SOLID OXIDE FUEL CELL OPERABLE AT DECREASED TEMPERATURE USING LaGaO$_3$ PEROVSKITE OXIDE ELECTROLYTE

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ABSTRACT

LaGaO$_3$-based perovskite oxide doped with Sr and Mg exhibits wholly ionic conduction over a wide oxygen partial pressure. In this study, SOFCs where LaGaO$_3$-based perovskite type oxide is applied as the electrolyte, were studied for the decreased temperature solid oxide fuel cells. The power generation characteristics of cells were strongly affected by the electrode, both anode and cathode. It became clear that Ni and LnCoO$_3$ (Ln: rare earth) are suitable for anode and cathode, respectively. Rare earth cations in the Ln-site of Co-based perovskite cathode also have a great effect on the power generation characteristics. In particular, a high power density could be attained in the temperature range from 973 to 1273 K by using a doped SmCoO$_3$ for the cathode. The maximum power density of the SOFC, which consisted of Ni anode and Sm$_{0.6}$Sr$_{0.4}$CoO$_3$ cathode attained a value as high as 0.44 W/cm$^2$ at 1073 K.

INTRODUCTION

Solid oxide fuel cell (SOFC) provides a new and clean electric power generation system. At present, Y$_2$O$_3$ stabilized -ZrO$_2$ (YSZ) is commonly used for the electrolyte of solid oxide fuel cell. Since 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 the high power density of SOFCs when YSZ is used as electrolyte. On the other hand, all advantages of SOFC such as a high efficiency and a variety of usable fuels can be obtained at a decreased temperature such as 1073 K. Furthermore, choice of the materials for cell stacking becomes wide; in particular, a cheap refractory metal such as a stainless steel will be used by decreasing the operating temperature down to 1100 K. Consequently, decrease in operating temperature is of importance for the development of cheap but reliable cells (1). Decreasing the operating temperature requires the active electrode, in particular, cathode material, and the electrolyte with a low resistence. Ceria doped with Gd or Sm is generally considered for the electrolyte of SOFC operable in the decreased temperature range (1). However, ceria based oxide exhibits the n-type semi-conduction in the reducing atmosphere. Consequently, open circuit voltage becomes smaller than theoretical value when CeO$_2$ based oxide is used.

It is, therefore, of great importance to develop new electrolyte materials which exhibit high oxide ion conduction over a wide oxygen partial pressure. The reports on the oxide ion conductivity are limited for oxides with non-fluorite structure. In our previous study, oxide ion conductivity in oxide with perovskite structure was investigated and it was found that the LaGaO$_3$-based perovskite type oxide exhibits extremely high oxide ion conductivity (2), which is comparable with that of CeO$_2$-based
oxide. In particular, LaGaO$_3$ doped with Sr for La and Mg for Ga sites exhibits high oxide ion conductivity stably over a wide oxygen partial pressure range. The advantage of this oxide is that almost pure oxide ion conductivity is exhibited in both reducing and oxidizing atmosphere. It is, therefore, expected that the operating temperature of SOFC can be decreased by using LaGaO$_3$-based oxide for the electrolyte of SOFCs (3,4). In the present study, power generation characteristics of SOFC were investigated when LaGaO$_3$-based oxide is used as the electrolyte. In addition, the thermal expansion as well as the oxygen nonstoichiometry of LaGaO$_3$-based oxide were further investigated.

EXPERIMENTAL

Calculated amounts of commercial La$_2$O$_3$ (Wako, 99.99% purity), SrO and MgO (Wako, 99.9% purity), and Ga$_2$O$_3$ (Kishida, 99.99% purity) were mixed in a mortar with a pestle and then precalcined at 1273K for 6 h. The perovskite oxide of La$_{1-x}$Sr$_x$Ga$_{1-y}$Mg$_y$O$_3$ was used in this study. 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 vacuo. The disks were sintered at 1773 K for 6 h unless otherwise stated. Thus obtained disks were ground and polished with diamond wheels to 0.5 mm in thickness. LaCoO$_3$, LaFeO$_3$, LaCrO$_3$, and LaMnO$_3$-based perovskite type oxides for the cathode were prepared by calcining the precursors at 1473 K for 6 h. The precursors of these oxides were prepared by the evaporation to dryness of acetate solutions. The commercial metal without further purification was used for anode. Thus obtained cathode oxide and anode metal were applied on one face of LaGaO$_3$ disks (5 mm in diameter) with plating method, followed by calcining at 1173 K for 10 min.

