INTERMEDIATE TEMPERATURE SOLID OXIDE FUEL CELL USING Ni DOPED LaGaO₃ ELECTROLYTE

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ABSTRACT

Although the hole conduction appeared, it was found that doping by Ni is effective for improving the oxide ion conductivity in La₀.₈Sr₀.₂Ga₀.₈Mg₀.₂O₃. Considering the ionic transport number and the electrical conductivity, the optimized composition for Ni doped sample was La₀.₈Sr₀.₂Ga₀.₈Mg₀.₂Ni₀.₀₇O₃ (LSGMN). In agreement with the improved electronic conductivity, power density of the solid oxide fuel cell using LaGaO₃ electrolyte increased by doping small amount of Ni for Ga site. In particular, the power density of 224 mW/cm² at 873 K was attained on the cell using LSGMN for the electrolyte in spite of the usage of electrolyte plate with 0.5 mm thickness. In order to develop the inexpensive cathode oxide, effect of aliovalent cation doping for Co site of La₀.₉Sr₀.₁CoO₃ was further investigated. It was found that the cathodic overpotential decreased by doping Cu for Co site of LaCoO₃.

INTRODUCTION

At present, Y₂O₃ stabilized-ZrO₂ (YSZ) is commonly used as the electrolyte of solid oxide fuel cell (SOFC). Because the oxide ion conductivity of YSZ is insufficient for the electrolyte of fuel cells, a thin electrolyte film without gas leakage and an excessively high operating temperature such as 1273 K are essential for achieving the high power density. On the other hand, all advantages of SOFC such as a high efficiency and a variety of fuel can be obtained at intermediate temperatures such as 1073 K. Furthermore, the choice of the materials for cell stack becomes wider; in particular, cheap refractory metals such as a stainless steel become usable by decreasing the operating temperature down to 1100 K. Consequently, a decrease in the operating temperature becomes an importance subject for the development of the reliable and the inexpensive cells (1). Decreasing the operating temperature requires an electrolyte with low resistance and an active electrode, in particular, the cathode electrode (2). In our previous study, it was found that a LaGaO₃-based perovskite type oxide exhibits high oxide ion conductivity (3,4), which is comparable with that of CeO₂-based oxide. In particular, LaGaO₃ doped with Sr for La and Mg for Ga sites exhibits the high oxide ion conductivity over a wide range of oxygen partial pressure. Following our reports, the high oxide ion conductivity of this system has been confirmed by several researchers (4-7). The advantage of this oxide is that almost pure oxide ion conductivity is exhibited in both reducing and oxidizing atmospheres. It is reported that the electron and the hole conduction in this oxide are smaller than that of oxide ion by few orders of magnitude (8). It is, therefore, expected that the operating temperature of SOFC can be decreased by using LaGaO₃-based oxide for the electrolyte of SOFCs (9,10). On the other hand, doping the transition metal cations is
generally expected to be undesirable for an ionic conductor, since the electronic conduction will appear. However, in our previous study, it was found that doping Co is effective for improving the oxide ion conductivity when the amount of doped Co was less than 10 mol% to Ga site of La$_{0.8}$Sr$_{0.2}$Ga$_{0.8}$Mg$_{0.2}$O$_3$ (LSGM) (11). In accordance with the conductivity measurement, power density of the cell at intermediate temperature was also greatly improved by doping Co to Ga site of LaGaO$_3$. On the other hand, it was also found that doping Ni exhibited the positive effect on the electrical conductivity. In the present study, therefore, doping effects of Ni to Ga site of La$_{0.8}$Sr$_{0.2}$Ga$_{0.8}$Mg$_{0.2}$O$_3$ on the oxide ion conductivity were studied. Furthermore, the power generation characteristics of the cell using Ni doped LaGaO$_3$ based oxide were investigated systematically. On the other hand, SmCoO$_3$ was always used for the cathode of the intermediate temperature fuel cell in our previous study. However, a rare earth oxide of Sm$_2$O$_3$ is rather expensive and the usage of SmCoO$_3$ based oxide cathode is undesirable for a commercial cell from the cost point of view. Therefore, development of the cheap but highly active cathode is strongly required. In this study, doping effects of an aliovalent cation for Co site of La$_{0.9}$Sr$_{0.1}$CoO$_3$ on the overpotential of cathode were investigated for this purpose.

