Tohoku University

Graduate School of Environmental Studies

Development of Solid Oxide Fuel Cell Cathode with Ni-based Perovskite Oxide

(Ni 系ペロブスカイト酸化物を用いた SOFC カソードの開発)

A dissertation submitted for the degree of Doctor of Philosophy

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Chapter 1 General Introduction

1.1 Environment and Energy Problem

One of the serious problems which we faced is an environment and energy problem. Up to date, the energy sources which we used are causing an environmental problem. The energy sources are still dominated by the fossil fuel. Coal, petroleum, and natural gas are kind of fossil fuel, which have generated lots of carbon dioxide emissions since long time ago. The kinds of fossil fuels, which formed millions of years ago, and its existence is increasingly depleted, and become a threat to us. For example, the existence of oil resources has decreased since we hardly found new oil reserves. In addition, the depletion of oil reserves drives the price of oil becomes higher [1.1].

The advantage of Fossil fuel lies in the high rate conversion into electrical energy. Although the energy which produced from fossil fuels is great, but there are side effects to our earth. An Effect occurred as a result come from the reaction of fossil fuels which produce carbon dioxide. The carbon dioxide trapped in the earth's atmosphere which is raising the temperature of the earth which called greenhouse effect. Without we realize it, the days we use more fossil fuels the more we pollute our earth. The earth has been enduring all consequences from the use of fossil fuels since long time ago. But, there are other energy sources which give a hope to replace or to efficiently use of fossil fuel energy. These energy sources must be clean and also renewable. Energy resources which are being developed, among others, namely, fuel cell. Fuel cells are devices that capable to convert the chemical energy directly into electrical energy without combustion processes [1.2]. Fuel cells offer a clean energy source, high efficiency, quiet and very wide of application.

Table 1.1 Shows 5 types of Fuel Cells [1.2].

Type Fuel cell	PEMFC	PAFC	AFC	MCFC	SOFC
Electrolyte	Ion exchange membrane	Phosphoric acid	Alkaline electrolyte	Carbonate	Solid oxide
Ion diffusion	H^+	H^+	OH^-	CO_3^{2-}	O^{2-}
Operating temperature	70~90℃	200℃	60~80℃	660~700℃	700~1000℃
Efficiency	30~40%	35~42%	~70%	40~60%	40~65%
Fuel	H_2	H_2	H_2	$CH_4,$ CO, H_2	$CH_4,$ CO, H_2

There are five types of fuel cell which are classified by the electrolyte material: Polymer Electrolyte Membrane Fuel Cell (PEFC), Phosphoric-Acid Fuel Cell (PAFC), Alkaline Fuel Cell (AFC), Molten Carbide Fuel Cell (MCFC), and Solid Oxide Fuel Cell (SOFC). Among these four, SOFC is used in the high temperature around 1273 K which can rise the most efficient when the high temperature exhaust heat is used as a cogeneration system. At the same time, high temperature power generation allows the direct feed of various hydrocarbon fuels, which is preferred for the present practical use.

1.2 Solid Oxide Fuel cell

Solid Oxide Fuel Cell (SOFC) has several advantages such as high efficiency compared to other fuel cell types, have the flexibility in the use of fuel. Basically, SOFC

consist of following 4 components: electrolyte, cathode, anode, and interconnects as shown in the Fig. 1.1. All these components are made from ceramic which brings various stacking types for a single cell.
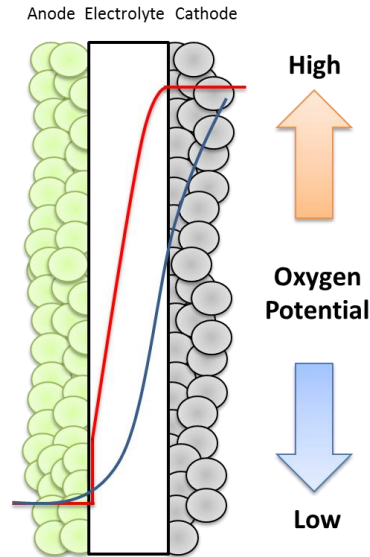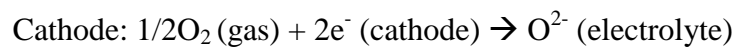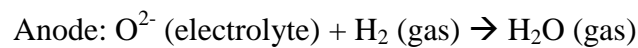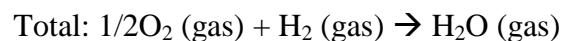

Figure 1.1 Scheme of Solid Oxide Fuel Cell

Generally, the reaction on the SOFC separated as two reactions on the cathode (air electrode) and anode side (fuel electrode). At the cathode, oxygen gas is reduced into oxide ions, and then incorporated to the electrolyte.

$$\text{Cathode: } 1/2O_2 \text{ (gas)} + 2e^- \text{ (cathode)} \rightarrow O^{2-} \text{ (electrolyte)}$$