Electrical power generation characteristics of a single SOFC were measured with the four probe method using humidified hydrogen (2 vol% H$_2$O) as fuel and oxygen as oxidizing agent. It is also noted that the theoretical electromotive forces estimated from the Nemst equation is 1.10 V under the used condition. Each gas was fed at 100 ml min$^{-1}$ and the molten Pyrex glass was used for sealing of cells. Overpotential of electrode was measured with current interruption method. Current pulse generated with the current pulse generator (Hokuto Denko, HC-111) was applied across the cathode and anode and the transient potential across the electrode and reference electrode put on the side of electrolyte was analyzed with the digital spectrum analyzer (Takeda Riken TR-9404).

Thermal expansion of LaGaO$_3$ was measured with the thermal mechanical analyzer (Rigaku) in air at a heating rate of 5 K/min. The expansion coefficient was estimated with comparison with Al$_2$O$_3$ standard sample. On the other hand, oxygen nonstoichiometry of LaGaO$_3$ based oxide was measured by thermal gravimetry (Carn, CN2000) with the gas flow system which could control the oxygen partial pressure.

RESULTS AND DISCUSSION

Property of the Acceptor Doped LaGaO$_3$ Oxide

Figure 1 shows the thermal expansion profiles of La$_{1-x}$Sr$_x$Ga$_{1-y}$Mg$_y$O$_3$ at $X=0.1$ and 0.2 in air. It is reported that crystal structure of non doped LaGaO$_3$ is rhombohedral at room temperature and it changes to orthorhombic at 313 K. However, no significant changes in the thermal expansion coefficient are observed around 300 K. Clearly, LaGaO$_3$ based oxide exhibits linear thermal expansion from room temperature to 1573 K and the average thermal expansion coefficient is about 11 x10$^{-6}$ K$^{-1}$, which is slightly larger than that of

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Y$_2$O$_3$-stabilized ZrO$_2$. Therefore, some of the materials used in the YSZ cell commonly investigated are also usable for the LaGaO$_3$ cell from the thermal expansion property. Increasing amount of Sr in La site increases the thermal expansion coefficient slightly. Thermal expansion profiles in CO and O$_2$ atmosphere were also measured but the thermal expansion coefficient was almost independent of the oxygen partial pressure. This suggests that LaGaO$_3$ based oxide is highly stable for the reduction and oxidation. The stability in the oxidation and reduction atmosphere was also confirmed with oxygen non-stoichiometry with thermal gravimetry. Figure 2 shows the non-stoichiometry of non-doped LaGaO$_3$ and LaGaO$_3$ doped with Sr as a function of oxygen partial pressure. Although small decrease in weight is observed in CO, oxygen non-stoichiometry is hardly observed over the wide oxygen partial pressure from 1 to 10$^{-20}$ atm. Consequently, it can be concluded that LaGaO$_3$ based oxide is stable for use as the electrolyte of SOFC.

Self diffusion coefficient of oxide ion in LaGaO$_3$ doped with Sr and Mg was measured with SIMS to estimate the oxide ion conductivity in LaGaO$_3$ based oxide by using SIMS. The isotopic ratio, $^{18}$O/$^{18}$O+$^{16}$O, on the surface of $^{18}$O treated sample was lower than 1% on the surface of the sample, while the diffusion length was attained to 400 μm when $^{18}$O exchange was performed at 1073 K for 540 s. This suggests that the surface of LaGaO$_3$ based oxide is inactive to the dissociation of oxygen molecule into oxide ion due to low concentration of free electron, however, mobility of oxide ion in bulk is extremely fast. Figure 3 shows the diffusion coefficient estimated with SIMS and the electrical conductivity by applying Nernst-Einstein equation. Clearly, the data obtained by the different methods are identical to within experimental error. Therefore, electrical conductivity of LaGaO$_3$ based oxide in the temperature range measured is wholly ionic.

