considered to be controlled by the nucleation reaction between the nucleation agent and the gaseous Cr species [51-54]. The nature of the nucleation agent strongly depends on the electrode material and

impurities [51-54].

Concerning the difference of chromium poisoning phenomena among cathode materials, $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ (LSCF) [47, 50] and $\text{LaNi}_{0.6}\text{Fe}_{0.4}\text{O}_3$ (LNF) [46, 58] have been proposed as potential cathode material which exhibit higher tolerance to chromium poisoning than lanthanum strontium manganite. However, there are several factors to be considered to understand the effect of cathode material. One is cathode polarization and the other is reactivity of the cathode material with chromium vapor.

Chemical reaction of the chromium vapor with LSM, leading to $(\text{Mn,Cr})_3\text{O}_4$ formation, occurs all over the cathode even with no cathode polarization. Although the chemical reaction slightly affects the cathode performance, the electrochemical deposition by cathode polarization near the electrolyte severely damages the cathode performance [34, 40-44, 47, 54, 61]. In the case of $(\text{La}_{0.6}\text{Sr}_{0.4})(\text{Co}_{0.2}\text{Fe}_{0.8})\text{O}_3$ (LSCF), chemical reactivity of LSCF with the chromium vapor is higher than that of LSM and formation of SrCrO_4 was significantly observed in the cathode. In most cases, the formation of SrCrO_4 was observed in the vicinity of the cathode surface, which does not directly affect the electrode reaction sites [38, 41-42, 45, 52-53, 55-57]. The phenomena are explained by three-dimensionally-extended electrode reaction sites due to the high ionic conductivity of LSCF, while the electrode reaction sites are limited to the cathode/electrolyte interface for LSM because it is a pure electronic conductor. Similar results as LSCF were observed for $(\text{La}_{0.8}\text{Sr}_{0.2})\text{FeO}_3$ (LSF) [43]. In the case of $\text{La}(\text{Ni}_{0.6}\text{Fe}_{0.4})\text{O}_3$ (LNF), it was assumed that higher tolerance to chromium poisoning can be obtained because of its lower chemical reactivity with the chromium vapor [42, 58].

2.3.2 Aim of this study

The objective of this study is to clarify theme mechanism of chromium poisoning phenomena commonly applicable to many SOFC cathode materials, by focusing on the influence of cathode polarization and microscopic distribution of the deposited chromium.

In chapter 4, chromium deposition kinetics and deposition profile are compared among three kinds of cathode materials, LSM, LSCF or LNF, by changing cathode

polarization. Influence of cathode polarization on the chromium deposition near the electrode reaction site is investigated.

In chapter 5, mechanism of chromium deposition on the zirconia and ceria electrolyte surface is investigated by analyzing elemental distribution around the boundary of the zirconia surface and the deposited chromium, especially focusing on oxygen concentration near the zirconia electrolyte surface.

In chapter 6, chromium poisoning phenomena for different cathode materials, $\text{Pr}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (PrSM), $\text{Nd}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (NdSM) and $\text{Br}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$ (BSCF) are studied by regulating cathode polarization constant. Chromium deposition kinetics and deposition profile are compared and the mechanism of the chromium deposition which predominantly affects the cathode performance will be revealed.

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CHAPTER 3

EXPERIMENTATION

3.1 Cell fabrication

Two types of the cell were fabricated as shown in **Figure 3-1**, in which the position of reference electrode was different from each other. The reference electrode was used to measure the electrochemical characteristics of anode and cathode. Platinum paste (U-3401, N.E. CHEMCAT, Japan) with a geometric area of ca. 0.04 cm^2 was painted as the reference electrode adjacent to the working electrode, i.e. the anode or the cathode. The distance between the edge of the anode and the reference electrode was adjusted to ensure at least 1 mm, which enables to detect the absolute potential accurately within electrolytes with the thickness of $200 \text{ }\mu\text{m}$ [1, 2]. Platinum mesh (80 mesh with the Pt wire diameter of $16 \text{ }\mu\text{m}$) as a current collector welded to a platinum lead wire, was attached to the top surfaces of these three electrodes.

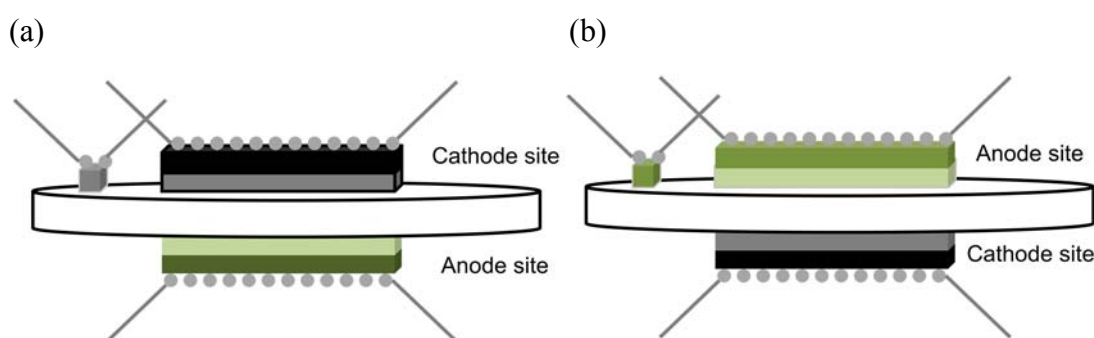


Figure 3-1. Configuration of SOFC single cells with (a) and (b) .

Electrolyte plates made of 8 mol% Y_2O_3 -92 mol% ZrO_2 (YSZ) with a thickness of $200 \text{ }\mu\text{m}$ and a diameter of 20 mm were used. Mixture of 56 wt% NiO and 44 wt% ScSZ (Sc_2O_3 -1 mol% CeO_2 -89 mol% ZrO_2 , Daiichi Kigenso Kagaku, JP) was used for the anode material. Anode was printed on the electrolyte plate and sintered at $1300 \text{ }^\circ\text{C}$ for 3 h. For the cermet (NiO-ScSZ) anodes, higher Ni content results in coarse microstructure via sintering and agglomeration of Ni particles, whereas network of zirconia within the anode prevents further coarsening. In addition, the cermet electrode can moderate the thermal expansion mismatch between the electrode material and the electrolyte material.

Therefore, in our laboratory, the weight ratio of 50:50 is currently employed for the Ni–ScSZ anode as an anode functional layer.

Besides, it is necessary to use an efficient current collector to lower the internal resistance of cells. Nickel in the anode takes care of this required function, and hence sufficient connectivity of Ni particles, continuity for electronic conduction, is needed [3].

In chapters 4-5, three kinds of cathode materials, $(\text{La}_{0.8}\text{Sr}_{0.2})_{0.98}\text{MnO}_3$ (LSM) (>99.9%, Praxair, USA), $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ (LSCF) (>99.9%, Praxair, USA), and $\text{LaNi}_{0.6}\text{Fe}_{0.4}\text{O}_3$ (LNF) were used as shown in **Table 3-1**. The LNF powder was synthesized by a solid-state reaction as follows. La_2O_3 (>99.9%, Kojundo Chemical, JP), NiO (>99.9%, Mitsuwa Chemical, JP) and $\alpha\text{-Fe}_2\text{O}_3$ (>99.9%, Kojundo Chemical, JP) powders were mixed and calcined at 1100 °C for 8 hours in air, ball-milled and heat-treated at 1200 °C for 24 hours, and then ball-milled for 48 hours. X-ray diffraction (XRD with $\text{CuK}\alpha$ radiation, Rigaku RINT Ultima III, Japan) was measured for the LNF powder as shown in **Figure 3-2**. Rhombohedral crystal structure was confirmed as reported in [4]. For the LSM cathode, mixture of LSM and ScSZ with a weight ratio of 1:1 was applied as a functional layer, and LSM powder was used as a current collection layer. The LSM cathode was sintered at 1200 °C for 5 hours. For the LSCF cathode, $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_2$ (GDC) (>99.9%, Rhodia, Tokushima, JP) layer was printed on the electrolyte plate with a thickness of 5 μm and sintered simultaneously with the anode at 1300 °C. LSCF was printed with a thickness of 30 μm on the GDC layer and sintered at 900 °C. For the LNF cathode, the LNF powder was printed with a thickness of 50 μm and sintered at 1100 °C for 4 hours. Material and thickness of each layer of the three cathodes are summarized in **Table 3-1** and the cross-sectional microstructures observed by SEM (Hitachi SU-6600) are shown in **Figure 3-3**. Electrode area was 8 mm $\times$ 8 mm (0.64 cm²). Platinum mesh was used as the current collector. Reference electrode was placed on the cathode side as shown in **Figure 3-1(a)**

Table 3-1: Chemical composition and thickness of each layer of the three cathodes in chapters 4-5.

	First layer	Second layer
LSM cathode	LSM/ScSZ (1:1), 30 μm	LSM, 20 μm
	LSM: $(\text{La}_{0.8}\text{Sr}_{0.2})_{0.98}\text{MnO}_3$ ScSZ: Sc_2O_3 -1 mol% CeO_2 -89 mol% ZrO_2	
LSCF cathode	GDC, 5 μm	LSCF, 30 μm
	GDC: $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_2$ LSCF: $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$	
LNF cathode	LNF, 40 μm	-
	LNF: $\text{LaNi}_{0.6}\text{Fe}_{0.4}\text{O}_3$	

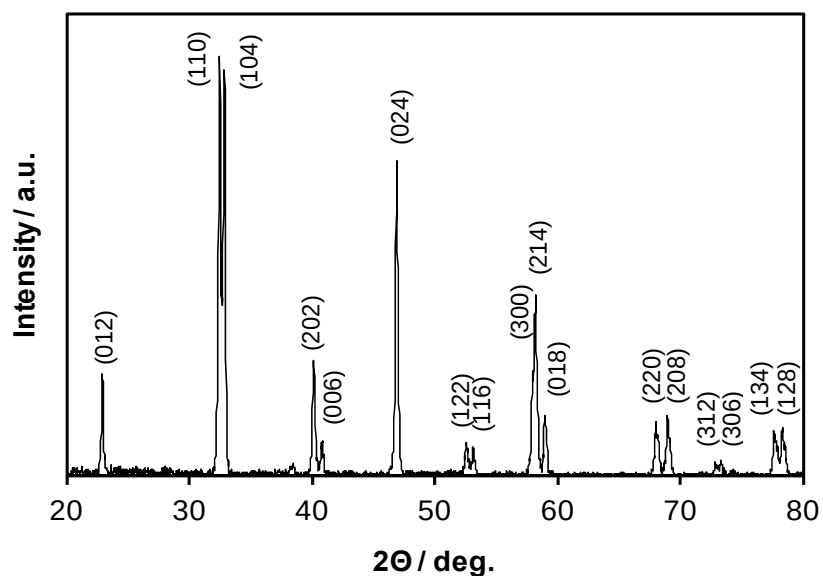
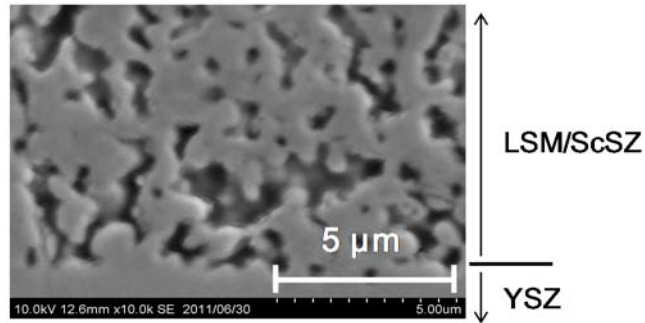
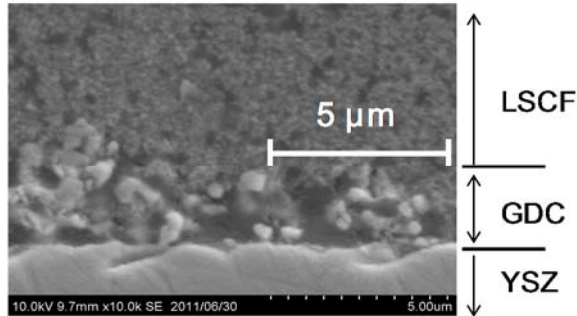


Figure 3-2. XRD pattern of the LNF powder synthesized in this study.

(a) LSM cathode



(b) LSCF cathode



(c) LNF cathode

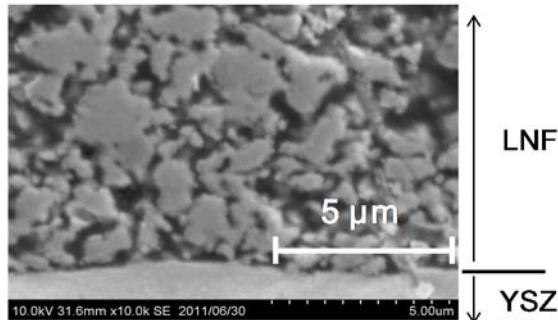


Figure 3-3. Cross-sectional microstructures of the three cathodes observed by SEM.

In chapter 6, four kinds of cathode materials, $(\text{La}_{0.8}\text{Sr}_{0.2})_{0.98}\text{MnO}_3$ (LSM), $\text{Br}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$ (BSCF), $\text{Pr}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (PrSM), and $\text{Nd}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (NdSM) were used as shown in **Table 3-2**. They were printed on the other side of the electrolyte plate and sintered. Heat-treatment condition was 1200 $^{\circ}\text{C}$ - 4 h for LSM, PrSM, NdSM, and 1100 $^{\circ}\text{C}$ - 5 h for BSCF. Electrode area was 8 mm $\times$ 8 mm (0.64 cm²). Pt mesh was used as the current collector. Reference electrode was placed on the anode side as shown in **Figure 3-1(b)**.

Table 3-2: Chemical composition and thickness of each layer of the four cathodes in chapter 6.

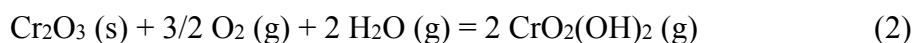
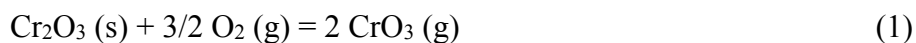
	First layer	Second layer
LSM cathode	LSM, 30 μm	LSM, 60 μm
	LSM: $(\text{La}_{0.6}\text{Sr}_{0.2})_{0.98}\text{MnO}_3$	
PrSMF cathode	PrSM, 30 μm	PrSM, 60 μm
	PrSM: $\text{Pr}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$	
BSCF cathode	BSCF, 30 μm	BSCF, 60 μm
	BSCF: $\text{Br}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$	
NdSM cathode	NdSM, 30 μm	NdSM, 60 μm
	NdSM: $\text{Nd}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$	

3.2 Electrochemical Characterization

3.2.1 Cell test with chromium poisoning

For the experiment of chromium poisoning, a chromium plate with 5 mm $\times$ 5 mm $\times$ 1 mm in size was placed on the current collector (Pt mesh) of the cathode. The chromium plate did not contact directly with the cathode.

The cell was set in the cell test equipment as schematically shown in **Figure 3-4** and heated by the electric furnace up to 850 $^{\circ}\text{C}$ in 4 hours to soften the glass seal, and was cooled down to the operating temperature of 700 $^{\circ}\text{C}$ in 1 hour. Cell tests were conducted at 700 $^{\circ}\text{C}$ by feeding air (0.15 l/min, 0.1 MPa) to the cathode and hydrogen to the anode (0.15 l/min, 0.1 MPa). The air used in this study was a compressor air, which was produced by an air compressor (0.7 -0.85 MPa) with an air dryer (5 - 15 $^{\circ}\text{C}$). The calculated concentration of water vapor in the cathode gas ranges from 1 hPa to 2.4 hPa. The surface of the chromium plate is oxidized under the cell operating condition, and chromium vaporizes by the following reactions.



The predominant vapor species is considered to be $\text{CrO}_2(\text{OH})_2 (\text{g})$ [5] and the equilibrium vapor pressure is estimated to be in the order of 10^{-4} - 10^{-3} Pa [6-8].

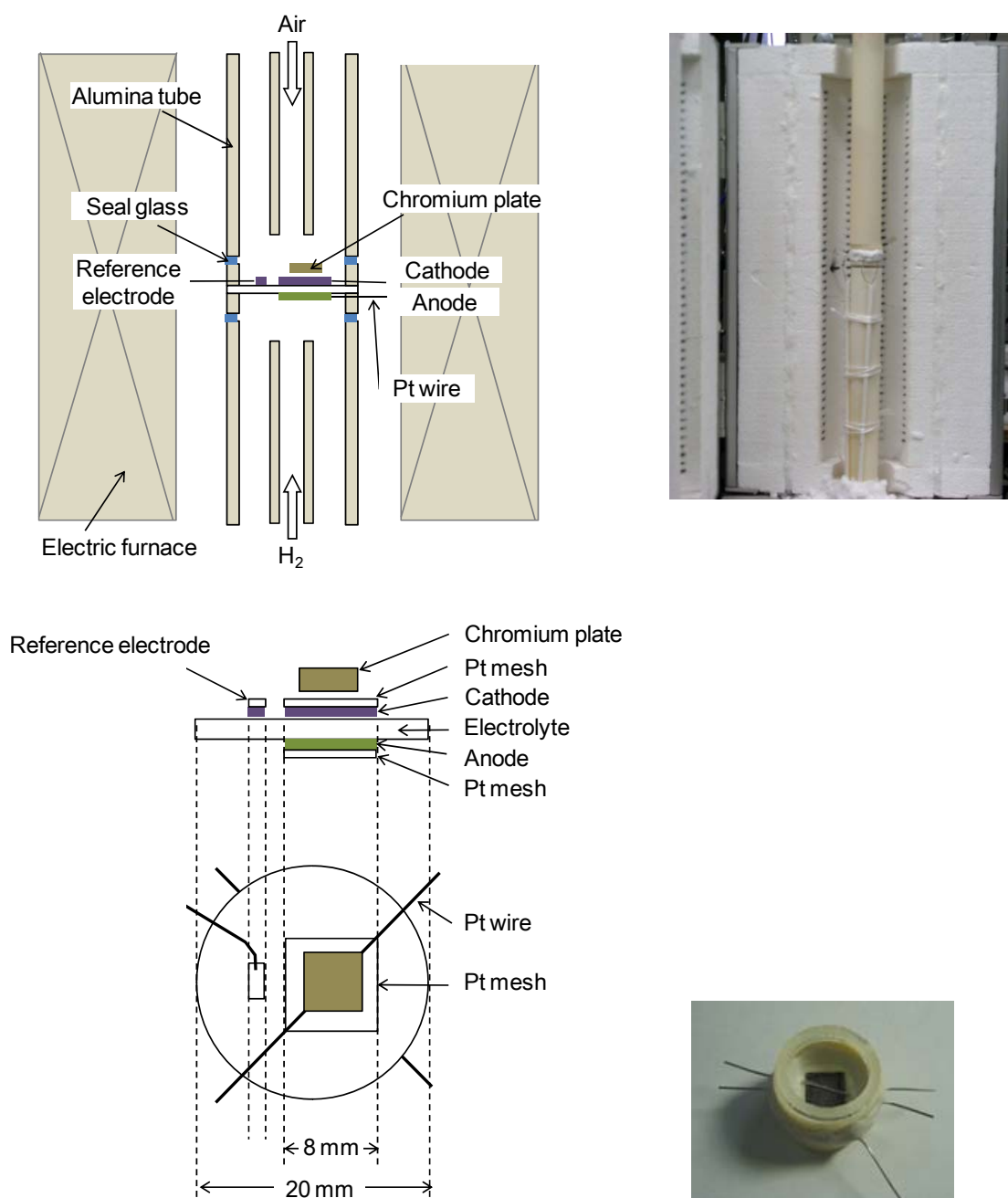


Figure 3-4. Schematic drawing of the test cell configuration.