At the anode, oxide ion oxidizes fuel and release electrons to the external circuit. In the case of hydrogen gas is used for the fuel, the reaction is

$$\text{Anode: } O^{2-} \text{ (electrolyte)} + H_2 \text{ (gas)} \rightarrow H_2O \text{ (gas)}$$

Then, the total reaction in the fuel cell can be expressed as an oxidation of hydrogen into water.

$$\text{Total: } 1/2O_2 \text{ (gas)} + H_2 \text{ (gas)} \rightarrow H_2O \text{ (gas)}$$

Currently, the researchers have been focused on the selection of materials that can provide high performance conversion, stability and thermodynamic efficiency at low

operating temperatures. The attentions have been devoted to the selection of materials which are capable of working at low temperatures. The existence of problems at the component materials also encourages researchers to continue looking for a replacement of conventional materials. Here, the properties and the material examples of SOFC described below.

Table 1.2 Required properties of component materials for SOFC

Component Properties	Anode	Electrolyte	Cathode	Interconnect
Ionic conductivity	High	High	High	Low
Electronic conductivity	High	Low	High	High
Chemical Stability	Reducing	Reducing/ Oxidizing	Oxidizing	Reducing/ Oxidizing
Morphology	Porous	Dense	Porous/Dense	Dense
Examples	Ni-YSZ	YSZ, GDC, LSGM	LSM, LSC, LSCF	LSrCrO3

1.3 SOFC Cathodes

An enormous amount of work has made SOFC closer to world-wide commercialization since several decades ago. Many of them focused on electrode materials, because the electrode overpotential is a large source of the resistance in SOFC [1.3]. Especially, oxygen reduction at the cathode is a difficult reaction to be activated [1.3]. Thus, a lot of efforts have been devoted to not only exploring new

cathode materials, but also elucidating the mechanism of oxygen reduction on cathodes in order to improve the cathode performance [1.3]. Several cathode materials were well studied over last several decades. For instance, $La_{1-x}Sr_xMnO_{3-\delta}$ (LSM), $La_{1-x}Sr_xCoO_{3-\delta}$ (LSC), and $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ (LSCF) have already been in the application stage.

A cathode material for SOFC should meet various requirements such as described in the following [1.4]:

1) High electronic conductivity,

2) High catalytic activity for oxygen reduction,

3) The chemical stability under the SOFC operating condition or cell preparation condition,

4) Has high morphological stability,

5) The thermal expansion coefficient that matches with an electrolyte.

For cathode material, it is preferred that materials with the electronic conductivity exhibits higher than c.a. 100 S/cm at SOFC operating atmosphere. Under these conditions, several spinel perovskite oxides with 3d metal transition can be selected. When Yttrium stabilized Zirconia (YSZ) is used for the electrolyte, the perovskite oxide with manganese, LSM, are generally used as the cathode. In other side, perovskite type oxides (ABO_3) containing Co ions the in their B sites are known to have much higher performance at SOFC operating temperature. However, the thermal expansion coefficients of these materials are much larger (22.0 x 10^{-6} K^{-1}) than that of $La_{0.8}Sr_{0.2}MnO_3$-δ (12.0 x 10^{-6} K^{-1}) [1.5]. In the recent years, LSC and LSCF are expected to be cathode material for SOFC, but there are several limitations on these materials.

Generally, the cathode SOFC faces several limitations, such as low conductivity, thermal expansion coefficient (TEC) that doesn't match with electrolyte, and chromia poisoning from metal separator make the performance of the cathode decreases. In order to overcome this problem, researcher have been looking for solution, such as exploring new cathode materials and also elucidating the mechanism of electrode reaction.

1.4 Ni based Perovskite Oxide

The material selection becomes important to obtain high electronic and ionic cathode. Several states the art of the cathode SOFC is Co-based perovskite oxide, such as: $La_{1-x}Sr_xCoO_{3-\delta}$ (LSC), and $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ (LSCF). The B-site of the perovskite structure is strongly connected with the oxygen as BO_6 octahedron and mainly determines the character of the perovskite-type oxide. So far, The Ni in the B-site of perovskite-type structure rarely studied. The $LaNiO_{3-\delta}$ is one of the "mother" composition for several cathode such as: $La(Ni,Fe)O_{3-\delta}$, and $La(Ni,Co)O_{3-\delta}$ which is rarely studied although it may have better performance.

Work from Bannikov et al. mentions that $LaNiO_{3-\delta}$ has a high performance on the electrical conductivity [1.6]. However, it suffers from the degradation above 1123 K in air due to the chemical instability. The Ni in the perovskite-type structure is unstable since Ni tends to become Ni^{2+} instead of Ni^{3+} [1.6, 1.7]. Many workers studied the $La_2NiO_{4-\pm}$ for cathode SOFC due to its stability and shows good performance on the electrochemical properties [1.8-1.10].