**EXPERIMENTAL**

**Preparation of LaGaO$_3$ Based Electrolytes Doped with Ni**

Calculated amounts of commercial La$_2$O$_3$ (Wako, 99.99% purity), SrCO$_3$ and MgO (Wako, 99.9% purity), Ga$_2$O$_3$ (Kishida, 99.99% purity), and NiO (99.5% Wako) were mixed in a mortar with a pestle and then precalcined at 1273K for 6 h (7) to prepare perovskite oxide of La$_{0.8}$Sr$_{0.2}$Ga$_{0.8}$Mg$_{0.2}$Ni$_x$O$_3$. The resulting powders were pulverized and isostatically pressed into a disk (20 mm in diameter and 0.6 mm thickness) at 274.6 MPa in vacuum. The disks were sintered at 1773 K for 6 h. XRD measurement was performed to analyze the purity of the specimens and it was confirmed that the specimens consisted of the single LaGaO$_3$ perovskite phase. Disks were ground and polished with a diamond wheel to 0.5 mm in thickness. The electrolytes of this thickness were always used for the fabrication of SOFC in this study.

Ln$_{1-x}$Sr$_x$CoO$_3$ (Ln=La, Sm)-based perovskite oxides were also prepared by a solid state reaction. Precursors of these oxides were prepared by the coprecipitation of acetate solutions. The obtained precursors were calcined at 1473 K for 6h in air. Single perovskite phase was confirmed by the X-ray diffraction analysis.

**Oxide Ion Conductivity and Power Generation Characteristics Measurement**

The electrical conductivity was measured as a function of temperature and oxygen partial pressure by a conventional dc four-probe method in a gas flow. Each measurement was performed for period longer than 1 h at each temperature and oxygen partial pressure in order to confirm a stable conductivity. The partial pressure of oxygen was controlled by mixing N$_2$, CO, or H$_2$ with O$_2$ and the oxygen partial pressure was monitored by a CaO stabilized ZrO$_2$ oxygen sensor that was attached close to the sample. The transport number of oxide ion was estimated by the electromotive forces of the H$_2$-O$_2$ gas concentration cell. The oxygen partial pressure was adjusted by adding 3 vol% H$_2$O to H$_2$.

The commercial NiO (Wako, 99.9%) without further purification was used for the anodes. The prepared cathode oxide and the anode metal oxide were applied on the surface of the electrolyte by painting the n-butyl acetic acid solvent (5mm in diameter).
After drying at room temperature, the specimens were calcined at 1173 K for 10 min to remove the organic solvent. Before measurement of power generation characteristics, NiO was reduced to Ni metal in a hydrogen stream at 1273 K. Molten Pyrex glass was used for sealing the cell. Commercial oxygen and hydrogen humidified with 3 vol% H$_2$O were used for the oxidant and the fuel, respectively, for the power generating measurements.

RESULTS and DISCUSSION

Effect of Ni Doping for Ga site of LaGaO$_3$ on Oxide Ion Conductivity

Figure 1 shows the Arrhenius plots of electrical conductivity of La$_{1-x}$Sr$_{0.2}$Ga$_{0.8}$Mg$_{0.2}$X$_{x}$O$_{3}$. In XRD measurement, no diffraction peaks from secondary phase were observed and the diffraction angle linearly increased with increasing Ni content. Therefore, it seems most likely that Ni successfully substituted the Ga site in LaGaO$_3$ perovskite lattice. In order to establish the optimum composition for Ni doped LSGM, the total amount of dopant in the Ga site was fixed at 20 mol% to get the same oxygen deficiency as that in parent LSGM provided that doped Ni would take divalent form. It is obvious that the electrical conductivity monotonously increased with increasing Ni content. At X=0.2, conductivity changed from a semiconductor to a metallic behavior. This is quite similar to that of Co doped sample.

Figure 2 shows the electrical conductivity of LaGaO$_3$ based oxide at 1173 K as a function of oxygen partial pressure. It is clear that the electrical conductivity was almost independent of the oxygen partial pressure in the range from $P_{O_2}$=1 to $10^{-21}$ atm when Ni content was less than 10 mol% for Ga site. Therefore, oxide ion conductivity was still dominant at this Ni content. In contrast, the electrical conductivity of 20 mol% Ni doped sample decreased monotonously with decreasing the oxygen partial pressure. Consequently, the major charge carrier at this composition seems to be the electronic hole. Therefore, in analogy with Co doping effects, doping excess amount of Ni only enhances the electronic hole conduction and is undesirable for the pure oxide ion conductor. However, it is expected that doping Ni at less than 10 mol% is effective for improving the oxide ion conductivity.