3.2.2 Electrochemical performance of the cell

As described in chapter 1, the theoretical value of open circuit voltage (OCV) is given by the formula

$$E = \frac{-\Delta G}{4F} \quad (3.1)$$

This gives a value of about 1.2V for a cell operating below 100 °C. However, experimentally obtained OCV is often less than the theoretical value by fuel crossover or electron conduction through the electrolyte. Operational voltage decreases by the following three factors:

- Activation losses (ΔV_{act}), which are caused by the activation required to proceed reactions taking place at the electrode/electrolyte interfaces.
- Ohmic losses (ΔV_{ohm}), namely, the straightforward resistance to the flow of electrons through the electrode materials and the various interconnections, as well as the resistance to the flow of ions through the electrolyte materials.
- Mass transport or concentration losses (ΔV_{trans}), resulting from the change in concentration of the reactants near the electrode/electrolyte interface.

Therefore the actual cell voltage V can be described as:

$$V = E - \Delta V_{act} - \Delta V_{ohm} - \Delta V_{trans} \quad (3.2)$$

where the main cell voltage drop comes from the activation losses and ohmic losses and they will be discussed as follows.

The activation loss may follow the Tafel equation:

$$\Delta V_{act} = A \ln\left(\frac{i}{i_0}\right) \quad (3.3)$$

where constant A is higher for a slow electrochemical reaction, constant i_0 is higher for a fast reaction, which is also called exchange current density, and i is the electrode current density resulting from the reaction.

The Tafel equation describes the behavior of one isolated reaction. In a SOFC system, we have two opposing reactions, anodic and cathodic. A phenomenological theory, which gives a quantitative relation between current density and activation polarization, is known as the Butler-Volmer equation as follows :

$$V = E - A \ln\left(\frac{i}{i_0}\right) \quad (3.4)$$

$$\frac{i}{i_0} = \exp\left(\frac{\alpha n F \eta_{act}}{RT}\right) - \exp\left(-\frac{(1-\alpha) n F \eta_{act}}{RT}\right) \quad (3.5)$$

where E is the OCV value calculated by equation 3.1.

The ohmic loss, at a given current density, can be given by:

$$\Delta V_{ohm} = IR_{total} = I(\rho_c l_c + \rho_e l_e + \rho_a l_a + R_{contact}) \quad (3.6)$$

where ρ_c , ρ_e , and ρ_a are the resistivities of cathode, electrolyte, and anode, and l_c , l_e , and l_a are the thickness of cathode, electrolyte, and anode, respectively. $R_{contact}$ is any possible contact resistance within the SOFC stacks. The ohmic loss can be described by applying an equivalent circuit comprising a simple resistor, and in most SOFCs, the main contribution to the ohmic loss is the ionic resistivity of electrolytes [5].

Therefore, under current load, the output voltage is given by:

$$V = V'_c - V'_a \quad (3.7)$$

$$= \text{OCV} - (\eta_a + \eta_c) - (IR_a + IR_c) \quad (3.8)$$

where V'_a and V'_c are the electrical potentials of the anode and the cathode under current load, respectively. η_a and η_c are the non-ohmic losses of the anode and the cathode; IR_a and IR_c are the anode-side and the cathode-side ohmic losses.

The potential between cathode-anode (V_{c-a}) and reference-anode (V_{re-a}) were

simultaneously monitored by applying the current interruption technique so as to measure ohmic (IR) and non-ohmic (η) losses of both the anode and the cathode side.

$$V_{c-a} = \text{OCV} - (\eta_a + \eta_c) - (IR_a + IR_c) \quad (3.9)$$

$$V_{re-a} = \text{OCV} - \eta_a - IR_a \quad (3.10)$$

In this study, OCV and reference-cathode and reference-anode were measured.

3.2.3 Cell test at a constant current density

In the chromium poisoning tests in chapters 4-5, current density was kept constant to measure the time dependence of overvoltage (overpotential or polarizatoion) of the cathode. Initial cell performance was measured by changing current density. Cathode potential was measured by a voltmeter between the cathode and the reference electrode. Cathode side ohmic loss was measured by an AC impedance analyzer at 10 kHz, which was also confirmed by the current interruption method. Cathode polarization was calculated by subtracting the cathode-side ohmic loss from the cathode potential. Next, cathode polarization was adjusted to the predetermined value ranging from 0 mV to 400 mV by controlling current density. The initial current density was kept constant for 100 hours and cathode polarization changed over time during the chromium poisoning test (**Figure 3-5**). Cathode polarization of 0 mV is equal to the condition of open circuit. Current density was different for each cathode because of the difference in the catalytic activity of the materials and the difference in the microstructure of the electrode. At the end of the cell test, the operating temperature was lowered to 500 °C in 40 minutes, keeping the cathode polarization constant by changing the current. The current was cut off at 500 °C and cooled down to the room temperature in 80 minutes.

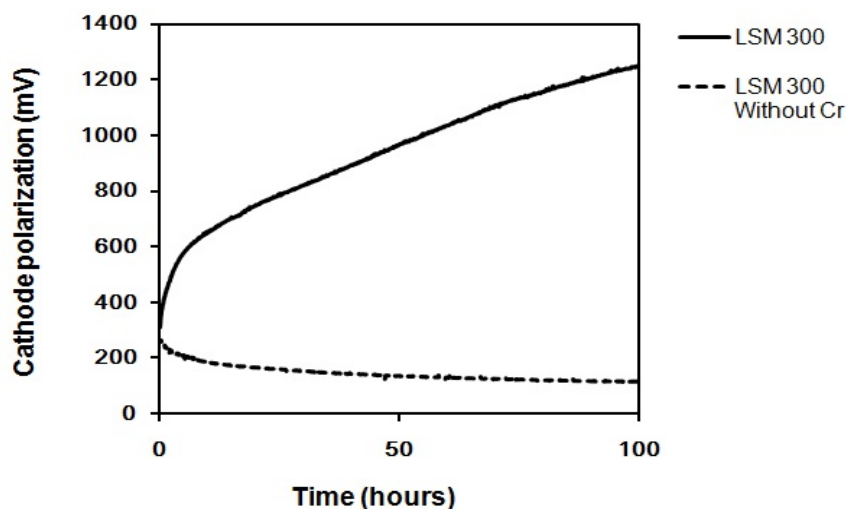


Figure 3-5. Change in the cathode polarization for 100 hours (a) with chromium and (b) without chromium, at a constant current density with an initial cathode polarization of 300 mV.

3.2.4 Cell test at a constant cathode polarization

Chromium poisoning tests in chapter 6 were conducted keeping the cathode polarization constant. The feedback control system shown in **Figure 3-6** to keep the cathode polarization constant was applied for 100 hours. **Figure 3-7** shows change of current density over time with and without chromium poisoning, under constant cathode polarization of 300 mV. **Figure 3-8** shows change of cathode polarization over time with and without chromium poisoning, under a constant cathode polarization of 200 mV. At the end of the chromium poisoning test, the operating temperature was lowered to 500 °C in 40 minutes, keeping the cathode polarization constant by changing the current. The current was cut off at 500 °C and cooled down to the room temperature in 80 minutes.

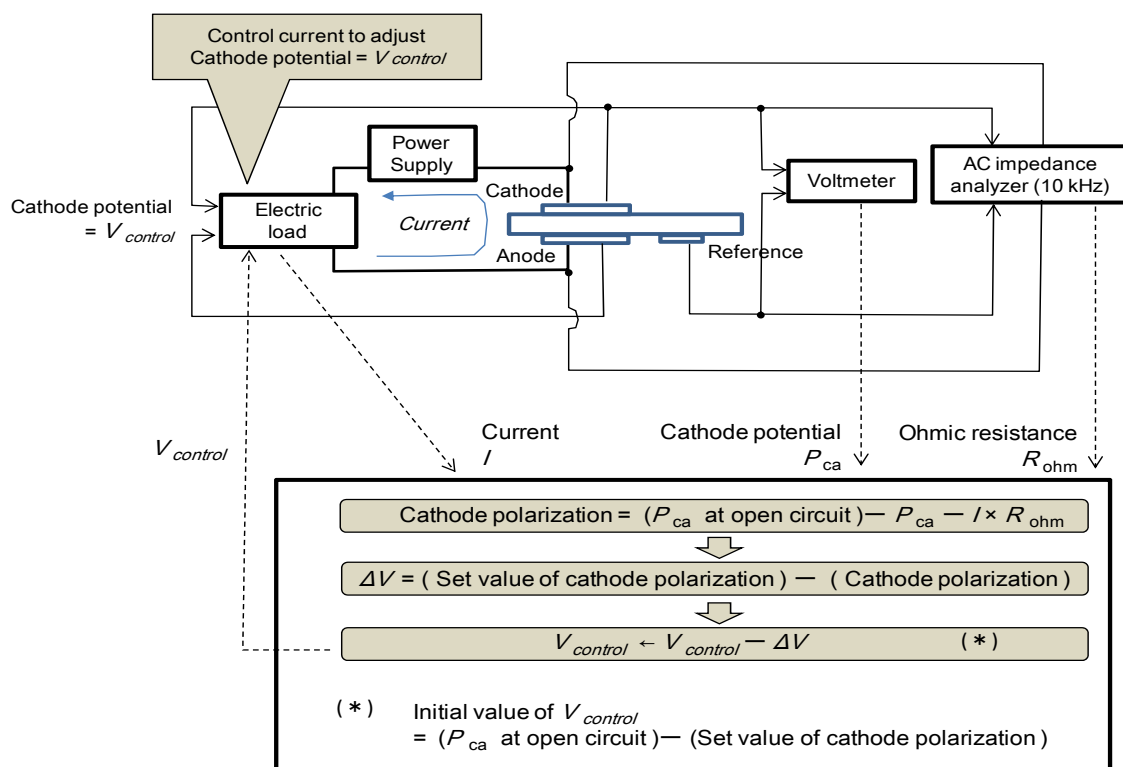


Figure 3-6. Feedback control system of the cell test to keep cathode polarization constant.

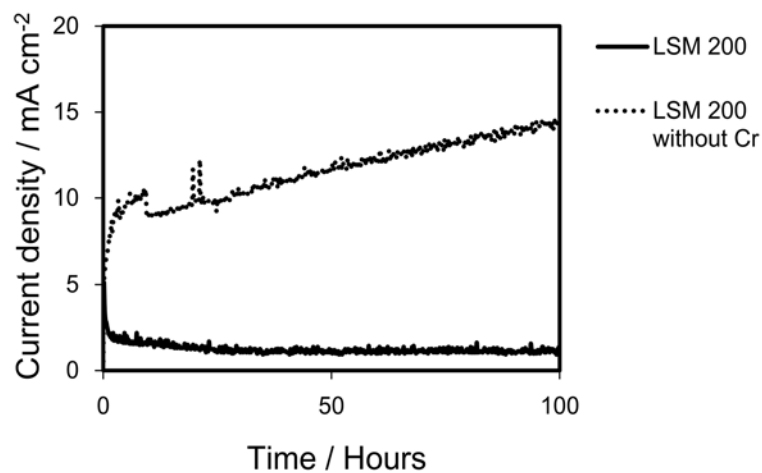


Figure 3-7. Change of current density over time (a) with chromium and (b) without chromium, under a constant cathode polarization of 300 mV.

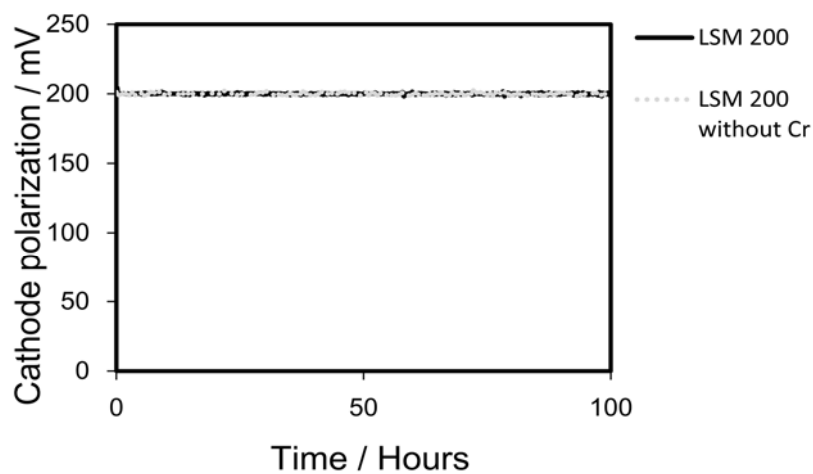


Figure 3-8. Change of cathode polatization over time (a) with chromium and (b) without chromium, under a constant cathode polarization of 200 mV.

3.3 Materials Characterization and Microscopic Analysis

3.3.1 X-ray diffraction

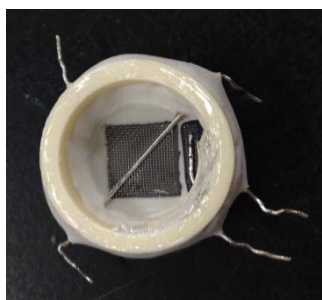
X-ray diffraction (XRD) yields the crystallographic structure of materials and is based on the elastic scattering of X-rays from the electron clouds of the individual atoms in the system, and powder XRD is a technique used to characterize the crystallographic phases, grain size, and preferred orientation in polycrystalline or powdered solid samples. It is usually used to identify unknown substances, by comparing diffraction data with a database maintained by the International Centre for Diffraction Data (ICDD). It may also be used to characterize heterogeneous solid mixtures to determine relative abundance of crystalline compounds and, when coupled with lattice refinement techniques, such as the Rietveld refinement, can provide structural information on unknown materials. In this study, the crystal structures of the cathode materials were determined using Rigaku RINT Ultima III. **Figure 3-2** shows the XRD patterns of LNF powders, which ensured single phase of the material before cell tests.

3.3.2 Sample preparation for microscopic analysis

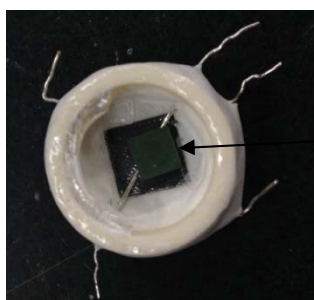
It is generally useful to examine a cross-section of the specimen. This allows observation of the microstructure and detection of any changes that have been produced by such as chemical reaction [9]. The cells after the chromium poisoning tests were embedded in a epoxy resin and they were cut for the cross-sectional observations.

By far the best type of mounting medium has been found to be the liquid epoxy resins. The sample after the cell test is positioned and the resin is poured in. The sample cup should be evacuated in a desiccator, left under vacuum for a few minutes, and then atmospheric pressure reapplied. This has the effect of removing air from porous structure of the electrode. This sort of mounting procedure requires several hours for hardening, preferably being left in a warm place overnight.

1) Cell after the chromium poisoning test



Anode side



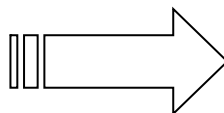
Chromium plate

Cathode side

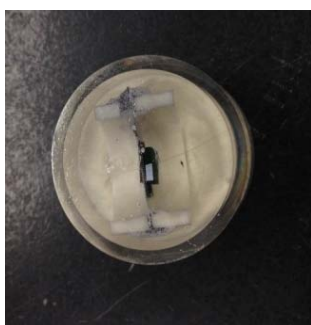
2) Mounting



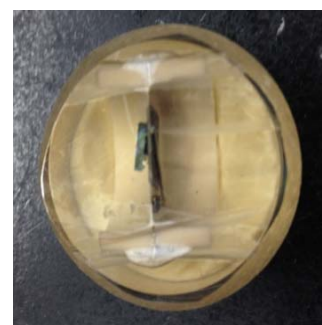
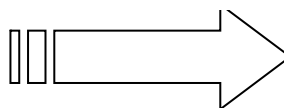
Input liquid epoxy resins



3) Cutting and polishing



Polishing and Coating Carbon



4) SEM and WDS analysis sample

**Figure 3-9.** Sample preparation for microscopic analysis.

After the mounting, the sample is cut by a low speed cutting machine in a plane of the cross-sectional observation and polished to obtain a smooth surface.