To enhance the chemical stability the $LaNiO_{3-\delta}$, the B-site is doped with other metal transition such as: Fe, and Co. The double B-site cation is not only enhances the chemical stability, but it can cause the enhancement of the performance such as high electronic conductivity. Since the BO_6 octahedron mainly determines the character of

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the perovskite-type oxide, then the double B-site cation will has complex characteristic [1.11]. By two different metals in B-site, the doped perovskite-type oxide may have both characters of the dopant and it is interesting to study.
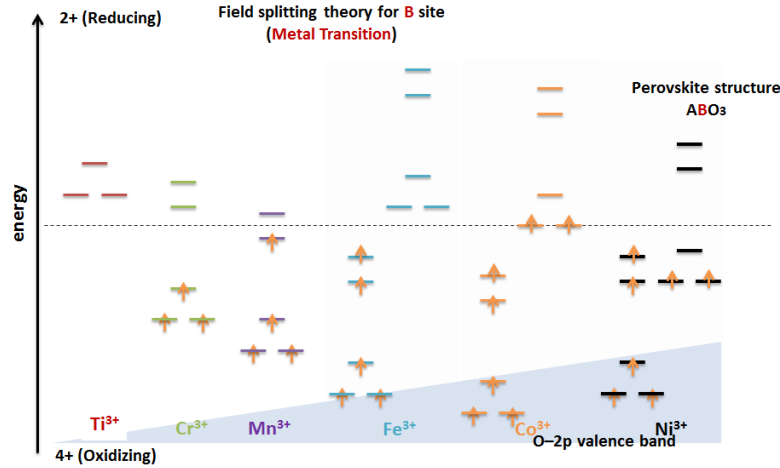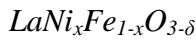

Figure 1.2 Schematic of energy levels for d electron in M^{3+} transition metal

$LaNi_xFe_{1-x}O_{3-\delta}$

$LaNi_xFe_{1-x}O_{3-\delta}$ is relatively new cathode material. This material is very attractive since it has several advantages to replace conventional SOFC cathode materials. Currently, state the art of cathode material for SOFC is perovskite type oxides (ABO_3) containing Co ions in their B-sites are known to have much higher conductivity. However, the thermal expansion coefficients of these materials are much larger ($22.0 \times 10^{-6} K^{-1}$) than of $La_{0.8}Sr_{0.2}MnO_{3-\delta}$ ($12.0 \times 10^{-6} K^{-1}$) [1.5]. This high thermal coefficient is commonly shared by the Ln(Sr)CoO3 (Ln = La, Pr, Nd, SM, Eu) series of ABO_3 type oxides [1.5]. The researcher found that $LaNi_xFe_{1-x}O_{3-\delta}$ has both a high electronic conductivity and thermal expansion ($11.4 \times 10^{-6} K^{-1}$) that matches with zirconia and ceria-based electrolyte [1.5].

Chiba et al. are the most recent researcher who has been investigating the $LaNi_xFe_{1-x}O_{3-\delta}$. They successfully measured the $LaNi_xFe_{1-x}O_{3-\delta}$ with various

compositions in order to find the electronic conductivity of $LaNi_xFe_{1-x}O_{3-\delta}$ [1.5]. From their result that found, the composition of iron $= 0.4$ shows the highest electronic conductivity among the others compositions as shown Fig 1.2.
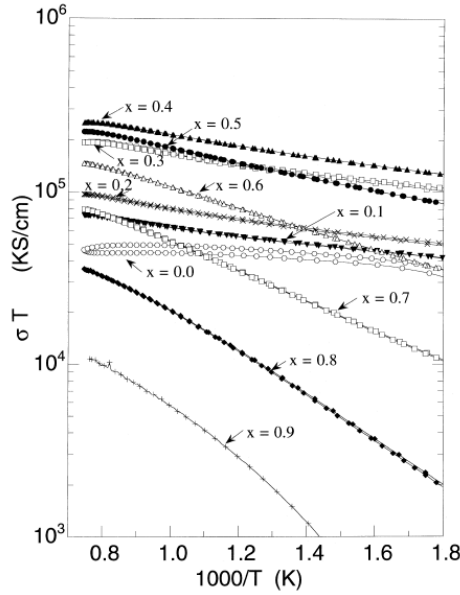

Figure 1.3 Electronic conductivity of $LaNi_xFe_{1-x}O_{3-\delta}$ versus operating temperature measurement shows that iron fraction is equal to 0.4 is the highest electronic conductivity.