The improvement in oxide ion conductivity by doping with Ni was further studied with the H$_2$-O$_2$ gas concentration cell. Figure 3 shows the temperature dependence of the transport number of oxide ion which was estimated by the electromotive forces in H$_2$-O$_2$ gas concentration cell. The transport number of oxide ion decreased with decreasing temperature. Since it is well-known that the activation energy for the hole conduction is far smaller than that of oxide ion, the electronic hole conduction became dominant with decreasing temperature. This was also confirmed by increase in $P_{O_2}$ dependence of conductivity with decreasing temperature. On the other hand, in good agreement with the results in Fig.2, it is obvious that the estimated transport number of oxide ion decreased with increasing Ni content at the same temperature. However, the transport number of oxide ion was still higher than 0.7 at all temperatures when the Ni content was less than 10 mol%. Therefore, it can be said that the oxide ion conductivity in LaGaO$_3$ based oxide increased by doping small amount of Ni for Ga site. Since the electrical conductivity was almost independent of the oxygen partial pressure from $P_{O_2}$=1 to $10^{-4}$ atm, Ni doped LaGaO$_3$ exhibited the oxide ion conductivity stably over the wide range of oxygen partial pressure. This Ni doping effect on conductivity is quite similar with that of Co doping. Therefore, Ni doped LaGaO$_3$ is usable for an electrolyte of the intermediate
temperature SOFCs, which is similar to Co doped one.

**Power Generation Characteristic of SOFC Using Ni Doped LaGaO₃**

The power generation characteristics of Ni doped LaGaO₃ were studied in detail. In order to determine the most suitable composition, the open circuit potential and the maximum power density of the cell at 1073 K is shown in Fig. 4 against the Ni content in LaGaO₃ based oxide. It is clear that the maximum power density monotonously increased with increasing Ni content and attained a maximum value at 7 mol% Ni doping to Ga site of LaGaO₃. At this composition, the maximum power density was higher than 800 mW/cm² at 1073 K in spite of the usage of 0.5 mm thick electrolyte. On the other hand, open circuit potential was monotonously decreased with increasing Ni content. This is in good agreement with increase in the hole conduction which was suggested by the electrical conductivity measurements. The improved power density also confirmed that the oxide ion conductivity improved by doping Ni for the Ga site. The optimized composition for the electrolyte of SOFC seems to exist at La₀.₈Sr₀.₂Ga₀.₈Mg₀.₁₃Ni₀.₀₇O₃ which is denoted as LSGMN in the following part.

Figure 5 shows the internal resistance of the cells as a function of Ni content. Clearly, the main internal resistance of the present cell was the electric resistance (IR loss) which almost corresponded to that of the electrolyte. In agreement with the improved oxide ion conductivity, it is obvious that IR loss monotonously decreased with increasing Ni content. On the other hand, the cathodic overpotential of the present cell was quite small, since Sm₀.₅Sr₀.₅CoO₃ exhibits high activity for the cathodic reaction at intermediate temperatures. In contrast, the anodic overpotential was larger than that of cathode. This suggests that the activity of pure Ni metal for the anodic reaction is not sufficient at intermediate temperatures. It is noted that the anodic overpotential decreased by doping Ni for LaGaO₃ electrolyte. At present, mechanisms for the decrease in anodic overpotential by doping Ni for electrolyte were not clear. However, it is anticipated that the hole conduction in Ni doped LaGaO₃ based oxide may have some relationship for improving the anodic performance. Similar positive effects by electronic conduction in electrolyte on the electrode reaction were reported on the cell using CeO₂ based oxide. In any case, it is obvious that the improved power density of the cell by using Ni doped LaGaO₃ based oxide for the electrolyte can be assigned to the decrease in IR loss. On the other hand, hole conduction was significantly appeared at the excess amount of Ni doped for Ga site and the cell was internally short circuited. Therefore, although the IR loss monotonously decreased with increasing Ni content, the maximum power density decreased by doping the excess amount of Ni.