3.3.3 *Micromachining by focused ion beam (FIB)*

Focused ion beam, also known as FIB, is a technique used particularly in the semiconductor industry, materials science, and increasingly in the biological field for site-specific analysis, deposition, and ablation of materials. In this study, FIB micro-machining systems FB-2100 (Hitachi High Technology, Japan) or Quanta 3D 200i (FEI) were used for sample preparation for STEM analysis by picking up micrometer-size (ca. $8\ \mu\text{m} \times 8\ \mu\text{m}$, thickness 50 nm - 100 nm) samples.

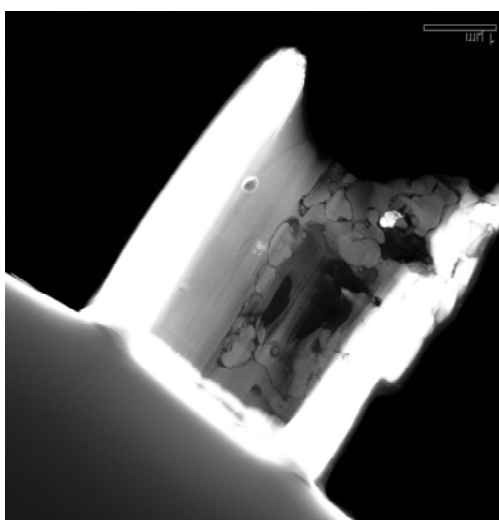


Figure 3-10. STEM sample prepared by FIB.

3.3.4 *Observation by SEM and STEM*

Scanning electron microscope (SEM) is a type of electron microscope that images the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern. The electron interacts with the atoms that make up the sample producing signals

that containing information about the sample's surface topgraph, composition, and other properties. A field emission gun is a type of electron gun in which a sharply-pointed Müller-type emitter is held at several-kilovolt negative potential relative to a nearby electrode, so that there is a sufficient potential gradient at the emitter surface to cause field electron emission. Therefore, more coherent electron beam with up to three orders of magnitude greater current density or brightness than can be achieved with conventional thermionic emitters made of tungsten. Scanning electron microscope with field emission gun (FE-SEM) exhibited significantly improved signal-to-noise ratio and spatial resolution, and greatly increased emitter life and reliability compared with thermionic devices have been achieved (**Figure 3-11**).

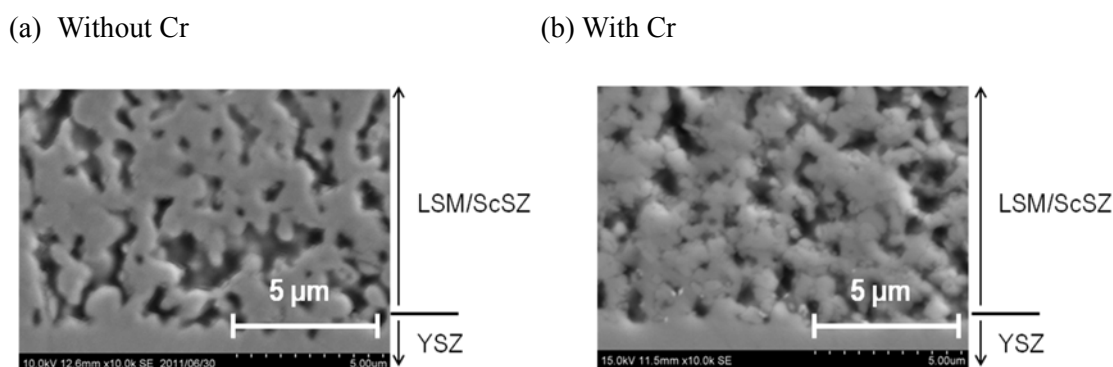


Figure 3-11. Microstructures of the cathode observed by FE-SEM (chapter 5).

A scanning transmission electron microscope (STEM) is focusing the electron beam into a narrow spot which is scanned over the sample in a raster. The rastering of the beam across the sample makes these microscopes suitable as analysis techniques for mapping by energy dispersive X-ray (EDX) spectroscopy and electron energy loss spectroscopy (EELS). These signals can be obtained simultaneously, allowing direct correlation of image and quantitative data. By using a STEM and a high-angle detector, it is possible to form atomic resolution images where the contrast is directly related to the atomic number (Z-contrast image). In this study, STEM-EDX (Hitachi HD2300A, equipped with EDAX Genesis) or STEM-EDS-EELS (JEOL JEM-ARM200F equipped

with JED-2300T, GIF Quantum) with Cs-corrected STEM-EDS-Dual EELS (simultaneous low-loss/core-loss/EDS signal) spectrum imaging acquisition system were employed to observe the microstructure change in cathodes after poisoning tests. STEM-EDX images observed by HD2300A are shown in **Figure 3-12**.

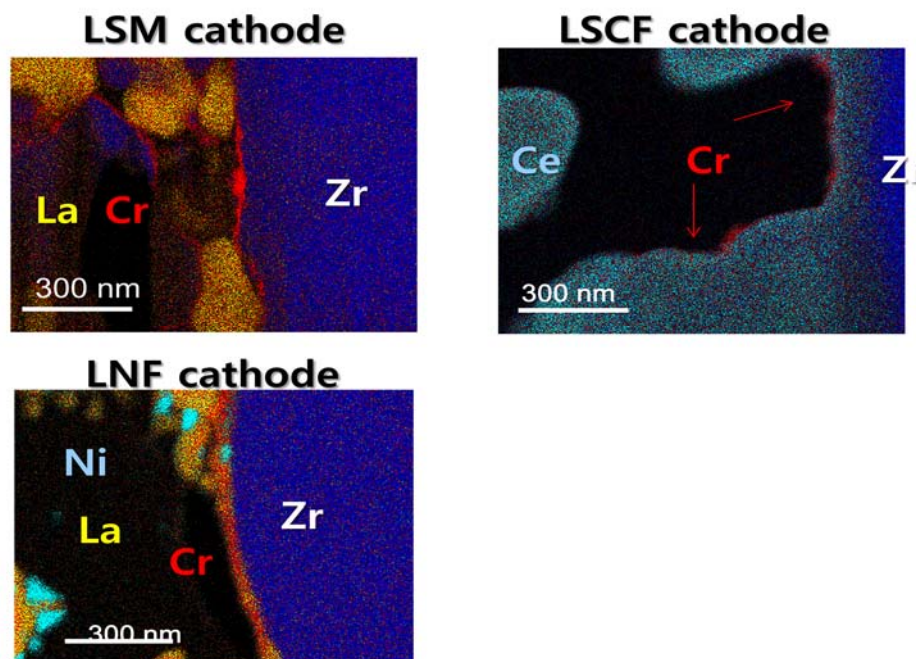


Figure 3-12. STEM-EDX mapping after the Cr poisoning at 200 mV (chapter 5).

3.3.5 SEM-WDX analysis for the measurement of chromium distribution

WDX Analysis stands for Wavelength Dispersive X-ray analysis. It is sometimes referred to as WDS analysis. WDX analysis works in pretty much the same way as EDX analysis, except that its detector classifies and counts the impinging X-rays in terms of its characteristic wavelengths. The detector system uses an X-ray analyzing crystal that only allows the diffraction of desired wavelengths into the X-ray detector for counting. Advantages of WDX analysis over EDX analysis include: 1) a much better energy resolution, preventing many peak overlapping errors frequently encountered in EDX analysis; and 2) lower background noise allowing a more accurate

quantitative analysis. Its disadvantages include: 1) higher time consumption; 2) greater sample damage and chamber contamination because of the high beam currents required; and 3) high cost.

Cross-sectional chromium distribution across the whole cathode was observed by SEM-WDX (Hitachi SU-6600 equipped with EDAX Trident). Line scan of WDX was conducted in thickness direction of the cathode by a beam current of 30 nA at a low magnification ($\times 500$). Chromium concentration was estimated by comparing the intensity of WDX from the cathode with that from the chromium plate assuming that the intensity of WDX is proportional to the concentration. At least five lines were measured for each cathode and average data was applied for the concentration and distribution of chromium in the cathode.

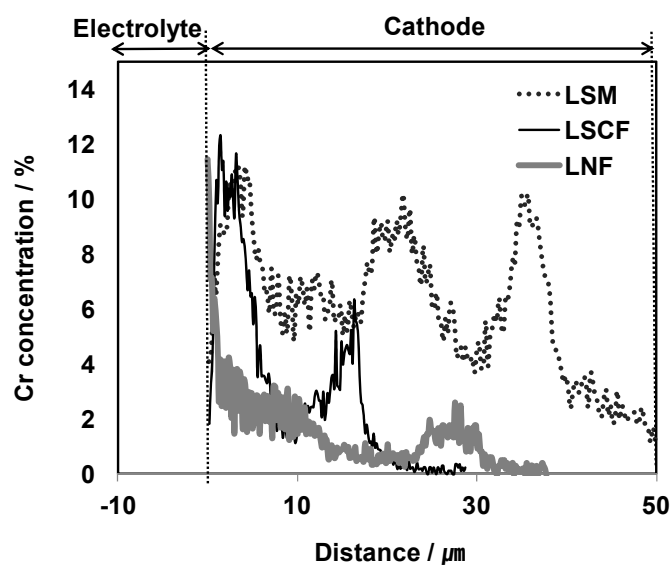


Figure 3-13. Cross-sectional chromium distribution in the cathodes by WDX after the chromium poisoning tests in which the initial cathode polarization was adjusted to 300 mV.

References:

- [1] J. Winkler, P. V. Hendriksen, N. Bonanos, and M. Mogensen, "Geometric Requirements of Solid Electrolyte Cells with a Reference Electrode," *J. Electrochemical Soc.*, **145**, pp. 1184 (1998).
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CHAPTER 4

Comparison of chromium poisoning phenomena among conventional cathode materials LSM, LSCF, and LNF

Abstract^{1 2}:

Chromium poisoning phenomena are compared among three SOFC cathodes using $(\text{La}_{0.8}\text{Sr}_{0.2})_{0.98}\text{MnO}_3$ (LSM), $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$ (LSCF), and $\text{LaNi}_{0.6}\text{Fe}_{0.4}\text{O}_3$ (LNF) at 700°C by changing cathode polarization (0 - 400 mV). Chromium vapor deposited near the electrolyte for LSM and LNF, and the amount of deposition increased with increasing cathode polarization. In the case of LSCF, chromium deposited the cathode surface under smaller cathode polarization (≤ 200 mV). However, chromium deposition near the cathode/electrolyte interface similarly increased for the three cathodes under larger cathode polarization (≥ 300 mV). Cathode polarization facilitated the chromium deposition and there seemed to be no correlation with the current density.

¹ Eunjoo Park, Shunsuke Taniguchi, Jyh-Tyng Chou, Yuya Tachikawa, Yusuke Shiratori, and Kazunari Sasaki, *ECS transactins*, **50**(30), pp. 21-26 (2013)

² Eunjoo Park, Shunsuke Taniguchi, Takeshi Daio, Jyh-Tyng Chou, and Kazunari Sasaki, *Int.. J. Hydrogen Energy*, **39**, pp. 1463-1475 (2013)

4.1 Introduction

Concerning the difference of chromium poisoning phenomena among cathode materials, $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ (LSCF) and $\text{LaNi}_{0.6}\text{Fe}_{0.4}\text{O}_3$ (LNF) have been proposed as potential cathode materials which exhibit higher tolerance to chromium poisoning than lanthanum strontium manganite [1-3].

As mentioned in section 2.3, there are roughly two types of reactions in the chromium poisoning phenomena. One is chemical reaction and the other is electrochemical deposition. Chemical reactivity with the chromium vapor varies by cathode materials, and it may prevent diffusion of chromium vapor into the cathode, decreasing deposition at the cathode/electrolyte interface. Although LSCF and LNF have been proposed as potential cathode materials which exhibit higher tolerance to chromium poisoning, it is not clear which type of reactions dominates the chromium deposition under different cathode polarization conditions for each cathode material. Concerning the electrochemical deposition, two types of mechanism have been proposed as a predominant deposition process. One is a reaction of oxygen vacancy with the chromium vapor and the other is a contribution of nuclei such as Cr-Mn-O or Cr-Sr-O.

In this chapter, change of the chromium deposition profile in the cathode is investigated by changing cathode polarization for three kinds of cathodes using LSM, LSCF, and LNF. Cathode polarization was regulated to the predetermined value from 0 mV to 400 mV at the initial stage and the chromium poisoning tests were conducted for 100 hours under the constant current densities. Cathode polarization was increased up to a larger value (>200 mV) than the real application of SOFC to investigate the effect of electrochemical deposition.

4.2 Experimental

Three kinds of cathode materials, $(\text{La}_{0.8}\text{Sr}_{0.2})_{0.98}\text{MnO}_3$ (LSM), LSCF, and LNF were used as described in **chapter 3**. For the LSM cathode, mixture of LSM and ScSZ with a weight ratio of 1:1 was applied as a functional layer, and LSM powder was used

as a current collection layer. The LSM cathode was sintered at 1200 °C for 5 hours. For the LSCF cathode, $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_2$ (GDC) layer was printed on the electrolyte plate with a thickness of 5 μm and sintered simultaneously with the anode at 1300 °C. LSCF was printed with a thickness of 30 μm on the GDC layer and sintered at 900 °C. For the LNF cathode, the LNF powder was printed with a thickness of 50 μm and sintered at 1100 °C for 4 hours. Electrode area was 8 mm $\times$ 8 mm (0.64 cm²). Platinum mesh was used as the current collector. Reference electrode was placed on the cathode side as shown in **Figure 3-1(a)**. The cell was set in the cell test equipment as shown in **Figure 3-4**. The electric furnace was heated up to 850 °C in 4 hours to soften the glass seal, and cooled down to the cell operating temperature of 700 °C in 1 hour. Cell tests were conducted at 700 °C feeding air (150 ml/min) to the cathode and hydrogen to the anode. First, cathode polarization was measured by changing current density. Cathode polarization was calculated by subtracting cathode side ohmic loss (measured at 10 kHz) from the cathode potential measured between the cathode and the reference electrode. Second, cathode polarization was adjusted to the predetermined value from 0 mV to 400 mV by controlling current density, and the initial current density was kept constant for 100 hours. Current density was different for the three cathodes according to the cathode performance (LSCF > LSM > LNF). At the end of the cell test, temperature of the furnace was cooled naturally with keeping the cathode polarization constant until 500 °C by changing the current, then the fuel and the current were cut off.

After the cell test, cross-sectional chromium distribution in the cathode was measured by SEM-WDX (SU-6600, Hitachi). Chromium concentration was estimated by comparing the intensity of WDX from the cathode with that from the chromium plate. At least five lines were measured for each cathode and average data was applied for the concentration and distribution of chromium in the cathode.

4.3 *Results and discussion*

4.3.1 *Distribution of chromium after the poisoning test*

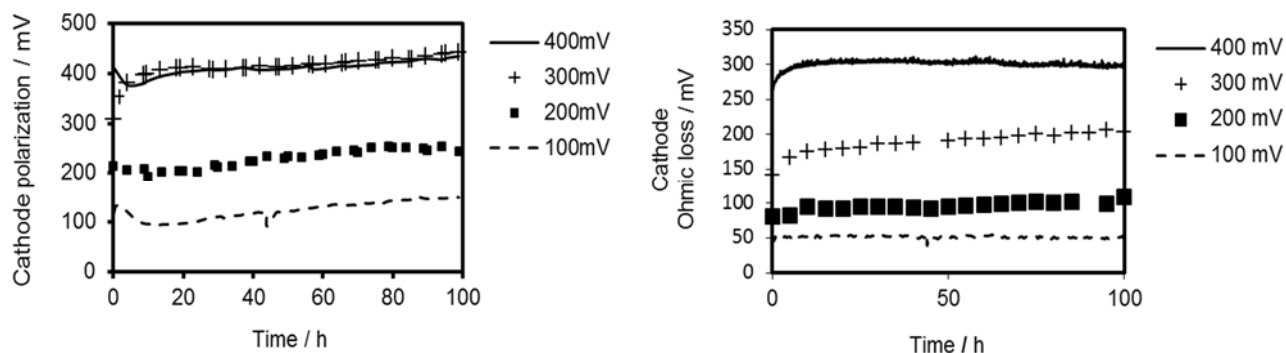
Table 4-1 shows the initial cell performance in the chromium poisoning tests. Cell performance was different among the three cathodes because of the difference in the catalytic activity of the materials and the difference in the microstructure as shown in **Figure 3-3**. Cell performance varied even in the same cell specification, which seemed to be caused by the difference in the ohmic resistance. The possible cause of the variation may come from difference in contact resistance between the cathode and the Pt current collector. Therefore, cathode polarization did not correspond to the current density in magnitude.

Figure 4-1 shows change in cathode polarization and cathode-side ohmic loss with time by the chromium poisoning under the condition of initial cathode polarization ranging from 100 mV to 400 mV. In most cases, cathode polarization increased with time. The increase in cathode polarization with time was more significant for the case with larger initial cathode polarization. In some cases, cathode polarization decreased in the initial stage and tended to increase afterward. The enhancement of the cathode performance with time in the initial stage suggests activation of the cathode as reported in [4-5]. The reason is explained by morphological changes induced by the current leading to an increase in the Three-Phase-Boundary length.

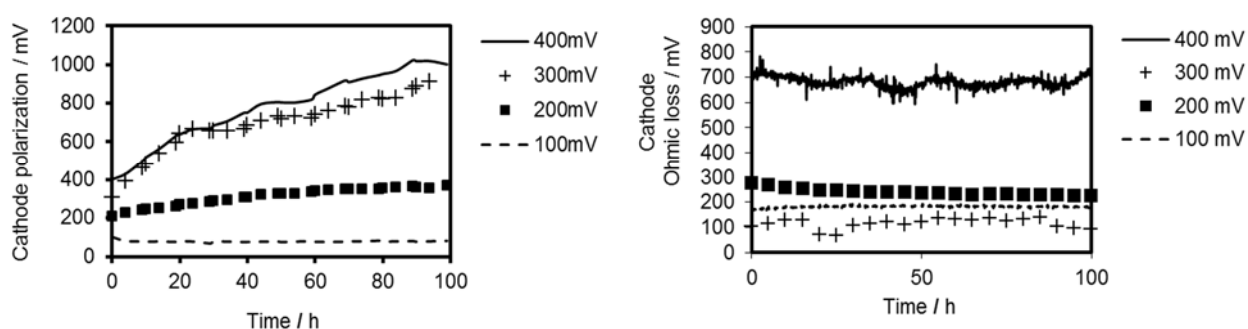
Table 4-1: Initial cell performance in the chromium poisoning tests.