Another advantage of this material is the durability against sulfur or chromium cathode poisoning from vapor from metal separator of SOFC. Several conventional cathode materials, $La_{1-x}Sr_xMnO_{3-\delta}$, $La_{1-x}Sr_xCoO_{3-\delta}$, and $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$, has low durability against this poisoning. Absolutely, this is one of the weaknesses of conventional cathode material, but $LaNi_{1-x}Fe_xO_{3-\delta}$ has relatively high durability against that poisoning compared to conventional materials [1.12]. The chemical reactivity of $LaNi_xFe_{1-x}O_{3-\delta}$ was studied and reported by Komatsu et al. The chemical reactivity of $LaNi_{0.6}Fe_{0.4}O_{3-\delta}$ with Cr_2O_3 has been investigated in order to examine the long-term stability of the $LaNi_{0.6}Fe_{0.4}O_{3-\delta}$ phase at 1073 K. The chemical stability of

$LaNi_{0.6}Fe_{0.4}O_{3-\delta}$ was compared with that of $La_{0.8}Sr_{0.2}MnO_{3-\delta}$ under the existence of Cr_2O_3. They found that the $LaNi_{0.6}Fe_{0.4}O_{3-\delta}$ phase maintains the hexagonal crystal system when heated up in air up to 1000 h. In the $LaNi_{0.6}Fe_{0.4}O_{3-\delta}$ -Cr_2O_3 mixture, the $LaNi_{0.6}Fe_{0.4}O_{3-\delta}$ phase kept its pristine crystal structure. In the $La_{0.8}Sr_{0.2}MnO_{3-\delta}$ -Cr_2O_3 mixture, $La_{0.8}Sr_{0.2}MnO_{3-\delta}$ reacted with Cr_2O_3 and produced a significant amount of $MnCr_2O_4$. $LaNi_{0.6}Fe_{0.4}O_{3-\delta}$ showed a much better chemical stability against Cr_2O_3 than $La_{0.8}Sr_{0.2}MnO_{3-\delta}$.

Numerous studies on this material so far concerned only the performance, and just a few did the mechanism of the oxygen reduction process. Thus, the electrochemical kinetics on this electrode material is not clear yet. In this study, electrochemical oxygen reduction process on a $LaNi_{1-x}Fe_xO_{3-\delta}$ electrode was investigated to determine the reaction mechanism in order to improve its performance.

$LaNi_xCo_{1-x}O_{3-\delta}$

The relatively new cathode material, $La(Ni,Co)O_{3-\delta}$, is expected as one of the alternative cathode of SOFC. At this cathode, the double B-site cations cause the relatively high performance of the electrode. Generally, the B-site metal has a strong connection with the oxygen form BO_6 octahedron. The BO_6 octahedron mainly determines the electronic structure of the perovskite-type oxide [1.11]. When the B-site is doped with transition metal, it may lead to a change in the strong connection of BO_6 octahedron and the defect chemical properties of double B-site cathode is supposed to be complex [1.11]. The study of the defect structure is important because the defect structure explains how the oxygen vacancy is generated at the cathode.

So far, $La(Ni,Co)O_{3-\delta}$ series have been reported to have a high electrical conductivity (1300 Scm^{-1} at 1073 K) [2,3]. Moreover, the thermal expansion coefficient (14-17 x 10^{-6}

K^{-1}) is tolerable for the use with oxide ion conducting electrolytes [1.13, 1.14]. It can also be expected that a chromia tolerance of La(Ni,Co)O$_{3-\delta}$ is higher than the cathode materials with Sr in the composition. Hjalmarsson et al. reported that LaNi$_{0.6}$Co$_{0.4}$O$_{3-\delta}$ doesn't have an oxygen vacancy in the air up to 1273 K which is measured by thermogravimetry [1.15]. However, there is limited knowledge of p(O$_2$) dependence on the oxygen vacancy concentration and the defect chemistry and other basic properties of LaNi$_{0.6}$Co$_{0.4}$O$_{3-\delta}$ so far. Systematical study of basic properties and of the electrode reaction mechanism is needed as an aid to enhance the performances

1.6 Scope of this study

The main object of this study is development of Ni-based perovskite oxide. The objective of this thesis is separated into two parts. The first part will be divided into three chapters, where it will determine the basic properties of LaNi$_x$Fe$_{1-x}$O$_{3-\delta}$ and LaNi$_x$Co$_{1-x}$O$_{3-\delta}$ and understanding the factor that limiting of these materials. The second part will discuss about how to improve the electrochemical performance of the LaNi$_x$Fe$_{1-x}$O$_{3-\delta}$ and LaNi$_x$Co$_{1-x}$O$_{3-\delta}$ by several methods. In this part, the purpose of this study will be explained.