Figure 6 shows the temperature dependence of the maximum power density of the cell using LSGMN for electrolyte. For the present cell, pure Ni is used as the anode. However, it is well-known that Ni easily aggregates at a high current density and the power density decreases with the passage of time. Therefore, the power generation characteristic at temperatures higher than 1173 K was not measured in this study. It is obvious that the LSGMN cell exhibited the notably large power density and the high power density was sustained at low temperatures. Although the thickness of the used electrolyte was as low as 0.5mm, the maximum power density of the cell attained a value of 224 mW/cm² at 873 K, which was the largest power density attained in our previous study. The maximum power density of cell with Y₂O₃-stabilized ZrO₂ electrolyte is 0.3 and 0.07 W/cm² at 1293 and 1073 K, respectively, when O₂ is used as oxidant. Considering the power density of YSZ cell and the thickness of electrolyte, the power density characteristic-
tics of SOFC in Fig. 6 were extremely high. Furthermore, large part of the internal resistance in the cell is the electrical resistance of electrolyte. Therefore, further improvement in the power density will be expected by decreasing the thickness of the electrolyte. Since the ionic conductivity of YSZ at 1273 K is almost the same as that of LSGMN at 923 K, it is expected that the equivalent performances would potentially be achieved at considerably low temperatures. This, in our view, will be the most significant achievement in this field.

Figure 7 shows the comparison of power generation characteristics of the cell utilizing the LaGaO₃ based oxide doped with Fe, Co, or Ni. Transport number of oxide ion in non doped and Fe doped LaGaO₃ is almost unity and it is much higher than those of Co or Ni doped specimens. In agreement with this result, open circuit potential of the cells decreased in the following order of the electrolyte, non-doped > Fe >> Ni > Co doped LaGaO₃. However, power density shows the almost opposite order and it increased in the following order. Ni > Co >> Fe > non-doped sample. It has been already reported that the maximum power density of the cell using Fe doped LaGaO₃ electrolyte exhibited a large power density at high temperature (0.7 W/cm² at 1073 K), however, it decreased drastically with decreasing temperature (12). This may result from the large activation energy for the oxide ion conduction in Fe doped LaGaO₃. On the other hand, Ni doped sample exhibited performance similar to Co doped sample, not only in the electrical conductivity but also in the power generating characteristics. However, considering the power density and the open circuit potential, LSGMN seems to be more desirable as an electrolyte for the intermediate temperature SOFC.

**Effect of Dopant on Cathodic Property of La₀.₉Sr₀.₁CoO₃**

The usage of LSGMN for the electrolyte leads to the sufficient power density even at 873 K as mentioned above. However, in the present cell, Sm₀.₅Sr₀.₅CoO₃ was used for cathode. SmCoO₃ based oxide cathode exhibits a small overpotential at intermediate temperatures, however, this oxide is expensive. Therefore, SmCoO₃ cathode is undesirable from the cost point of view. Therefore, an alternative and cheap oxide cathode material is required. Since it is reported that the electrical conductivity increases by doping aliovalent cation to Co site of LaCoO₃, the effect of dopant on Co site of La₀.₉Sr₀.₁CoO₃ was studied. This is because La₀.₉Sr₀.₁CoO₃ exhibited the smallest overpotential among LaCoO₃ oxide in our previous study (10). Table 1 summarizes the overpotential of metal cation doped LaCoO₃ and Sm₀.₅Sr₀.₅CoO₃ at the current density of 0.5 A/cm² at 1073 K. It is clear that cathodic property of La₀.₉Sr₀.₁CoO₃ is greatly affected by doping the aliovalent cation to Co site. Comparing with Sm₀.₅Sr₀.₅CoO₃, La₀.₉Sr₀.₁CoO₃ exhibited much larger cathodic overpotential, however, the overpotential decreased by doping Cu for Co site of LaCoO₃ based oxide. Impedance measurement suggested that the small resistance assigned to a diffusion step from the oxygen adsorption site to a triple or two phase boundary was the origin for a small overpotential of SmCoO₃ based oxide cathode at intermediate temperatures. On the other hand, it is expected that doping Cu to Co site of LaCoO₃ is effective to improve the mixed oxide ion conductivity. Consequently, doping Cu to Co site of LaCoO₃ was effective for decreasing the cathodic overpotential at intermediate temperatures. In any case, this study revealed that LaCoO₃ based oxide doped with Cu or Ni was an active cathode for intermediate temperature SOFC. A power generating performance similar to that of a cell using Sm₀.₅Sr₀.₅CoO₃ cathode will be obtained even if the inexpensive similar to that of a La₀.₉Sr₀.₁Co₀.₉Cu₀.₁O₃ is used for cathode.
CONCLUSIONS