	Cathode polarization / mV	Cathode-side ohmic loss / mV	Cathode-side ohmic resistance / $\Omega \text{ cm}^2$	Current density / mA cm^{-2}
LSM cathode	100	46	0.421	109
	200	80	0.141	563
	300	141	0.360	391
	400	265	0.605	437
LSCF cathode	100	172	0.392	438
	200	278	1.224	227
	300	103	0.489	211
	400	713	0.913	781
LNF cathode	100	44	0.282	156
	200	55	1.403	39
	300	39	0.579	67
	400	43	1.776	24

(a) LSM cathode



(b) LSCF cathode



(c) LNF cathode

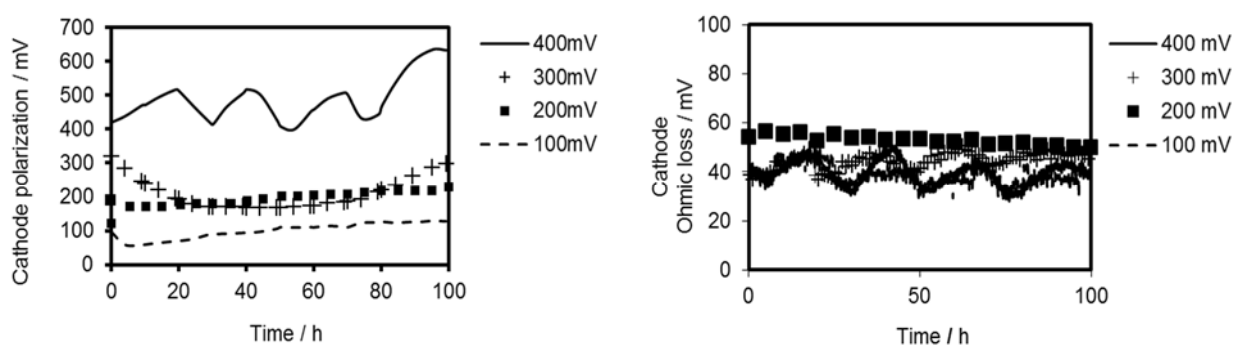


Figure 4-1. Change in the cathode polarization and cathode ohmic loss with time for the three cathodes, (a) the LSM cathode, (b) the LSCF cathode, and (c) the LNF cathode, under the conditions of initial cathode polarization ranging from 100 mV to 400 mV.

Figure 4-2 shows the cross-sectional chromium distribution across the whole cathode by SEM-WDX after the chromium poisoning tests. GDC layer is included in the LSCF cathode in the figure. The chromium observed in the cathode came from outside (right-hand side) diffusing in as a vapor and reacted with the cathode material. Chromium concentration near the cathode/electrolyte interface under the cathode polarization of 0 mV was on the same level as the background of WDX, in other words the lower detection limit, for the three cathodes. We confirmed in another experiment that the chromium distributions did not change so much from the initial during the chromium poisoning test at open circuit for 100 hours, in which chromium had been already contained by the pre-treatment at 850 °C. Chromium distribution changed depending on the initial cathode polarization. In the case of the LSM cathode, chromium was observed almost uniformly in the whole cathode after the test at 0 mV (open circuit), except in the area near the electrolyte with smaller concentration. With increasing cathode polarization, chromium deposition increased significantly near the cathode/electrolyte interface as reported in [6] and it also increased in other part of the cathode. In the case of the LNF cathode, larger concentration of chromium was observed in the outer half of the cathode than the inner half of the cathode after the test at 0 mV. With increasing cathode polarization, chromium deposition increased significantly near the cathode/electrolyte interface and it also increased in other part of the cathode, similarly with the LSM cathode. In the case of the LSCF cathode, larger amount of chromium deposited near the cathode surface under the smaller cathode polarization of 100 mV and 200 mV as reported in [7]. The cause of this phenomena may be related to the higher chemical reactivity of SrO [8, 9] in LSCF and the high ionic conductivity in LSCF which can spread cathode reaction site [10]. However, with increasing cathode polarization, chromium deposition increased significantly near the cathode/electrolyte interface as observed in the LSM cathode and the LNF cathode. The chromium distribution under the initial cathode polarization of ≥ 300 mV was concentrated to the electrode side, although these operating conditions are not realistic in the real SOFC applications.

4.3.2 *Influence of cathode polarization on the chromium deposition*

Figure 4-3(a) shows the relationship between the peak chromium concentration near the cathode/electrolyte interface ($\leq 10\ \mu\text{m}$) in **Figure 4-1** and the initial cathode polarization. Focusing on the deposition near the cathode/electrolyte interface, where more amount of cathode reaction causing cathode polarization likely to occur, the chromium concentration increased with increasing the initial cathode polarization, in common for the three cathodes, although quantitative values of the chromium concentration include a certain amount of error because different cathode microstructures influence the SEM-WDX intensity. Cathode polarization increased with time especially in the case of larger initial cathode polarization because current density was kept constant during the cell test. However, similar relationship was obtained in **Figure 4-3(b)** for the final cathode polarization at the end of the cell test as shown in **Figure 4-3(a)**. For the practical application, it is considered that the LSCF cathode shows the highest tolerance to chromium poisoning because it generates the lowest cathode polarization under the same current density and the deposition locates near the cathode surface, which does not directly affect the electrode performance.

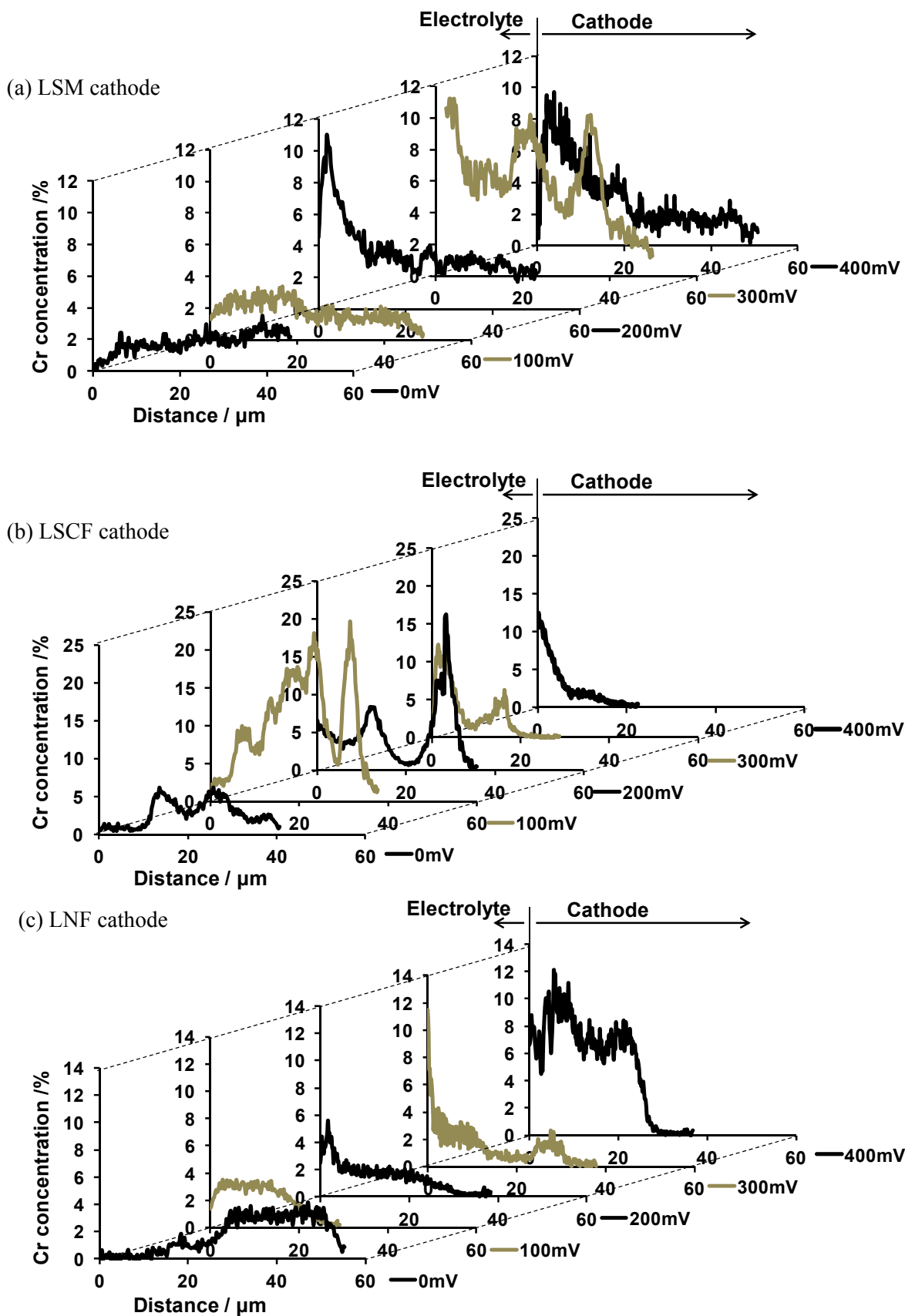


Figure 4-2. Distribution of chromium in the three cathodes, (a) the LSM cathode, (b) the LSCF cathode, and (c) the LNF cathode, after the cell tests with the chromium poisoning.

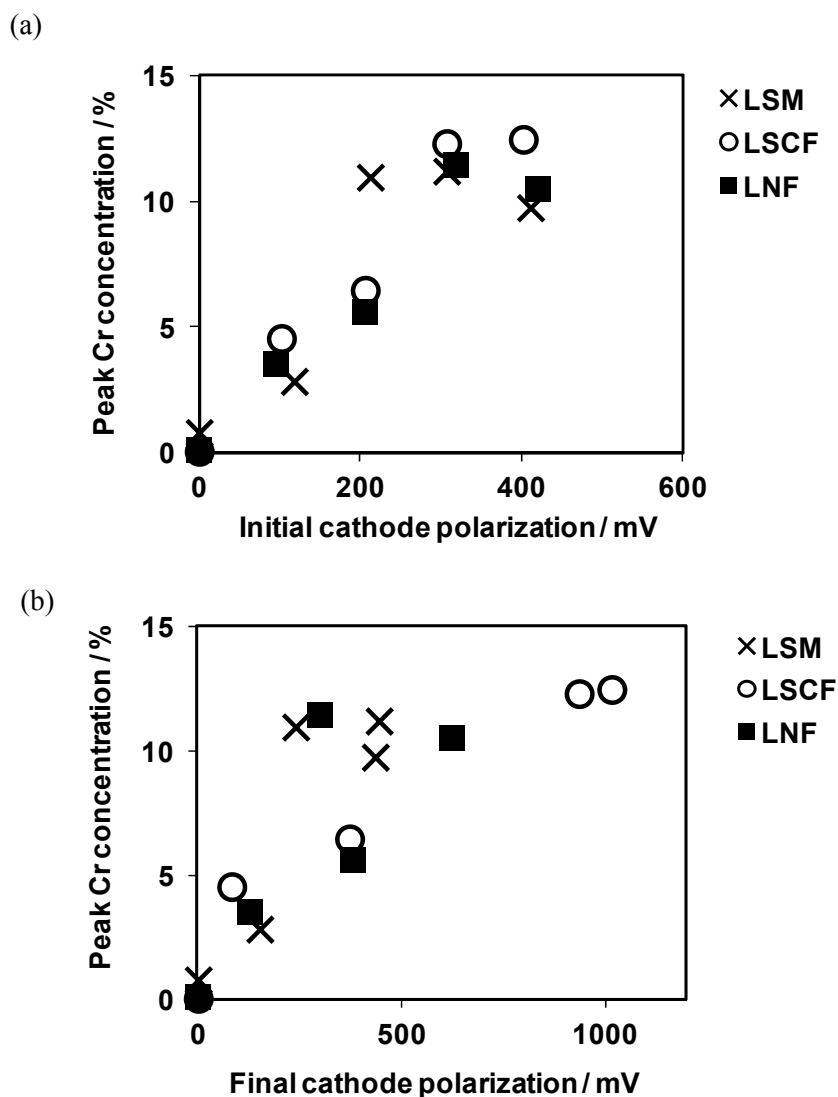


Figure 4-3. Influence of cathode polarization on the amount of chromium deposition near the cathode/electrolyte interface. (a) Influence of initial cathode polarization and (b) influence of final cathode polarization.

Figure 4-4 shows the relationship between the current density and the peak chromium concentration. In general, cathode polarization increases with increasing current density. In this study, however, current density necessarily did not correspond to the cathode polarization in magnitude because of the difference in contacting and microstructure. High concentration of chromium deposition was observed even at a low current density in the case of the LNF cathode, and no correlation was found between

the current density and the peak chromium concentration while cathode polarization had a strong influence. Therefore, chromium deposition seemed to be caused predominantly by cathode polarization with little impact of current density.

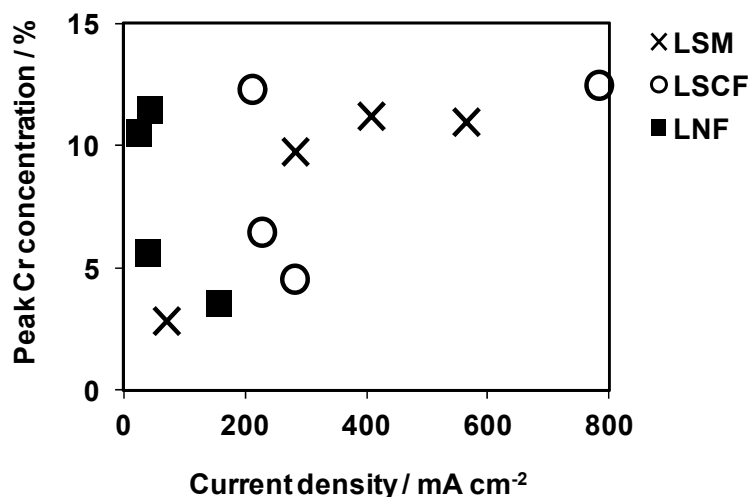


Figure 4-4. Relationship between the current density and the amount of chromium deposition near the cathode/electrolyte interface.

4.4 Conclusion

Chromium vapor deposited near the electrolyte for the LSM cathode and the LNF cathode, and the amount of the deposition increased with increasing cathode polarization. In the case of the LSCF cathode, chromium deposited near the cathode surface under smaller cathode polarization (≤ 200 mV). Under larger cathode polarization (≥ 300 mV), however, chromium deposition near the cathode/electrolyte interface similarly increased for the three cathodes. Cathode polarization facilitated the chromium deposition and there seemed to be no correlation with the current density. For the practical application, it is considered that the LSCF cathode shows the highest tolerance to chromium poisoning because it generates the lowest cathode polarization under the same current density and the deposition locates near the cathode surface, which does not directly affect the electrode performance.

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CHAPTER 5

Influence of cathode polarization on the chromium deposition near the cathode/electrolyte interface of SOFC

Abstract³ :

Mechanism of chromium deposition at the cathode/electrolyte interface was investigated by utilizing S-TEM analysis. Microscopic distribution of the deposited chromium, which was located on the surface of LSM, LSCF, LNF grains, and also on the surface of zirconia and ceria, seemed to correspond to the distribution of oxygen vacancy by cathode polarization at the electrode reaction sites. Chromium deposition on the zirconia surface seemed to be assisted by metal oxides segregated from the cathode material, which can conduct electron required for generating oxygen vacancy continuously. Oxygen deficiency on the surface of the deposited chromium was confirmed and interdiffusion of chromium and zirconium caused by cathode polarization was also suggested.

³ Eunjoo Park, Shunsuke Taniguchi, Takeshi Daio, Jyh-Tyng Chou, and Kazunari Sasaki, *Int. J. Hydrogen Energy*, **39**, pp. 1463-1475 (2013)

5.1 Introduction

In chapter 4, we have confirmed that cathode polarization facilitated chromium deposition near the cathode/electrolyte interface similarly for the LSM cathode, the LSCF cathode, and the LNF cathode, although chromium deposition for the LSCF cathode located near the cathode surface under smaller cathode polarization (≤ 200 mV).

In this chapter, mechanism of chromium deposition at the cathode/electrolyte interface was investigated in detail by utilizing STEM analysis. Distribution of chromium deposition after the cell tests were analyzed especially near the cathode/electrolyte interface. Mechanism of the electrochemical chromium deposition was discussed by considering the influence of cathode polarization, difference among cathode materials, contribution of current density, and microscopic distribution of the deposited chromium. Elemental distribution around the boundary of the zirconia surface and the deposited chromium was also measured focusing on oxygen distribution to confirm the mechanism.

5.2 Experimental

After the SEM-WDX measurements described in chapter 4, micrometer-size (ca. $8\ \mu\text{m} \times 8\ \mu\text{m}$, thickness 50 -100 nm) samples were picked up by utilizing FIB (Focused Ion Beam) micromachining system, Quanta 3D 200i (FEI) or FB-2100 (Hitachi). Cross-sectional elemental analysis in microscopic area near the cathode/electrolyte interface was conducted by STEM-EDX-EELS (Scanning Transmission Electron Microscopy- Energy Dispersive X-ray Spectroscopy- Electron Energy-Loss Spectroscopy, JEOL JEM-ARM200F equipped with JED-2300T, GIF Quantum) with Cs-corrected STEM-EDX-Dual EELS (simultaneous low-loss/coreloss/EDX signal) spectrum imaging acquisition system.