In chapter 2, the basic properties of LaNi$_x$Fe$_{1-x}$O$_{3-\delta}$ and LaNi$_x$Co$_{1-x}$O$_{3-\delta}$ will be discussed in the terms of electronic conduction mechanism, defect chemical model, transport properties, lattice parameter, and thermal expansion coefficient. All the basic properties are needed in order to give a basic parameter to understand the electrode reaction mechanism on the next chapter. In this part, the characteristic of the LaNi$_x$Fe$_{1-x}$O$_{3-\delta}$ and LaNi$_x$Co$_{1-x}$O$_{3-\delta}$ will also be discussed in order to give insight on the advantage and disadvantage of these materials.
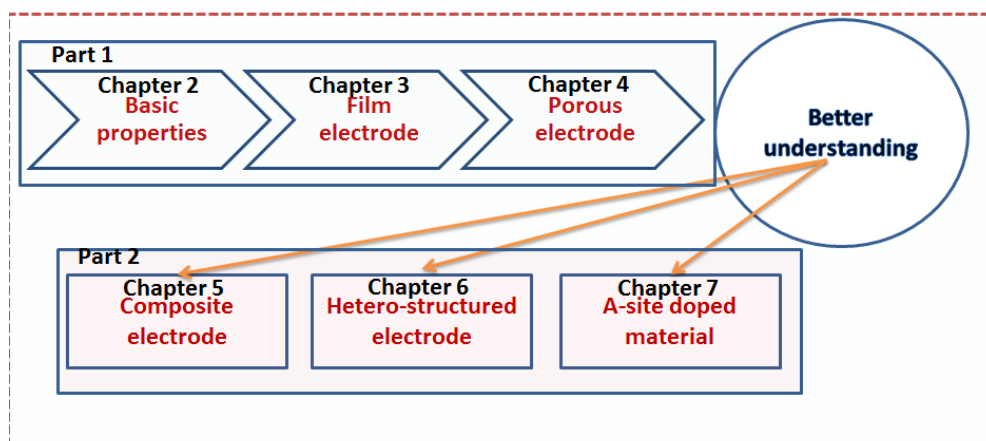
Figure 1.4 The scheme of the research plan in this study. The part 1 of this study is needed to understand the basic properties and performance of Ni-based perovskite oxide. The part 2 of this study will be about how to improve the cathode performance.

In the chapter 3, the dense film electrode of $LaNi_{0.6}Fe_{0.4}O_{3-\delta}$ and $LaNi_{0.6}Co_{0.4}O_{3-\delta}$ will be discussed prior to the porous electrode. The study of film electrode is needed in order to understand the reaction mechanism. Moreover, the rate limiting step or factor that limiting these electrodes will be determined. The advantage of the film electrode compared to the porous electrode is it has less complex oxygen reduction mechanism pathways. The study on it is important and will give another insight on how the oxygen molecules extracted into oxide ion on the electrode. The hypothesis on the film electrode will be used in order to understand the porous electrode on the next chapter.

In the chapter 4, the result in the chapter 2 and 3 will be used to understand the reaction mechanism on porous electrode. The study of porous electrode has advantages compared to dense film electrode. It is being realistic from the application of the cathode SOFC. However, the oxygen reduction mechanism is complex since the geometry and morphological affect to reaction pathways. In this part, the understanding

of the electrode reaction mechanism will be discussed in order to enhance the electrode performance.

In the chapter 5, the composite electrode between mixed ionic and electronic conductor ($LaNi_xFe_{1-x}O_{3-\delta}$ and $LaNi_xCo_{1-x}O_{3-\delta}$) and ionically conductiong oxide ($Ce_{0.9}Gd_{0.1}O_{1.95}$) will be discussed in the terms of electrochemical performance. Moreover, the reason of the enhancement of composite electrode compared to single phase porous electrode will be explained here.

In the chapter 6, the second attempt to enhance the electrode performance by adding the dissimilar structure into $LaNi_xFe_{1-x}O_{3-\delta}$. The hetero-structured electrode between the $LaNi_xFe_{1-x}O_{3-\delta}$ and $La_2NiO_{4\pm\delta}$ will be discussed in the terms of electrochemical performance. Moreover, the composite electrode of $LaNi_xFe_{1-x}O_{3-\delta}$ - $La_2NiO_{4\pm\delta}$ as volume ratios will be discussed in order to get understanding on the two dissimilar structure of mixed ionic and electronic conductor.

In the chapter 7, this part will be discussed about the exploring new cathode material. The strontium was doped into $LaNiO_{3-\delta}$, and $LaNi_xCo_{1-x}O_{3-\delta}$. The electrochemical study on these materials will be discussed in this part.

In the chapter 8, general conclusion of this study will be summarized. The result of the study on the development Ni-based perovskite oxide of $LaNi_xFe_{1-x}O_{3-\delta}$ and $LaNi_xCo_{1-x}O_{3-\delta}$ cathode will be stated, in accordance with the result of this study.