Although the hole conduction was slightly observed at the oxygen partial pressure higher than $10^{-5}$ atm, oxide ion conductivity increased by doping Ni for Ga site of LaGaO$_3$. In accordance with the improved oxide ion conductivity, the power density of the cell also increased greatly by doping Ni for LaGaO$_3$ electrolyte. The highest power density in our previous study was attained with a cell using La$_{0.8}$Sr$_{0.2}$Ga$_{0.8}$Mg$_{0.13}$Ni$_{0.07}$O$_3$ electrolyte. Since the valence number of Ni in crystal lattice seems to be $+2$ or $+3$, it is anticipated that the number of oxygen vacancy was almost unchanged or decreased by doping Ni. Consequently, the increased oxide ion conductivity may be assigned to an improved mobility of oxide ion. This is because the ionic size of Ni$^{2+}$ is almost the same as that of Ga$^{3+}$. Any way, this study revealed that Ni doped LaGaO$_3$ based oxide was an attractive fast oxide ion conductor for the intermediate temperature solid oxide fuel cell. Also, LaCoO$_3$ doped with Sr and Cu for La and Co sites respectively was promising as an inexpensive but active cathode for the intermediate temperature SOFC.

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Fig. 1 Arrhenius plots of electrical conductivity of La$_{0.8}$Sr$_{0.2}$Ga$_{0.8}$Mg$_{0.2-x}$Ni$_x$O$_3$ (P$_{O_2}$=10$^{-5}$ atm, Pt electrode)

Fig. 2 Electrical conductivity of LaGaO$_3$ based oxide doped with Ni at 1173 K as a function of oxygen partial pressure.

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Fig. 3 Temperature dependence of the transport number of oxide ion in Ni doped LaGaO$_3$ based oxide. The transport number was estimated with the electromotive forces of H$_2$-O$_2$ gas concentration cell.

$$H_2 + 3\text{vol}\%H_2O, \text{Ni} \mid \text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2-x}\text{Ni}_x\text{O}_3, \text{Sr}_{0.5}\text{Sm}_{0.5}\text{CoO}_3, O_2$$

Fig. 4 Open circuit potential and the maximum power density of the cell at 1073 K as a function of the Ni content in LaGaO$_3$ based oxide.

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Fig. 5 Internal resistance of the cells using Ni doped LaGaO$_3$ based oxide at 1073 K as a function of Ni content. Internal resistance was measured with the current interruption method at 1.0A/cm$^2$.

Fig. 6 Temperature dependence of the maximum power density of the cell using LSGMN for electrolyte. Anode; Ni, Cathode: Sm$_{0.9}$Sr$_{0.1}$CoO$_3$, Thickness of electrolyte; 0.5mm
Fig. 7 Comparison of the power generation characteristic of the cell using LaGaO₃ based oxide doped with Fe, Co, or Ni at 873 K.

Table 1 Overpotential of metal cation doped LaCoO₃ and Sm₀.₅Sr₀.₅CoO₃ at 1073 K at the current density of 0.5 A/cm².

| Cathode material | Cathodic Overpotential /mV | Activation energy for cathodic reaction /eV |
|------------------|---------------------------|-------------------------------------------|
| Sm₀.₅Sr₀.₅CoO₃   | 14                        | 0.443                                      |
| La₀.₉Sr₀.₁CoO₃   | 37                        | 0.443                                      |
| La₀.₉Sr₀.₁Co₀.₉M₀.₁O₃ M= Fe | 36                        | 0.445                                      |
|                  | Ni                        | 41                                         |
|                  | Mn                        | 44                                         |
|                  | Cu                        | 28                                         |
| Ba₀.₉La₀.₂Fe₀.₈Co₀.₂O₃   | 33                        | 0.755                                      |

Anode; Ni, Electrolyte; La₀.₉Sr₀.₁Ga₀.₈Mg₀.₂O₃