5. 3 *Results and discussion*

Figure 5-1 shows the cross-sectional chromium distribution across the whole cathode by SEM-WDX after the chromium poisoning tests. GDC layer is included in the LSCF cathode in the figure. The chromium observed in the cathode came from outside (right-hand side) diffusing in as a vapor and reacted with the cathode material. Chromium concentration near the cathode/electrolyte interface under the cathode polarization of 0 mV was on the same level as the background of WDS, in other words the lower detection limit, for the three cathodes. We confirmed in another experiment that the chromium distributions did not change so much from the initial during the chromium poisoning test at open circuit for 100 hours, in which chromium had been already contained by the pretreatment at 850 °C. Chromium distribution changed depending on the initial cathode polarization. In the case of the LSM cathode, chromium concentration of around 2 % was observed almost uniformly in the whole cathode after the test at 0 mV (open circuit) except in the area near the electrolyte with a lower concentration. With increasing cathode polarization, chromium deposition increased significantly near the cathode/electrolyte interface as reported in [1] and it also increased in other part of the cathode. In the case of the LNF cathode, chromium concentration of 3 % was observed in the outer half of the cathode and lower concentration of less than 1 % was observed in the inner half of the cathode after the test at 0 mV. With increasing cathode polarization, chromium deposition increased significantly near the cathode/electrolyte interface and it also increased in other part of the cathode, similarly with the LSM cathode. In the case of the LSCF cathode, chromium concentration varied from place to place, with the highest concentration of 6 % and the lowest concentration of 1 % after the test at 0 mV. Higher chemical reactivity of LSCF than LSM or LNF might probably caused the higher concentration of chromium observed in the cathode. Larger amount of chromium was deposited near the cathode surface under the smaller cathode polarization of 100 mV and 200 mV as reported in [2]. The cause of this phenomena is not clear, but it may be related to the higher chemical reactivity of SrO [3, 4] in LSCF and the high ionic conductivity in

LSCF the use of which can expand cathode reaction sites [5]. However, with increasing cathode polarization, chromium deposition increased significantly near the cathode/electrolyte interface as observed in the LSM cathode and the LNF cathode.

Figures 5-1 - 5-5 show the results of microscopic elemental analysis by STEM-EDX near the cathode/electrolyte interface after the chromium poisoning tests with the initial cathode polarization of 200 mV. For the LSM cathode, most of the chromium deposition was located on the ScSZ surface and on the LSM surface as shown in **Figure 5-1(a)(b)**. **Figure 5-1(c)** shows the quantitative distribution from the inside of the ScSZ grain to the adjacent ScSZ grain through the LSM grain in between. The chromium concentrations were about 4 at% at the LSM grain interface, and 1 at% at the center of the LSM grain. This result indicates the diffusion of the deposited chromium from the surface into the LSM grain. **Figure 5-1(d)** shows the quantitative distribution from the outside of the ScSZ grain to the inside. High concentration of chromium was observed on the surface of the ScSZ grain. Manganese was also observed slightly outside and a little overlapping with the chromium deposition, which seemed to have diffused during the cell fabrication at 1200 °C or diffused under the cathodic polarization condition in the chromium poisoning test. Under a large cathodic polarization condition, the manganese oxides can be precipitated from the A-site deficient LSM [6,7], and can diffuse on the surface of zirconia. The manganese observed near the chromium might have assisted the chromium deposition by conducting electron as discussed below. In the case of the LSCF cathode, chromium deposition was observed on the surface of the GDC layer and on the LSCF grain as shown in **Figures 5-2 - 5-5**. The deposition on the surface of the GDC layer was similar to the results reported in [8,9]. Segregation of strontium was observed in the LSCF grains and it was located in the same area of the chromium deposition as shown in **Figure 5-4**, which indicates the formation of SrCrO_4 [6,10,11]. In the case of the LNF cathode, chromium deposition was observed on the surface of the YSZ electrolyte and on the LNF grains, similarly to the LSM cathode as shown in **Figure 5-5**. Ni-rich segregation was identified on the edge of the LNF grains as reported in [9]. In the

middle of the LNF grains, the chromium concentration was about 1 at%, which was lower than that at the surface, indicating that chromium had diffused into the LNF cathode from the surface. High concentration of chromium was observed on the surface of the YSZ electrolyte and nickel was also observed slightly outside and a little overlapping with the chromium deposition as shown in **Figure 5-5(d)**. The nickel observed near the chromium deposition had been segregated from the LNF grain and might have assisted the chromium deposition by conducting electron, similarly to manganese in the LSM cathode.

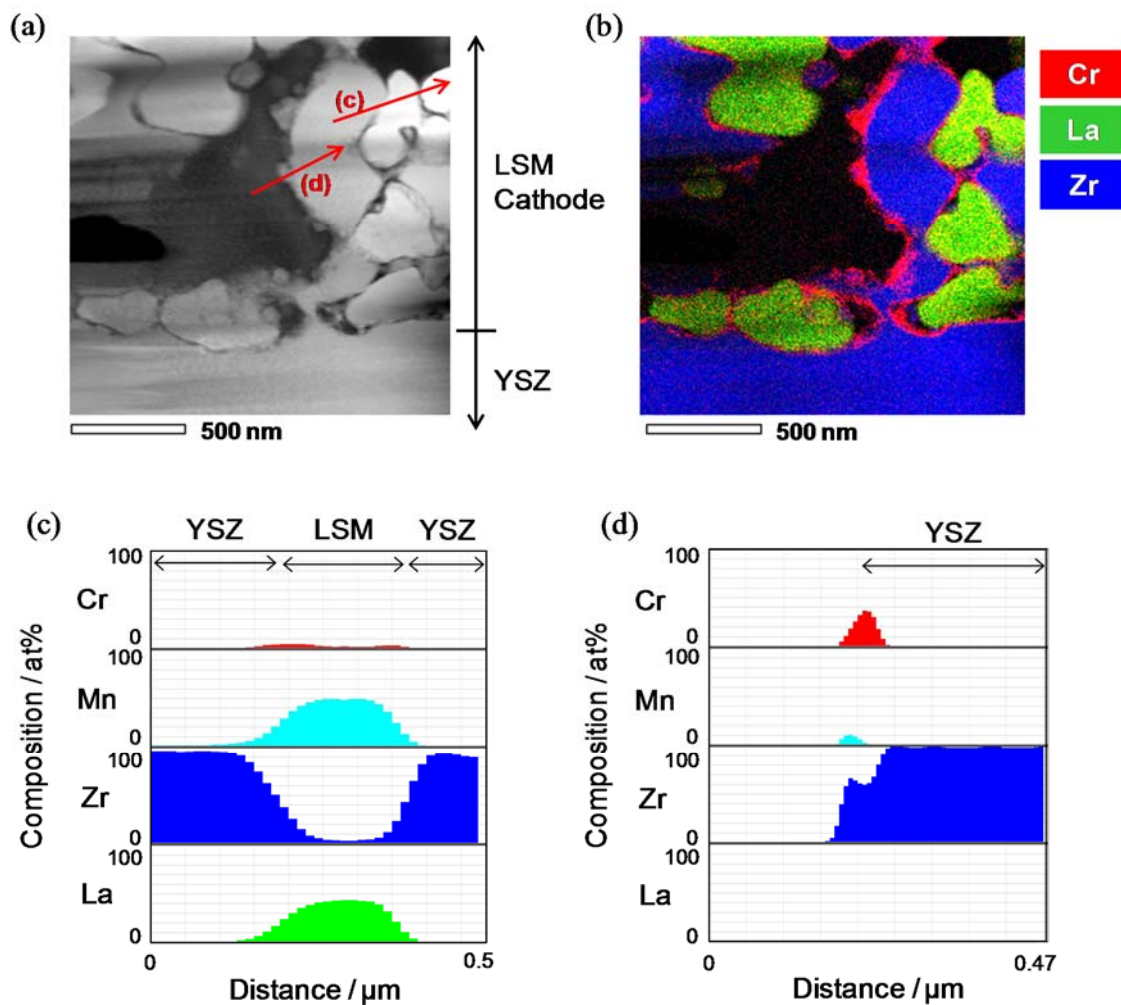


Figure 5-1. STEM-EDX analysis for the LSM cathode around the cathode/electrolyte interface after the chromium poisoning test with the initial cathode polarization of 200 mV: (a) Bright-field image, (b) EDX count maps of Cr, La and Zr, (c-d) compositional profile of Cr, Mn, Zr and La along the lines shown in (a).

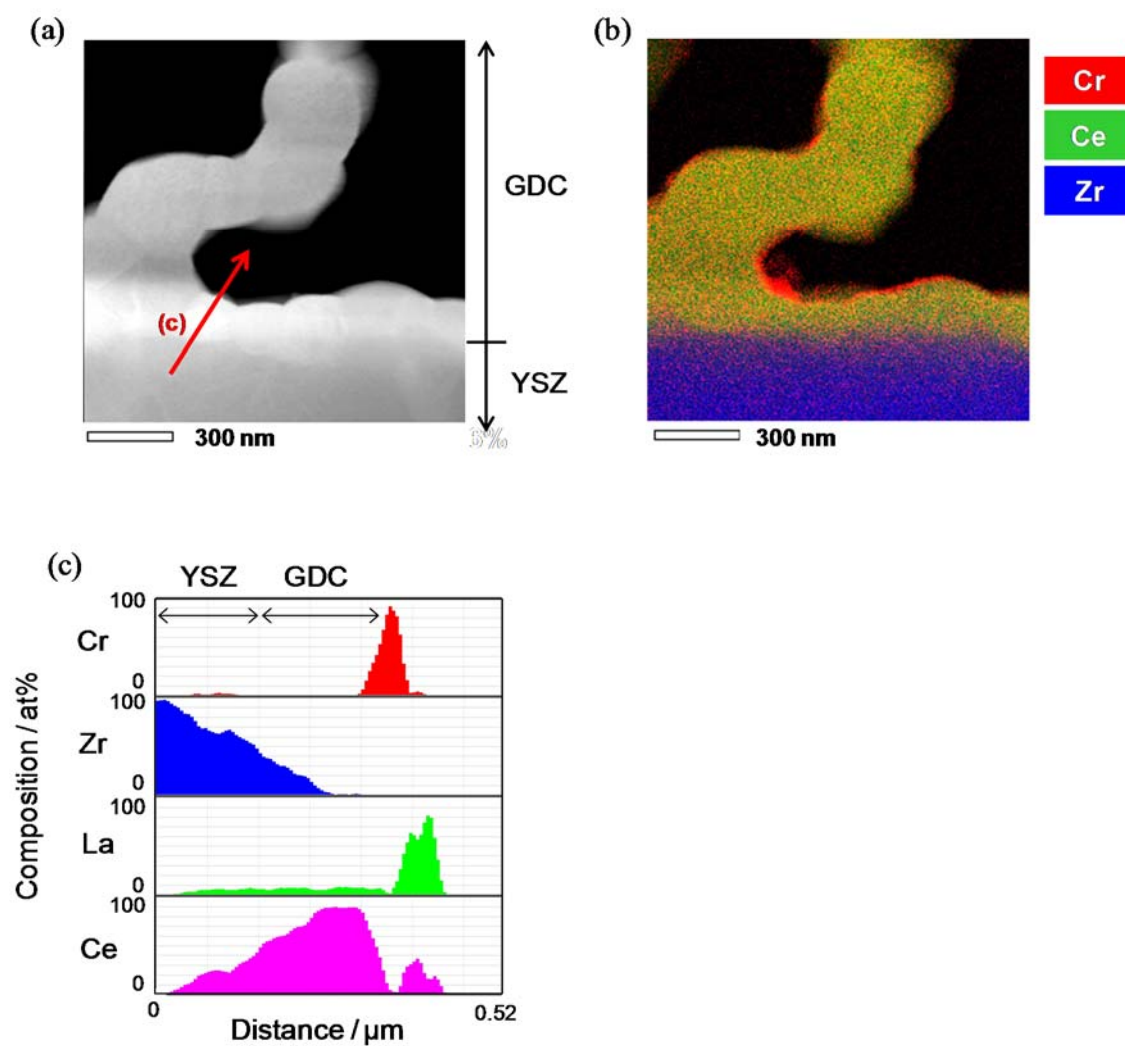


Figure 5-2. STEM-EDX analysis for the LSCF cathode around the GDC layer after the chromium poisoning test with the initial cathode polarization of 200 mV: (a) Bright-field image, (b) EDX count maps of Cr, Ce and Zr, (c) compositional profile of Cr, Zr, La and Ce along the lines shown in (a).

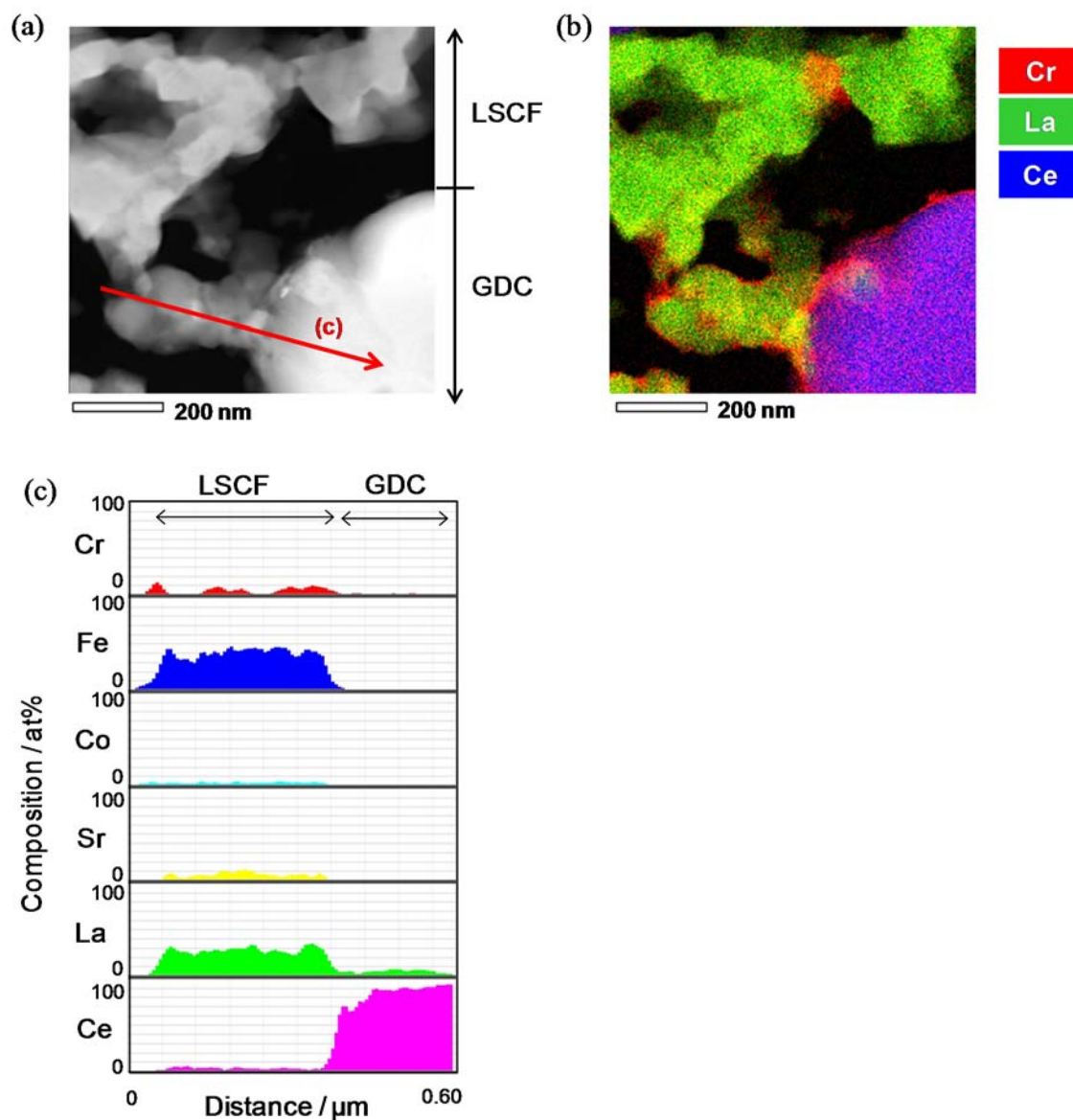


Figure 5-3. STEM-EDX analysis for the LSCF cathode around the LSCF/GDC interface after the chromium poisoning test with the initial cathode polarization of 200 mV: (a) Bright-field image, (b) EDX count maps of Cr, La and Ce, (c) compositional profile of Cr, Co, Sr, La and Ce along the lines shown in (a).

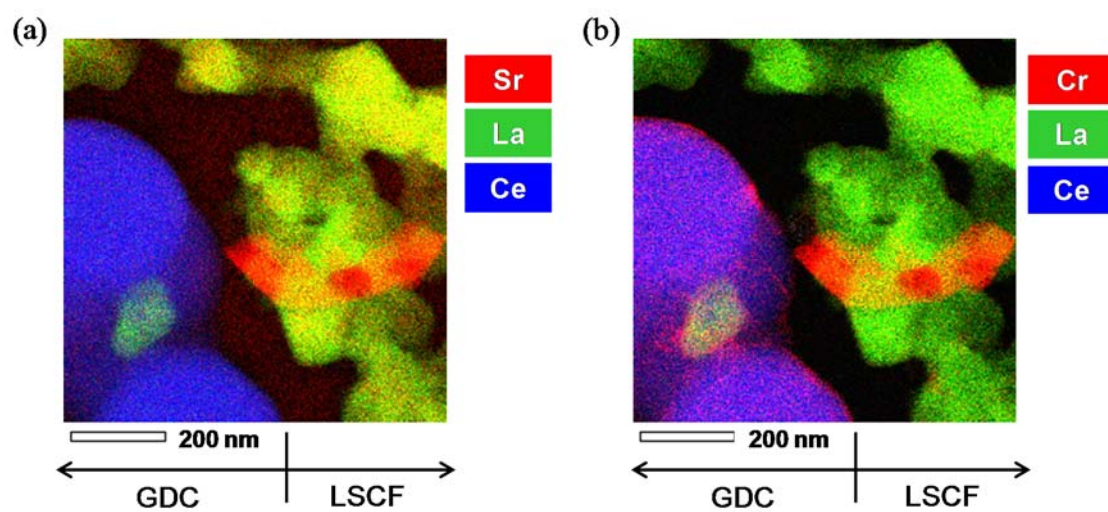


Figure 5-4. STEM-EDX analysis for the LSCF cathode in another area near the LSCF/GDC interface than **Figure 5-3** after the chromium poisoning test with the initial cathode polarization of 200 mV. The EDX count maps of (a) Sr, La, Ce and (b) Cr, La, Ce.