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Chapter 2 Basic Properties of $LaNi_{1-x}M_xO_{3-\delta}$ (M = Fe, Co and x = 0.2, 0.4, 0.6, 0.8)

The electrochemical performance of solid oxide fuel cell cathode depends on their ability to reduce and transport the oxygen through their bulk or surface. This ability corresponds to their oxygen vacancy concentration and transport properties. Thus, it is important to understand the properties as an aid for further research. So far, the basic properties of Ni-based perovskite oxide haven't been studied yet. In order to understand the factor limiting of their electrochemical performance, it is necessary to understand their basic properties. Therefore, the basic properties of $LaNi_{1-x}M_xO_{3-\delta}$ (M= Fe, Co) were studied in the terms of electronic conductivity, oxygen nonstoichiometry, oxygen transport properties, lattice parameter, and thermal expansion coefficient. The basic properties of $LaNi_{1-x}M_xO_{3-\delta}$ (M= Fe, Co) will be discussed in this chapter and will be used as an aid for further study in the next chapter.

Chapter 3 Determination of Rate Limiting Step on LaNi$_{0.6}$M$_{0.4}$O$_{3-\delta}$ film Electrode (M = Fe, Co)

Electrochemical properties of LaNi$_{0.6}$Fe$_{0.4}$O$_{3-\delta}$ and LaNi$_{0.6}$Co$_{0.4}$O$_{3-\delta}$ film electrodes were measured by electrochemical impedance spectroscopy as functions of temperature, T, oxygen partial pressure, $P(O_2)$, and thickness of the film electrode to determine the rate determining step of oxygen reduction process. From its chemical capacitance, the oxygen reduction process was limited on the surface, which had good agreement with the isotope exchange depth profile measurement. The result of this study will be used for determining reaction mechanism of porous electrode at the next chapter.

Chapter 4 Reaction Mechanism of LaNi$_{0.6}$M$_{0.4}$O$_{3-\delta}$ Porous Electrode (M = Fe, Co)

LaNi$_{0.6}$Fe$_{0.4}$O$_{3-\delta}$ and LaNi$_{0.6}$Fe$_{0.4}$O$_{3-\delta}$ porous electrode was measured as a function of temperature (923~1153K) and oxygen partial pressure (10^{-3}~1 bar) by impedance spectroscopy. Analysis of the electrode kinetics using appropriate equivalent circuits that the origins of electrochemical processes were separately identified yields value for area specific conductivity and chemical capacitance. Chemical capacitance was used to determine the rate determining step and also the reaction zone of the electrode. Determination of The electrode reaction length (ERL) indicates extends of reaction beyond the electrode/electrolyte interface. It shows that adsorption and or dissociation of oxygen molecules is near the boundary of electrode/electrolyte.

Chapter 5 The Effect of $Ce_{0.9}Gd_{0.1}O_{1.95}$ Coexistence on the Oxygen Exchange Kinetics on Perovskite Oxide Electrodes

The composite electrode between mixed ionic and electronic conductor and ionic conducting oxide has been studied in order to get better performance of solid oxide fuel cell cathode. The contact area between electronic and ionic conducting part is believed as the reason that electrode performance enhances drastically compared to the single phase porous electrode. The question has been rising on the reason of enhancement of composite electrode. In the composite electrode, the effective reaction length, the length of the oxygen reduction reaction takes place, should be increased due to the increasing the contacting area between electronic and ionic conducting part. However, in our study on $LaNi_{0.6}Co_{0.4}O_{3-\delta} - Ce_{0.9}Gd_{0.1}O_{1.95}$ and $LaNi_{0.6}Fe_{0.4}O_{3-\delta} - Ce_{0.9}Gd_{0.1}O_{1.95}$ composite electrode, the effective reaction length was not enhances despite the electrochemical performance increased drastically. There is another factor as the reason of the enhancement on the composite electrode. Therefore, in this study, several experiments were performed to elucidate the reason of enhancement on the composite electrode.

In this study, the composite electrode of $La_{0.6}Sr_{0.4}CoO_{3-\delta} - Ce_{0.9}Gd_{0.1}O_{1.95}$ was studied as well. The $La_{1-x}Sr_xCoO_{3-\delta}$ is state the art of solid oxide fuel cell cathode, which has very high electronic and ionic conductivity. The composite electrode of $La_{0.6}Sr_{0.4}CoO_{3-\delta} - Ce_{0.9}Gd_{0.1}O_{1.95}$ will give another insight on the oxygen reduction process of composite electrode. Several experiments on $La_{0.6}Sr_{0.4}CoO_{3-\delta} - Ce_{0.9}Gd_{0.1}O_{1.95}$ has been done in order to give another point of view on the composite electrode.

Chapter 6 Hetero-Structured Electrode of Ni-based Perovskite Electrode

The dissimilar structure between the two oxides attracts the attention since it could enhance the cathode performance significantly. This strategy has been used to develop a hetero-structure electrode which could has a higher performance than a single phase electrode. In this study the hetero-structure of $LaNi_{0.6}Fe_{0.4}O_{3-\delta}$ (Perovskite oxide) film electrode and $La_2NiO_{4-\pm}$ (Rudlesden-popper) porous electrode was studied. The enhancement of the cathode performance was observed and the reaction mechanism in the hetero-structure was studied in this part. Moreover, the hetero-junction of two mixed conductors was also studied in the form of the composite electrode. The performance and reaction mechanism of the dissimilar structure between the two oxides will be discussed in this part.

Chapter 7 Exploring New Cathode Material of Ni-Based Perovskite Structure

$LaNi_{0.6}Fe_{0.4}O_{3-\delta}$ and $LaNi_{0.6}Co_{0.4}O_{3-\delta}$ is cathode solid oxide fuel cell which Strontium-free. One of the ways to enhance the cathode performance is to enhance the amount of oxygen vacancy concentration. When an aliovalent dopant (dopant which has different valence) is doped to the A-site perovskite oxide, the oxidation state of the substitution ion would be different from the host ions. As the effect, to compensate the formation of oppositely charged defects, the electroneutrality would be needed. Thus, the oxygen vacancy is expected to generate in this state and enhance the ionic conductivity of the cathode. Therefore, in this part, as the first step the $LaNiO_{3-\delta}$ was doped with strontium and measured its electrochemical performance.

Chapter 8 General Conclusion

A relatively new cathode material, $LaNi_{1-x}Fe_xO_{3-\delta}$ and $LaNi_{1-x}Co_xO_{3-\delta}$, as promising cathode solid oxide fuel cell (SOFC) was investigated in order to elucidate the electrochemical oxygen reduction process and improving the electrochemical performance. The scientific findings of this study are explained in this part.

In chapter 2, basic properties of the $LaNi_{1-x}Fe_xO_{3-\delta}$ and $LaNi_{1-x}Co_xO_{3-\delta}$ was investigated in the terms of electronic conduction mechanism, oxygen nonstoichiometry, defect chemical model, transport properties, lattice parameter, and thermal expansion coefficient. The $LaNi_{1-x}Fe_xO_{3-\delta}$ has metal-like conduction mechanism and hopping conduction mechanism which depend on the Ni content in the structure. The Ni rich composition has metal-like conduction mechanism; meanwhile the Fe rich is hopping conduction mechanism. On the other side, the $LaNi_{1-x}Co_xO_{3-\delta}$ has metal-like conduction mechanism. The defect chemical model was estimated based on the electronic conduction mechanism. For example, the defect chemical model of Fe rich of $LaNi_{1-x}Fe_xO_{3-\delta}$ was well-fitted with small Polaron model. In other side, the delocalized model is well-fitted to experimental data for $LaNi_{1-x}Co_xO_{3-\delta}$.

The transport properties of $LaNi_{1-x}Fe_xO_{3-\delta}$ and $LaNi_{1-x}Co_xO_{3-\delta}$ shows that both of materials have relatively high oxygen surface exchange constant, k^*, although the diffusivity, D^*, indicate these materials have low ionic conductivity. It shows that both of material are mixed ionic and electronic conductor. The determination of oxygen vacancy concentration from D^* has good agreement with the high temperature gravimetry measurement for $LaNi_{1-x}Co_xO_{3-\delta}$ case. The oxygen nonstoichiometry at high oxygen partial pressure is independent over the oxygen partial pressure and the plateau region was observed. The result of oxygen nonstoichiometry at high $p(O_2)$ ($1 - 10^{-4}$ bar)

was in good agreement with the lattice expansion which was almost independent over the $p(O_2)$.

In the chapter 3, Oxygen reduction process of $LaNi_{0.6}Fe_{0.4}O_{3-\delta}$ and $LaNi_{0.6}Co_{0.4}O_{3-\delta}$ film electrode has been determined by electrochemical measurement and secondary ion mass spectrometry measurement. It shows that the $LaNi_{0.6}Fe_{0.4}O_{3-\delta}$ and $LaNi_{0.6}Co_{0.4}O_{3-\delta}$ has surfaced reaction as limiting step of oxygen reduction, which is determined by the change of chemical capacitance inside the electrode. In the case of $LaNi_{0.6}Fe_{0.4}O_{3-\delta}$, the comparison of the electrodes with different thickness showed that chemical capacitance was proportional to the film thickness. The chemical capacitance is 0 when the thickness of the film is 0, which indicate the contribution of additional capacitance can be ignored.

In the isotope diffusion profile, there has been small gradient in the electrode layer just below the surface, which suggests some contribution of the subsurface transport resistance to the impedance spectra. The sub-surface layer is an indication that incorporation process during the oxygen reduction process is slow reaction. The slow incorporation process in the $LaNi_{0.6}Fe_{0.4}O_{3-\delta}$ and $LaNi_{0.6}Co_{0.4}O_{3-\delta}$ gives a big hint in order to enhance the electrode performance.