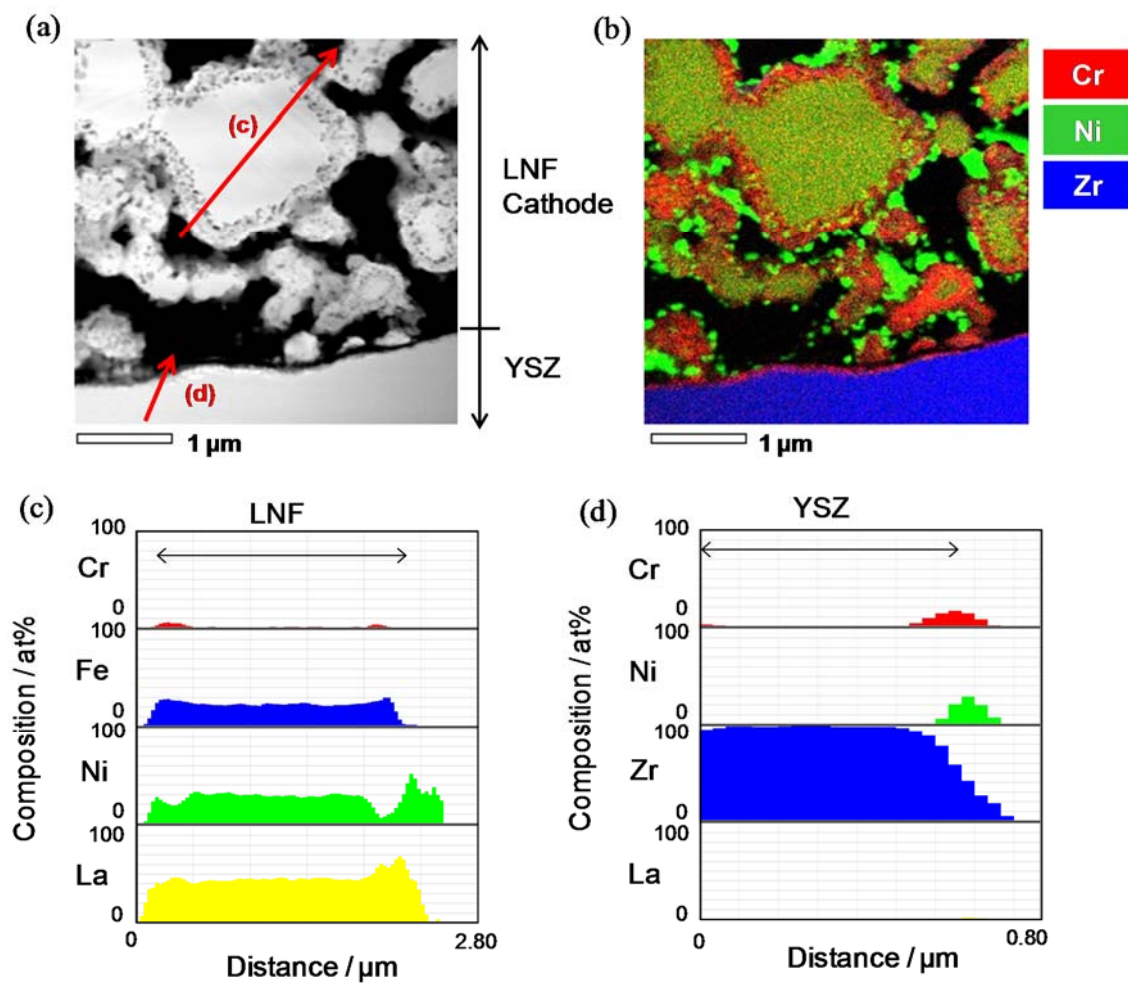


Figure 5-5. STEM-EDX analysis for the LNF cathode around the cathode/electrolyte interface after the chromium poisoning test with the initial cathode polarization of 200 mV: (a) Bright-field image, (b) EDX count maps of Cr, Ni and Zr, (c-d) compositional profile of Cr, Fe, Ni, Zr and La along the lines shown in (a).

Considering the fact that the amount of the chromium deposition near the cathode/electrolyte interface increased with increasing cathode polarization as shown in **Figure 4-3**, the microscopic distribution of the chromium deposition observed in **Figures 5-1 - 5-5** suggests the positions where local cathode polarization was induced. In general, cathode polarization causes the change in oxygen activity at the electrode reaction site by the following equations,

$$\eta = - (RT / 2 F) \ln [a_o / P_{O_2}^{1/2}] \quad (1)$$

η : cathode polarization

a_o : oxygen activity at the electrode reaction site

P_{O_2} : oxygen partial pressure in the gas phase.

Oxygen vacancy $Vo^{\bullet\bullet}$ should increase at the electrode reaction sites with increasing cathode polarization, corresponding to the decrease in oxygen activity.

Figure 5-6 shows the results of STEM-EDX-EELS analysis across the boundary of the zirconia and the deposited chromium for the LSM cathode with the initial cathode polarization of 200 mV. Oxygen deficient region with a thickness of about 10 nm was observed by EELS in the outer side of the deposited chromium. The profile is believed to reflect the distribution of oxygen during the cell test because of the procedure at the end of the cell test, in which the temperature was lowered by keeping the cathode polarization. The oxygen deficient state on the surface must have interacted with chromium vapor and facilitated deposition of chromium. Concentrations of zirconium and chromium gradually changed on both sides of the boundary, suggesting interdiffusion, to the distance of about 20 nm. Manganese was observed close to the deposited chromium.

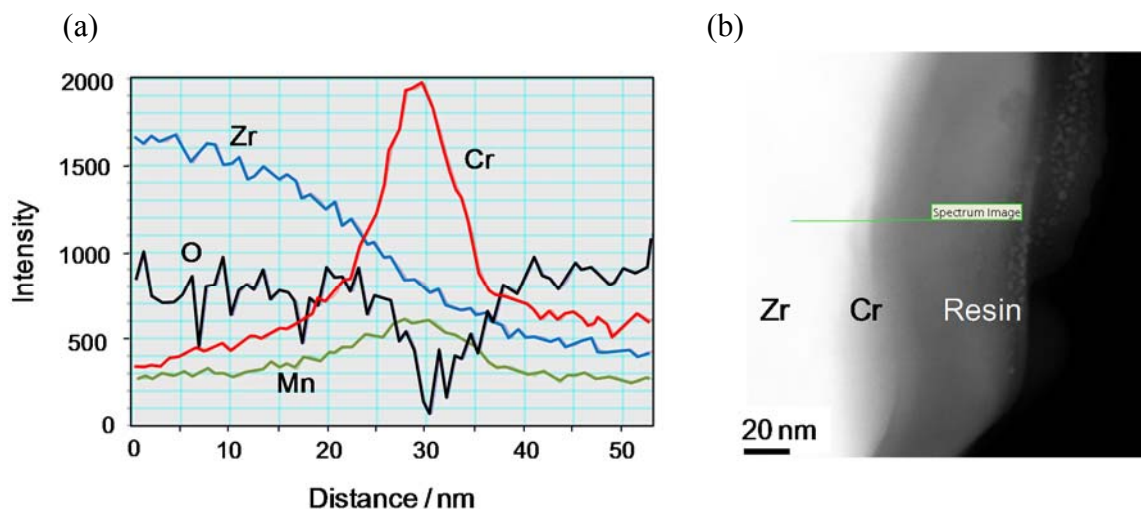
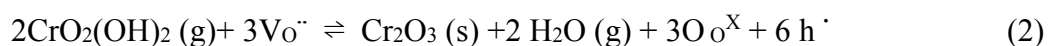


Figure 5-6. STEM-EDX-EELS analysis across the boundary of the zirconia surface and the deposited chromium for the LSM cathode with the initial cathode polarization of 200 mV: (a) EDX count profile of Zr, Cr, Mn and EELS count profile of O, (b) ADF(Annular Dark Field) image.

Basic reaction of the chromium deposition is considered to be consistent with the equation described in [5],



Chromium deposition is facilitated by cathode polarization with little correlation with the current density of SOFC as confirmed by **Figure 4-4**. In this study, chromium deposition has been carried out under cathodic polarization which changes over time, and higher cathodic polarization may also have caused the change in the surface of the cathode grain by such as segregation. Therefore it is unreasonable to compare deposition kinetics precisely and to discuss the chromium poisoning mechanism generally applicable to all conditions. Focusing on the chromium deposition on the zirconia electrolyte surface, electronic conducting media is required to generate oxygen vacancy and also to accept the chromium deposition. Because zirconia intrinsically has no electronic conductivity, it is considered that manganese oxide or

nickel oxide segregated from the cathode material and diffused to the zirconia surface played the role. Dissolution of these elements into zirconia may cause electronic conduction on the zirconia surface as described in [5].

The elemental distribution across the boundary of the zirconia and the deposited chromium in **Figure 5-6** can be explained by the mechanism illustrated in **Figure 5-7**. (i) Metal oxides (MOx) segregated from the cathode material such as manganese oxide or nickel oxide, which may be caused by cathode polarization, exist on the surface of zirconia. Oxygen vacancy is induced on the surface of zirconia via MOx when cathode polarization is applied. (ii) The oxygen vacancy on the surface interacts with chromium vapor and facilitates deposition of chromium. MOx assists the chromium deposition by conducting electron as well as by generating oxygen vacancy continuously. (iii) Oxygen deficiency in the surface region of zirconia facilitates diffusion of chromium and oxygen into zirconia. Zirconium also diffuses into the deposited chromium. (iv) The deposited chromium can also generate oxygen vacancy which can act as a deposition site. On the surface of the chromium deposition, a part of the chromium may exist in oxygen deficient state depending on the cathode polarization. MOx on the surface of zirconia can react with the deposited chromium and produce chemical reaction compound.

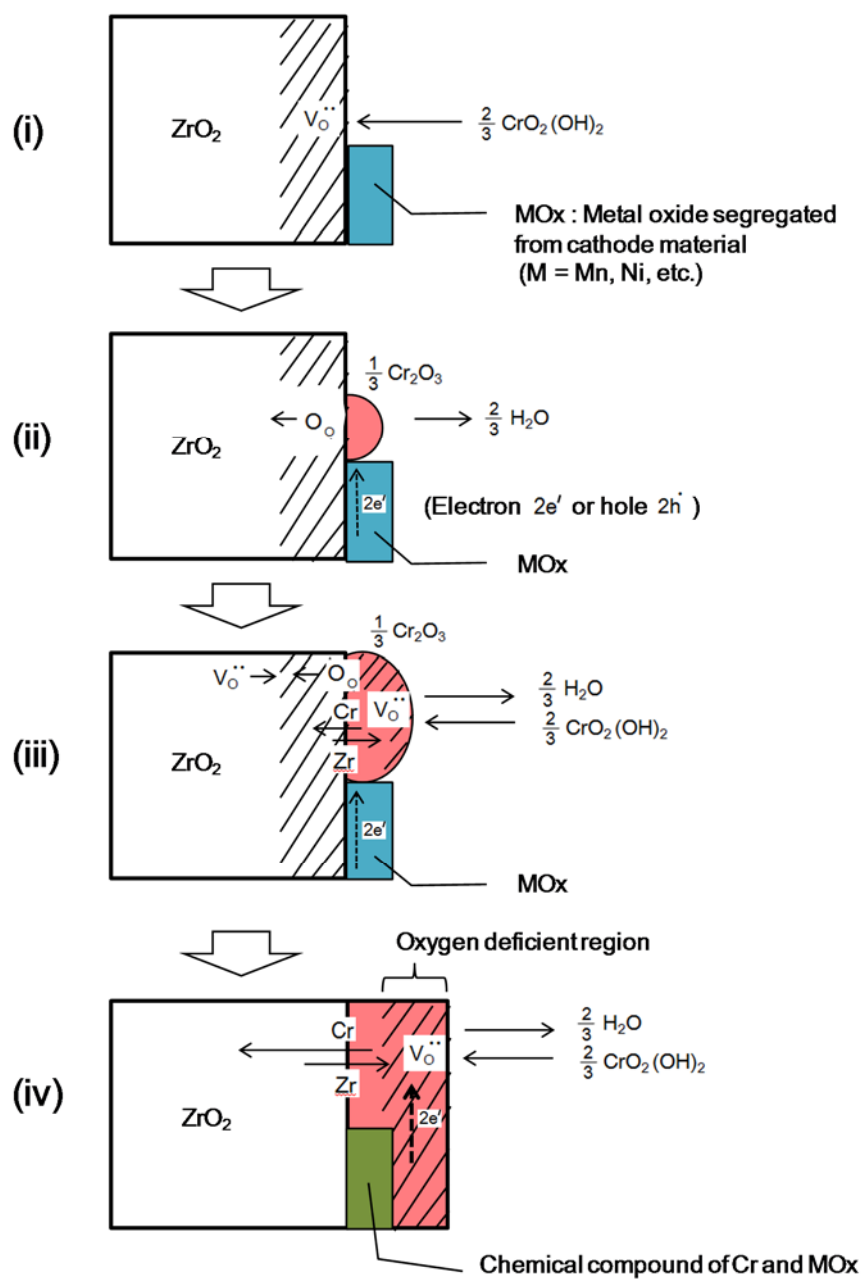


Figure 5-7. Mechanism of chromium deposition on the surface of zirconia electrolyte induced by cathode polarization and the subsequent elemental diffusion.

5. 4 Conclusion

Microscopic distribution of the deposited chromium, which was located on the surface of LSM, LSCF, LNF grains, and also on the surface of zirconia and ceria, seemed to correspond to the distribution of oxygen vacancy by cathode polarization at the electrode reaction sites. Chromium deposition on the zirconia surface seemed to be assisted by metal oxides segregated from the cathode material, such as manganese oxide for the LSM cathode or nickel oxide for the LNF cathode. The metal oxides seemed to provide electrons or holes required for generating oxygen vacancy and accepting the chromium deposition on the surface of zirconia. The deposited chromium can diffuse into the zirconia together with oxygen, which is facilitated by oxygen deficiency in the surface region of zirconia. Zirconium ions also diffuse into the deposited chromium. The surface of the deposited chromium may exist in an oxygen deficient state, depending on the cathode polarization, and can act as the deposition site.

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CHAPTER 6

Comparison of chromium poisoning among solid oxide fuel cell cathode materials

Abstract⁴ :

Chromium poisoning phenomena were studied for different kinds of cathode materials, $(\text{La}_{0.8}\text{Sr}_{0.2})_{0.98}\text{MnO}_3$ (LSM), $\text{Pr}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (PrSM), $\text{Nd}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (NdSM), $\text{Br}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$ (BSCF), using yttria-stabilized zirconia (YSZ) as electrolyte at 700 °C under constant cathode polarization conditions (≤ 300 mV). Deposition of chromium increased with increasing cathode polarization similarly for the four cathodes, although position of the deposition was different for the BSCF cathode. Chromium deposited near the cathode/electrolyte interface for the LSM cathode, the PrSM cathode and the NdSM cathode. Chromium deposition on the surface of the zirconia electrolyte was observed for the PrSM cathode and the NdSM cathode as previously observed in the LSM cathode. Oxygen deficiency in the deposited chromium on the surface of the zirconia electrolyte was also observed, thus the reaction mechanism of chromium vapor with the oxygen vacancy induced by cathode polarization was supported. The oxygen vacancy on the surface of the zirconia electrolyte seemed to be generated via metal oxides such as manganese oxide or neodymium oxide segregated from the cathode materials. Chromium deposited on the surface of the BSCF cathode. Cathode polarization seems to increase reactivity of BSCF and enhance trapping of chromium vapor near the cathode surface.

⁴ Eunjoo Park, Shunsuke Taniguchi, Takeshi Daio, Jyh-Tyng Chou, and Kazunari Sasaki, *Solid State Ionics* (Submitted)

6.1 Introduction

In the previous chapters, we confirmed that cathode polarization facilitated chromium deposition near the cathode/electrolyte interface similarly for the LSM cathode, the LSCF cathode, and the LNF cathode. We also observed chromium deposition on the zirconia electrolyte and oxygen deficiency in the deposited chromium for the LSM cathode, which seemed to support the mechanism that oxygen vacancy induced by cathode polarization facilitates chromium deposition. However, detailed discussion about the kinetics was difficult because these experiments were conducted under a constant current density with changing cathode polarization over time.

In this chapter, chromium poisoning phenomena were studied for different cathode materials, $\text{Pr}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (PrSM), $\text{Nd}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (NdSM) and $\text{Br}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$ (BSCF) under constant cathode polarization conditions. Cathode polarization was regulated to the predetermined values from 100 mV to 300 mV, and distribution of the chromium deposition were analyzed after cooling the cell with keeping the cathode polarization. Mechanism of the chromium deposition is discussed especially for the LSM cathode, the PrSM cathode and the NdSM cathode focusing on the surface of zirconia electrolyte, considering microscopic distribution around the boundary of the zirconia surface and the deposited chromium.

6.2 Experimental

Four kinds of cathode materials, $(\text{La}_{0.8}\text{Sr}_{0.2})_{0.98}\text{MnO}_3$ (LSM), $\text{Br}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$ (BSCF), $\text{Pr}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (PrSM), and $\text{Nd}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (NdSM) were used, and they were printed on the other side of the electrolyte plate and then sintered. Heat-treatment condition was 1200 °C - 4 h for LSM, PrSM, NdSM, and 1100 °C - 5 h for BSCF. Electrode area was 8 mm × 8 mm (0.64 cm²). Pt mesh was used as the current collector. Reference electrode was placed on the anode side as shown in **Figure 3-1(b)**. For the experiment of chromium poisoning, a chromium plate with 5 mm × 5 mm × 1 mm in size was placed on the current collector of the cathode side. The chromium plate did not contact directly with the cathode.

The cell was set in the cell test equipment as schematically shown in **Figure 3-4** and heated by the electric furnace up to 850 °C in 4 hours to soften the glass seal, and was cooled down to the operating temperature of 700 °C in 1 hour. The feedback control system shown in **Figure 3-5** to keep the cathode polarization constant was applied for 100 hours. At the end of the chromium poisoning test, the operating temperature was lowered to 500 °C in 40 minutes keeping the cathode polarization constant. The current was cut off at 500 °C and cooled down to the room temperature in 80 minutes.

The cells after the chromium poisoning tests were embedded in a epoxy resin and they were cut for cross-sectional observations. Cross-sectional chromium distribution across the whole cathode was observed by SEM-WDX (Scanning Electron Microscopy-Wavelength Dispersive X-ray Spectroscopy, Hitachi SU-6600 equipped with EDAX Trident) in thickness direction. Chromium concentration was estimated by comparing the intensity of WDX from the cathode with that from the chromium plate assuming that the intensity of WDX is proportional to the concentration. At least five lines were measured for each cathode and average data was applied for the concentration and distribution of chromium in the cathode. Cross-sectional elemental analysis in microscopic area near the cathode/electrolyte interface was conducted by STEM-EDX-EELS (Scanning Transmission Electron Microscopy- Energy Dispersive X-ray Spectroscopy- Electron Energy-Loss Spectroscopy, JEOL JEM-ARM200F equipped with JED-2300T, GIF Quantum) with Cs-corrected STEM-EDS-Dual EELS (simultaneous low-loss/core-loss/EDS signal) spectrum imaging acquisition system, after picking up micrometer-size (ca. 8 μm $\times$ 8 μm , thickness $\leq$ 50 nm) samples by utilizing FIB (Focused Ion Beam) micro-machining system (Hitachi FB-2100).

6. 3 *Results and Discussion*

Figure 6-1 shows change in the current density over time during the chromium poisoning tests. Reference experiments without chromium poisoning at 200 mV are also shown in this figure. Larger current density was obtained at the initial stage when larger cathode polarization was applied even though a little deviation appeared among cell performances for different cells. The deviation of cell performances may come from insufficient adhesion between the electrolyte and the cathode. Current density decreased rapidly at the beginning for the LSM cathode, the PrSM cathode, and the NdSM cathode. By comparing these changes to those without chromium at 200 mV, the rapid decrease in the current density seems to be affected by chromium poisoning. Chromium vapor had already diffused into the cathodes at the beginning of the cell tests by the pre-treatment at 850 °C. On the other hand, current density of the BSCF cathode increased at the initial stage and it was more stable than the case of the other three cathodes.

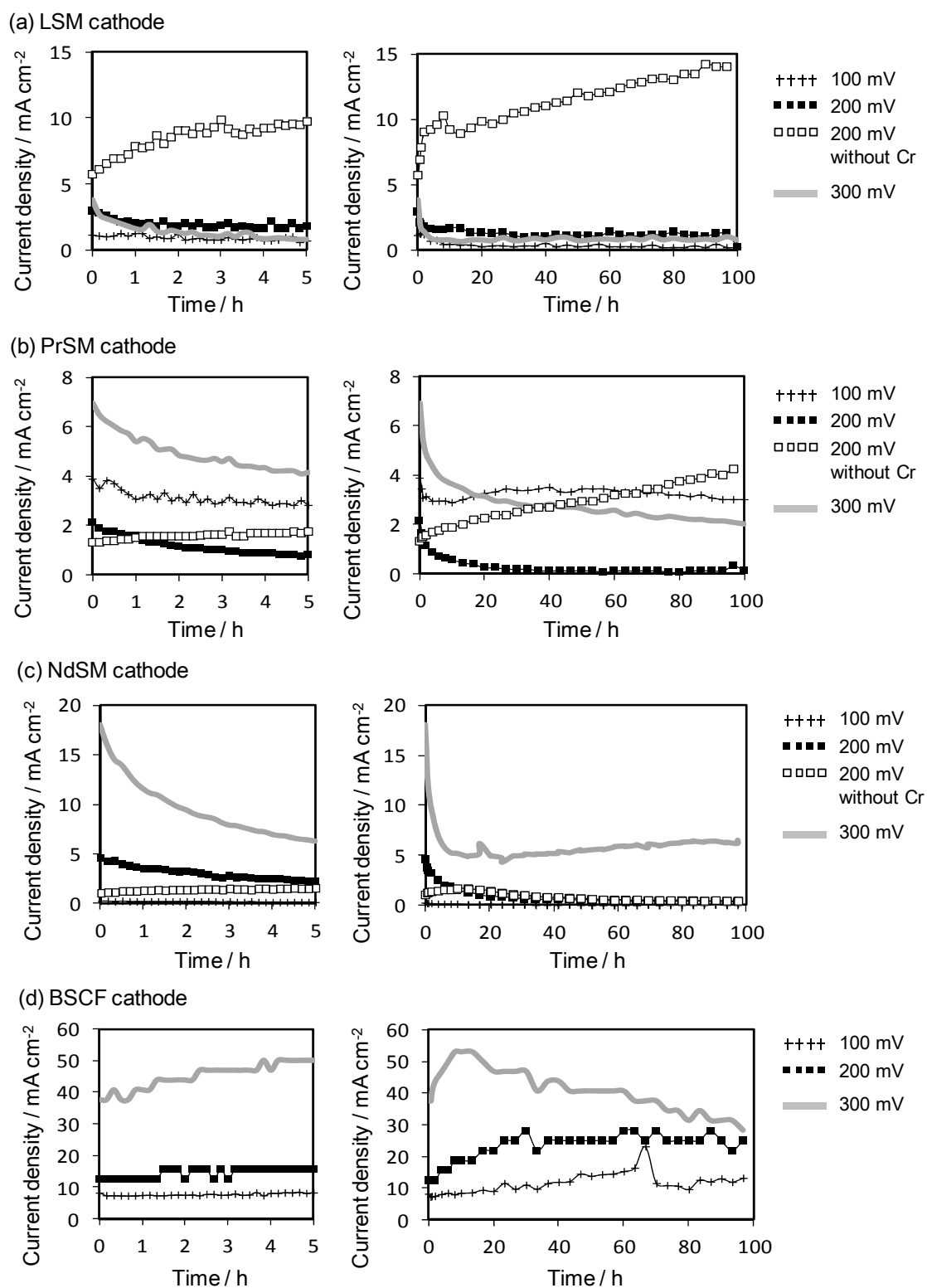
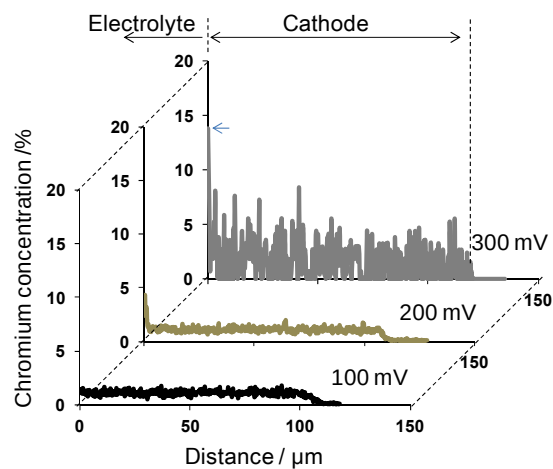


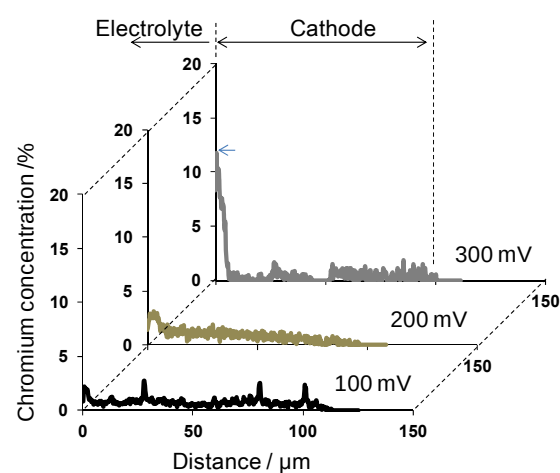
Figure 6-1. Change of current density over time during the chromium poisoning tests. Reference experiments without chromium poisoning at 200 mV are also shown in this figure.

Figure 6-2 shows the cross-sectional chromium distribution across the whole cathode by SEM-WDX after the chromium poisoning tests. The chromium observed in the cathode came from outside (right-hand side) diffusing in as a vapor and reacted with the cathode materials. Chromium distribution changed depending on the cathode polarization. We confirmed in another experiment that the chromium distributions did not change so much from the initial during the chromium poisoning test at open circuit for 100 hours [5], in which chromium had already been contained by the pre-treatment at 850 °C. With increasing cathode polarization, chromium deposition increased near the cathode/electrolyte interface for the LSM cathode, the PrSM cathode, and the NdSM cathode. In the case of the BSCF cathode, however, higher concentration of chromium appeared near the cathode surface at higher cathode polarization as observed in the preceding study using LSCF cathodes [5, 6-9]. The difference in the chromium distribution may be caused by higher reactivity of BSCF with chromium vapor. Cathode polarization seems to increase reactivity of BSCF and enhance trapping of chromium vapor near the cathode surface. This phenomenon may have close relationship with high ionic conductivity in BSCF.

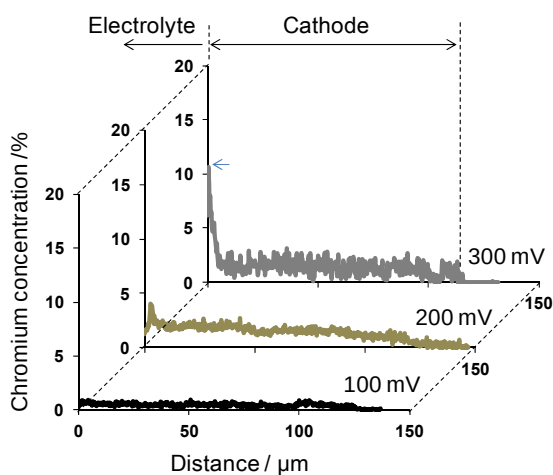
(a) LSM Cathode



(b) PrSM Cathode



(c) NdSM Cathode



(d) BSCF Cathode

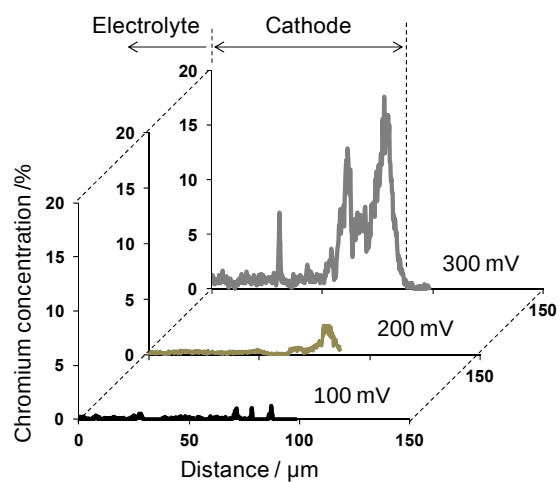


Figure 6-2. Distribution of chromim in the cathodes after the chromium poisoning tests.

Figure 6-3 shows relationship between cathode polarization and peak concentration of the chromium deposition in the cathodes after the chromium poisoning tests. As cathode polarization increased, the amount of chromium deposition increased for the four cathodes. Similar phenomena as the LSM cathode were confirmed for the PrSM cathode and the NdSM cathode, that is, chromium deposition mainly occurred at the cathode/electrolyte interface and it was enhanced by cathode polarization. The amount of chromium deposition similarly increased for the BSCF cathode with increasing cathode polarization, although the mechanism and position of the deposition are different from those of the other three cathodes.

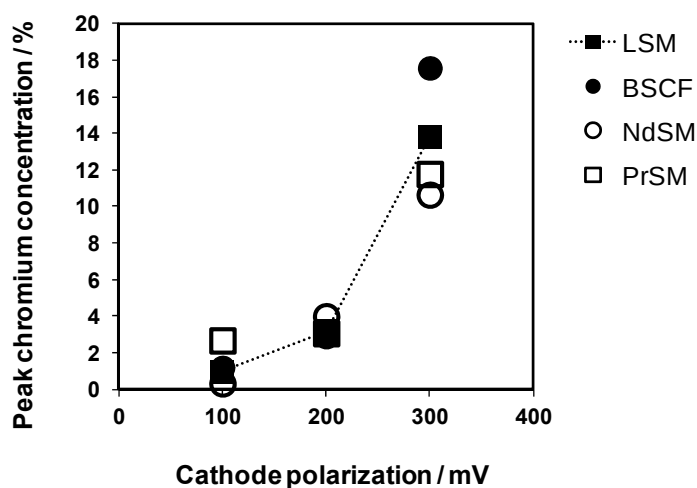


Figure 6-3. Relationship between cathode polarization and the peak concentration of chromium deposition in the cathode. The peak concentration was observed at the cathode/electrolyte interface for the LSM cathode, the PrSM cathode and the NdSM cathode, while it was located near the surface of the BSCF cathode.

Figure 6-4 shows the microscopic elemental distribution around the cathode/electrolyte interface of the PrSM cathode by STEM-EDX after the chromium poisoning test with cathode polarization of 200 mV. High concentration of chromium was observed on the surface of the zirconia electrolyte. Manganese was also observed overlapping with the deposited chromium. The manganese oxide was probably precipitated from PrSM under cathodic polarization condition as reported for LSM [10,11] or during the cell fabrication at 1200 °C, and had diffused on the surface of zirconia.

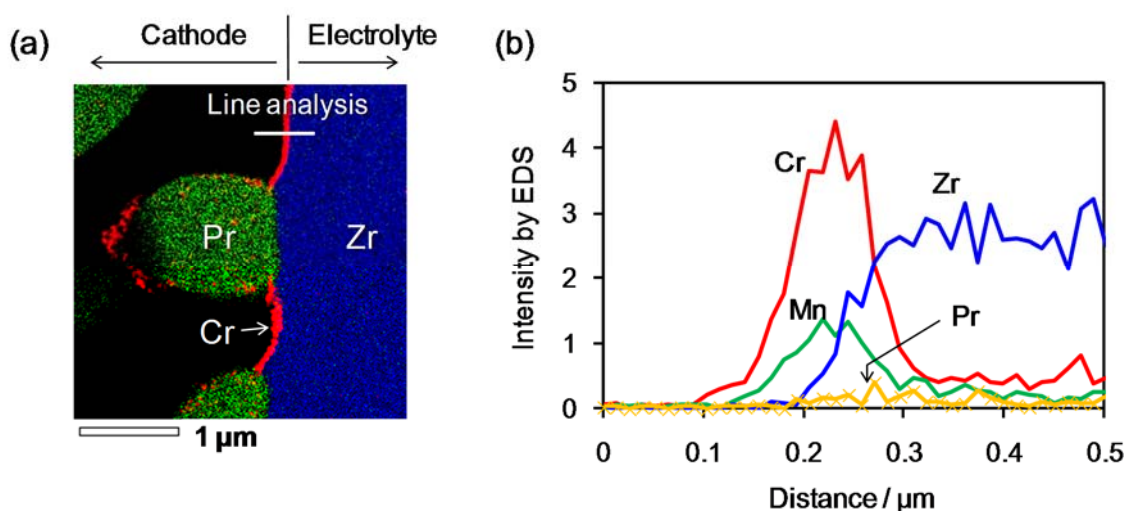


Figure 6-4. STEM-EDX(EDS) analysis of the PrSM cathode around the cathode/electrolyte interface after the chromium poisoning test with the initial cathode polarization of 200 mV: (a) EDS elemental maps of Pr, Zr, Cr and (b) EDS count profile of Pr, Zr, Cr, Mn along the line shown in (a).

Figure 6-5 shows the microscopic elemental distribution around the cathode/electrolyte interface of the NdSM cathode by STEM-EDX-EELS after the chromium poisoning test with cathode polarization of 200 mV. Neodymium existed from the surface to the inside of the zirconia electrolyte with a depth of several 100 nm, which had diffused under cathodic polarization condition or during the cell fabrication at 1200 °C. Oxygen deficient region with a thickness of about 10 nm was observed by EELS in the deposited chromium on the surface of zirconia electrolyte. The profile is

believed to reflect the distribution of oxygen during the cell test because the temperature was lowered by keeping the cathode polarization. The oxygen deficient state on the surface must have interacted with chromium vapor and facilitated chromium deposition.