In the chapter 4, Impedance spectroscopy was used to investigate the rate determining step and effective reaction length of the $LaNi_{0.6}Fe_{0.4}O_{3-\delta}$ and $LaNi_{0.6}Co_{0.4}O_{3-\delta}$ porous electrode. Based on the capacitance and Adler-Lane-Steele model, the effective reaction length (ERL) was estimated for the $LaNi_xCo_{1-x}O_{3-\delta}$ and $LaNi_{0.6}Fe_{0.4}O_{3-\delta}$ porous electrode. The ERL was near the triple phase boundary indicates that it has a slow bulk diffusion. This result is in good agreement with the ionic conductivity

which is explained in the chapter 2. The reaction pathways for oxygen could be passed through the surface diffusion as the bulk diffusion is slow reacting.

In other side, the electrode reaction mechanism was also determined based on the Adler model for "freestanding electrode". The model of incorporation process is in good agreement with the experimental data for the tendency of rate reaction constant on $p(O_2)$. This slow incorporation process was displayed as sub-surface resistance barrier at $LaNi_{0.6}Fe_{0.4}O_{3-\delta}$ and $LaNi_{0.6}Co_{0.4}O_{3-\delta}$ film electrode. In the case of porous electrode, the slow incorporation process associated to the short ERL. Therefore, in the porous case the oxide ion diffuses at the surface.

In the chapter 5, the composite electrode between mixed ionic and electronic conductor and ionic conducting oxide has been studied in order to get better performance of solid oxide fuel cell cathode. In our study on $LaNi_{0.6}Co_{0.4}O_{3-\delta}$ − $Ce_{0.9}Gd_{0.1}O_{1.95}$ and $LaNi_{0.6}Fe_{0.4}O_{3-\delta}$ − $Ce_{0.9}Gd_{0.1}O_{1.95}$ composite electrode, the effective reaction length was not enhances despite the electrochemical performance increased drastically. There is another factor as the reason of the enhancement on the composite electrode. From our study, $Ce_{0.9}Gd_{0.1}O_{1.95}$ existence of $LaNi_{0.6}Fe_{0.4}O_{3-\delta}$ will enhances the oxygen surface exchange which is demonstrated by the several experiments. One possible reaction pathway may involve the oxygen reduction (absorption and dissociation) process in the $LaNi_{0.6}Fe_{0.4}O_{3-\delta}$ film and $Ce_{0.9}Gd_{0.1}O_{1.95}$ porous (incorporation). This reaction pathway is possible since the $Ce_{0.9}Gd_{0.1}O_{1.95}$ has high diffusivity which oxide ion is preferable to transport inside $Ce_{0.9}Gd_{0.1}O_{1.95}$ porous. With this system the surface exchange kinetics enhance drastically.

In chapter 6, the $La_2NiO_{4\pm\delta}$ porous electrode was loaded into the $LaNi_{0.6}Fe_{0.4}O_{3-\delta}$ film electrode. The area specific conductivity was enhanced drastically compared to

bare $LaNi_{0.6}Fe_{0.4}O_{3-\delta}$ film electrode and also $La_2NiO_{4\pm\delta}$ porous electrode. From our analysis, the enhancement of the area specific conductivity didn't come from the enhancement of surface area. The surface area which associated with the effective reaction length didn't enhance as the chemical capacitance of the hetero-structure electrode has a lower value than bare $LaNi_{0.6}Fe_{0.4}O_{3-\delta}$ film electrode. The enhancement of the hetero-structure also cannot be explained only by considering the parallel pathways for oxygen species.

In chapter 7, one of the ways to enhance the cathode performance is to enhance the amount of oxygen vacancy concentration is explained in this chapter. When the equivalent dopant is doped to the A-site perovskite oxide, the oxidation state of the substitution ion would be different from the host ions, and the electroneutrality would be needed to compensate the formation of oppositely charged defects. Thus, the oxygen vacancy is expected to generate in this state and enhance the ionic conductivity of the cathode. Although the enhancement of the area specific conductivity wasn't large, but it showed that the A site depend was increasing their area specific conductivity compared to pure $LaNiO_{3-\delta}$. In other side, when B-site doped by Co, their area specific conductivity was slightly decreased. It could be due to the structure on $La_{0.98}Sr_{0.02}NiO_{3-\delta}$ more stable when Co was duped into B-site.

Through the work in this thesis, the systematic evaluation of basic properties and oxygen reduction process at single phase porous electrode are successfully demonstrated. Moreover, the enhancement of the electrode performance was improved after the rate limiting step of the electrode distinguished. Finally, the study sincerely hopes will be useful for a researcher on the designing high performance of cathode solid oxide fuel cell.

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Research Related to Presentation and Publication

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