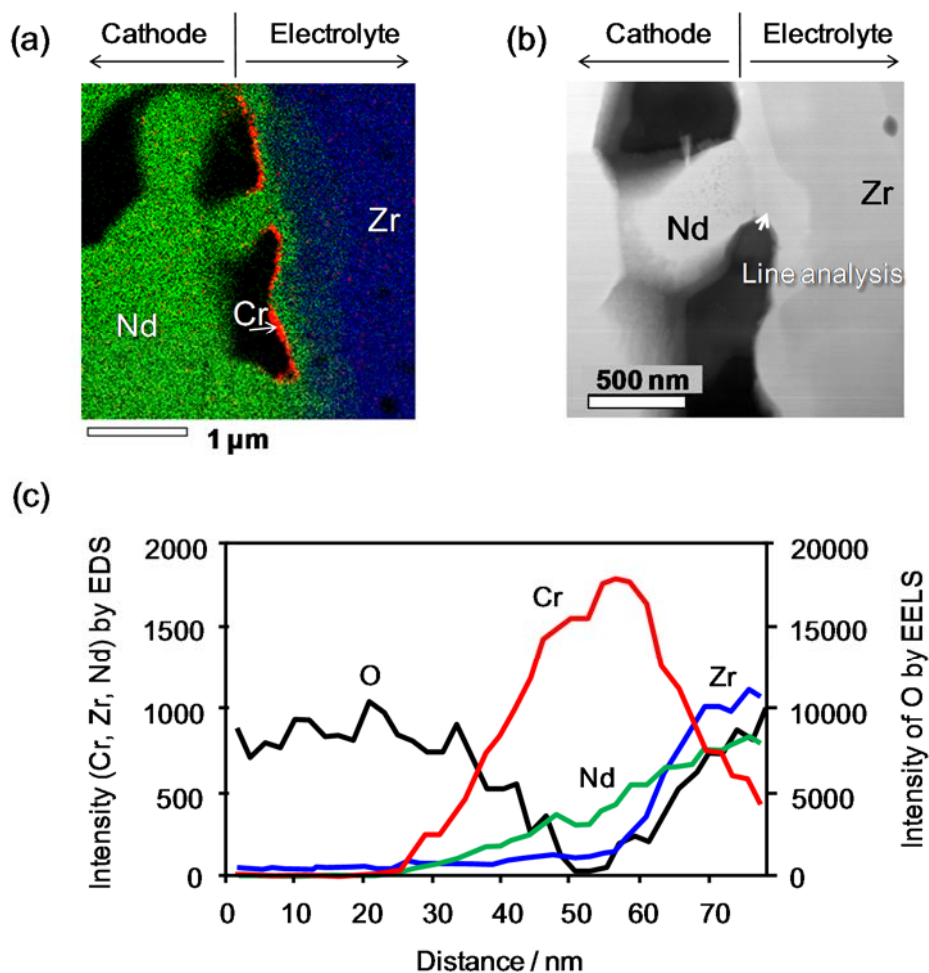


Figure 6-5. STEM-EDX(EDS)-EELS analysis of the NdSM cathode around the cathode/electrolyte interface after the chromium poisoning test with the initial cathode polarization of 200 mV: (a) EDS elemental maps of Nd, Zr, Cr, (b) ADF(Annular Dark Field) image, (c) EDS count profile of Zr, Cr, Nd and EELS count profile of O along the line shown in (b).

Concerning the chromium deposition at the cathode/electrolyte interface by cathode polarization for the LSM cathode, the PrSM cathode, and the NdSM cathode, predominant mechanism is discussed as follows. Chromium deposited on the surface of the zirconia electrolyte at the cathode/electrolyte interface as shown in **Figures 6-4 -6-5**. Because zirconia intrinsically has no electronic conductivity, electronic conducting media is required to generate oxygen vacancy on the surface of zirconia. Manganese oxide or neodymium oxide (MOx) segregated from the cathode materials must have served as the electronic conductor. They may also dissolve into the zirconia electrolyte and cause electronic conduction on the zirconia surface. Oxygen vacancy is induced on the surface of the zirconia via MOx when cathode polarization is applied. The oxygen vacancy on the surface interacts with chromium vapor and facilitates deposition of chromium. MOx assists the chromium deposition by conducting electron as well as by generating oxygen vacancy continuously. Oxygen vacancy may also be induced on the surface of MOx. It is considered that the two kinds of oxygen vacancies on the surface can interact with chromium vapor and facilitates deposition of chromium as shown in **Figure 6-6**. The deposited chromium can also generate oxygen vacancy which can act as a deposition site. On the surface of the chromium deposition, a part of the chromium may exist in oxygen deficient state depending on the cathode polarization. MOx on the surface of the zirconia can react with the deposited chromium and produce chemical compound. The oxygen deficiency on the surface of zirconia can facilitate interdiffusion of zirconium and chromium. Chromium deposition occurs even on the zirconia electrolyte surface and it affects cathode performance, therefore it is suggested that the similar phenomena may occur with other cathode materials.

In the case of the BSCF cathode, higher reactivity of BSCF with chromium vapor prevents diffusion of chromium vapor to the electrode reaction site and cause little degradation of cathode performance. However, influence of much longer term should be investigated.

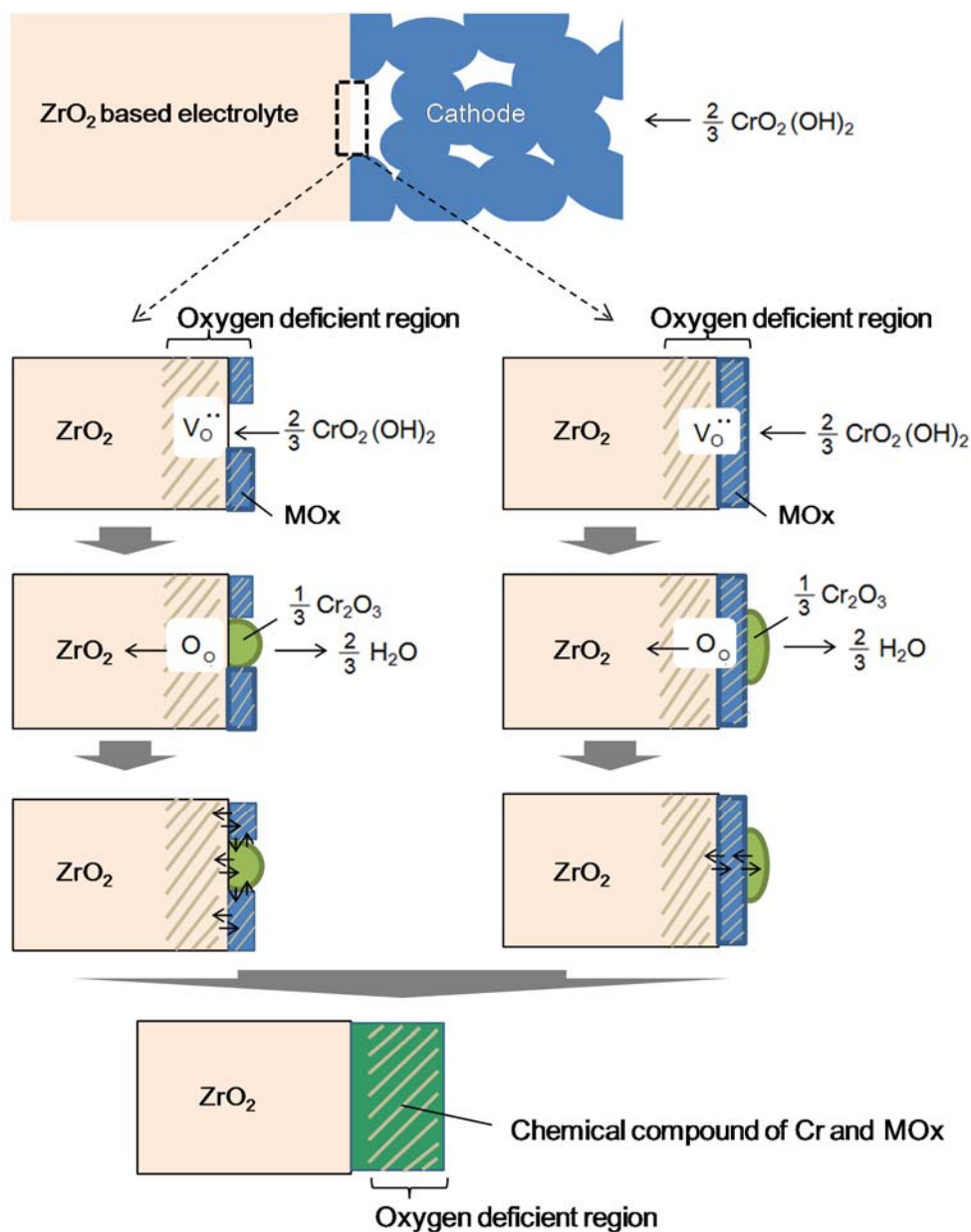


Figure 6-6. Mechanism of chromium deposition on the surface of zirconia electrolyte induced by cathode polarization. MOx: manganese oxide or neodymium oxide segregated from the cathode material.

6. 4 Conclusion

Deposition of chromium was facilitated with increasing cathode polarization similarly for the LSM cathode, the PrSM cathode, the NdSM cathode, and the BSCF cathode. The deposition occurred near the cathode/electrolyte interface for the LSM cathode, the PrSM cathode, and the NdSM cathode. Oxygen deficiency was observed in the deposited chromium on the surface of the zirconia electrolyte, thus the mechanism of the reaction of chromium vapor with the oxygen vacancy was confirmed. The oxygen vacancy on the surface of the zirconia electrolyte seemed to be generated via metal oxides such as manganese oxide or neodymium oxide segregated from the cathode materials. Chromium deposition occurs even on the zirconia surface, therefore similar phenomena may occur with other cathode materials. In the case of the BSCF cathode, chromium deposition occurred on the surface of the cathode, which may be caused by higher reactivity of BSCF with chromium vapor. Cathode polarization seems to increase reactivity of BSCF and enhance trapping of chromium vapor near the cathode surface, thus causes little degradation of cathode performance.

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CHAPTER 7

CONCLUSIONS

7.1 *Chromium Poisoning Mechanisms*

This dissertation deals with chromium poisoning phenomena of SOFC cathodes which has been one of the major technological issues to ensure the long-term durability of SOFCs. Mechanism of chromium poisoning in SOFC cathodes was investigated using $(\text{La}_{0.8}\text{Sr}_{0.2})_{0.98}\text{MnO}_3$ (LSM), $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ (LSCF), $\text{LaNi}_{0.6}\text{Fe}_{0.4}\text{O}_3$ (LNF), $\text{Pr}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (PrSM), $\text{Nd}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (NdSM) or $\text{Br}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$ (BSCF) as cathode materials. Kinetics of chromium deposition in each cathode were compared by changing cathode polarization. Microscopic distribution of the chromium deposition in the cathodes and elemental distribution around the deposited chromium were analyzed in detail.

This dissertation clarified that cathode polarization facilitates chromium deposition in the cathode for all the cathode materials investigated. The chromium deposition profiles were classified into the following two types and the predominant mechanism seems to be different from each other.

(1) Chromium deposits near the cathode/electrolyte interface for the LSM cathode, the LNF cathode, the PrSM cathode, and the NdSM cathode.

(2) Chromium deposits on the surface of the LSCF cathode and the BSCF cathode. Cathode polarization seems to increase reactivity of LSCF and BSCF and enhance trapping of chromium vapor near the cathode surface. However, it is probable that similar degradation as (1) occurs after a longer-term operation, although the phenomena have not been clearly understood yet.

Concerning the chromium deposition at the cathode/electrolyte interface by cathode polarization for the LSM cathode, the LNF cathode, the PrSM cathode, and the NdSM cathode, predominant mechanism was concluded as follows. Cathode polarization causes the change in oxygen activity at the electrode reaction site by the following equations.

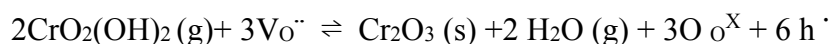
$$\eta = - (RT / 2 F) \ln [a_o / P_{O_2}^{1/2}]$$

η : cathode polarization

a_o : oxygen activity at the electrode reaction site

P_{O_2} : oxygen partial pressure in the gas phase.

Oxygen vacancy $V_o^{\cdot\cdot}$ should increase at the electrode reaction sites with increasing cathode polarization, corresponding to the decrease in oxygen activity. The oxygen deficient state on the surface must have interacted with chromium vapor and facilitated deposition of chromium. Basic reaction of the chromium deposition is considered to be



Focusing on the chromium deposition on the zirconia electrolyte surface, electronic conducting media is required to generate oxygen vacancy on the surface of zirconia because zirconia intrinsically has no electronic conductivity. Segregated oxides such as manganese oxide, nickel oxide or neodymium oxide (MO_x) must have served as the electronic conductor. They may also dissolve into the zirconia electrolyte and cause electronic conduction on the zirconia surface. Oxygen vacancy is induced on the surface of the zirconia via MO_x when cathode polarization is applied. The oxygen vacancy on the surface interacts with chromium vapor and facilitates deposition of chromium. MO_x assists the chromium deposition by conducting electron as well as by generating oxygen vacancy continuously. Oxygen vacancy may also be induced on the surface of MO_x . The deposited chromium can also generate oxygen vacancy which can act as a deposition site. On the surface of the chromium deposition, a part of the chromium may exist in oxygen deficient state depending on the cathode polarization. MO_x on the surface of the zirconia can react with the deposited chromium and produce chemical compound. The oxygen deficiency on the surface of zirconia can facilitate the interdiffusion of zirconium and chromium. Chromium deposition occurs even on the zirconia electrolyte

surface and it affects cathode performance, therefore it is suggested that the similar phenomena may occur with other cathode materials.

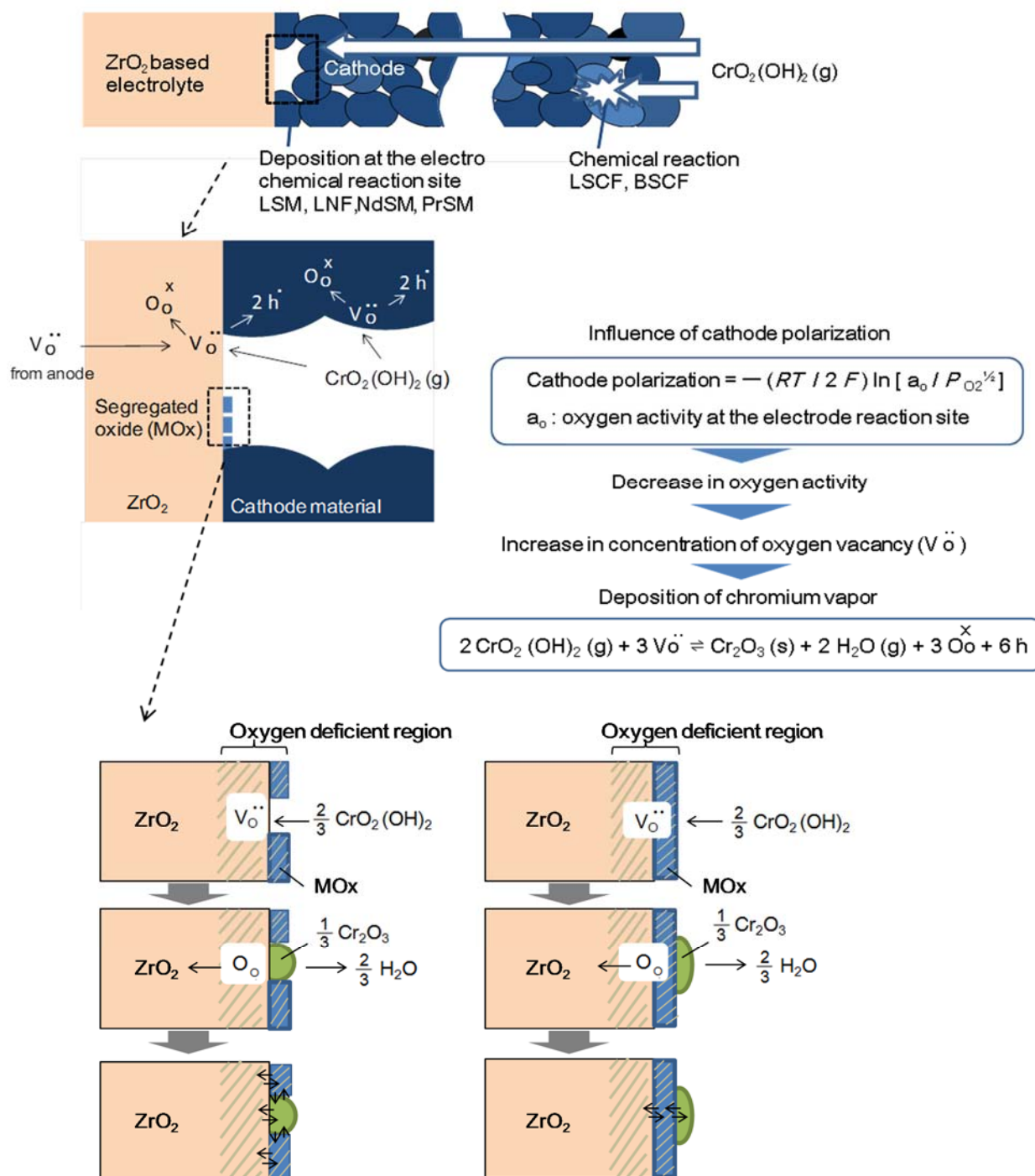


Figure 7-1. Mechanism of chromium deposition in SOFC cathodes.

7.2 *Outlook for Future Work*

We have clarified that chromium deposition is similarly enhanced by cathode polarization for all cathodes investigated in this study. Therefore, similar degradation may occur under the same cathode polarization condition.

For the practical application, the use of a cathode material which generates the lowest cathode polarization, such as LSCF, is one of the solutions as well as coating of the alloy components to reduce chromium vaporization. LSCF and BSCF seem to have another advantage because of the position of the chromium deposition. Chromium deposited on the surface of the LSCF cathode and the BSCF cathode, which seems to be caused by high reactivity of these materials with chromium vapor, thus the chromium deposition does not directly affect the cathode performance.

It was revealed that chromium deposits on the surface of zirconia electrolyte and it may cause severe damage to the cathode performance. The following studies may be valuable as the future work to tackle this issue and to create more durable SOFC cathodes.

- Understanding of dynamic change (such as vaporization) of the deposited chromium as well as change in the elemental distribution in detail, by changing cathode polarization dynamically. This allows us to design a durable cathode which facilitates dissipation of the deposited chromium.
- Visualization and quantification of oxygen vacancy near the surface of the electrolyte and cathode material by utilizing e.g. STEM-EDX-EELS.
- Investigation of other electrolyte materials than doped zirconia on the chromium deposition kinetics.