Effects of Electrode Materials on the Power Generation Characteristic of SOFC

Table 1 summarizes the effects of electrode material on the electrical power generation characteristics of SOFCs for which La$_{0.8}$Sr$_{0.2}$Ga$_2$Mg$_{0.1}$O$_{3-δ}$ was used as the electrolyte at the operating temperature of 1273 K. The open circuit voltages of SOFCs were slightly lower than that estimated from the Nernst equation due to a hole conduction in the high oxygen partial pressure range, however, the open circuit voltage attained to almost 1.10 V on each SOFC as shown in Table 1. This suggests that oxide ion conduction was dominant and stable in La$_{0.8}$Sr$_{0.2}$Ga$_2$Mg$_{0.1}$O$_{3-δ}$ over wide range of oxygen partial pressure, which is in good agreement with the results of self diffusion of $^{18}$O by SIMS. On the other hand, the maximum power density strongly depended on the electrode materials used for both cathode and anode. As shown clearly in Table 1, the maximum power density of cells increased in the following order, Pt $<$ La$_{0.8}$Sr$_{0.2}$CrO$_3$ $<$ (La$_{0.8}$Sr$_{0.2}$)$_2$MnO$_3$ $<$ La$_{0.8}$Sr$_{0.2}$FeO$_3$ $<$ La$_{0.8}$Sr$_{0.2}$CoO$_3$ for the cathode, and Ru $<$ Pt $<$ Co $<$ Ni for the anode. Although the maximum power density of the cell for which cathode and anode were both platinum was as low as 0.09 W/cm$^2$, it attained a value as high as 0.71 W/cm$^2$ in the cell where La$_{0.9}$Sr$_{0.1}$CoO$_3$ and Ni were used for the cathode and anode, respectively. The power density was also dependent on the amount of Sr doped for A site of LaCoO$_3$ as shown in Table 1. Considering the power density, Ni and La$_{0.9}$Sr$_{0.1}$CoO$_3$ are the most suitable for anode and cathode, respectively.

Figure 4 shows the temperature dependence of maximum power density of SOFC for which LaGaO$_3$ based oxide and YSZ electrolyte were used. Maximum power density of both cells decreased with decreasing the operating temperature. However, the decrease in the power density is smaller for LaGaO$_3$ cell than YSZ cell. Apparent activation energy of electrical conductivity for LaGaO$_3$ based oxide is 0.79 eV which is smaller than that for YSZ. Reflecting the difference in the activation energy of electrical conductivity, the
difference of power density between the LaGaO$_3$ cell and the YSZ cell becomes more significant with decreasing temperature. Consequently, the power density of LaGaO$_3$ cell is ca. 380 mW/cm$^2$ at 1073 K, which is larger than that of YSZ cell by an order of magnitude. Considering the 0.5mm thickness of electrolyte, this power density at 1073 K is considered as a high value among the reported ones.

Internal resistance of the present cell was analyzed with a current interruption method at 1273 and 1073 K and shown in Fig.5. The main reason for the voltage drop of the present cell is the electrical resistance at both temperatures. On the other hand, the overpotential of cathode is slightly smaller than that of anode at 1273 K but it drastically increases with decreasing operating temperature. At 1073 K, the overpotential of cathode is 3 times larger than that of anode. This suggests that decreasing the electrical resistance and increasing the activity of cathode are essential for the development of SOFC operable at decreased temperature. The electrical resistance of the present cell is larger than that of electrolyte resistance estimated with the electrical conductivity and the thickness of electrolyte. This suggests that all electrical resistance in the present cell is not brought about by the electrolyte resistance but some of it by electrical resistances such as a contact resistance. However, it is expected that the electrical resistance can be decreased by decreasing the thickness of electrolyte.

Figure 6 shows the effects of the thickness of electrolyte on the power density of the cell at 1073 K. Theoretically, the power density of the cell is inversely proportional to the thickness of electrolyte. However, the electrical resistance of the cell is not only consisted of the electrolyte resistance. As a result, the power density of the cell did not increase linearly with the thickness of electrolyte decreases. However, the power density increased with decreasing thickness of electrolyte and attained the maximum power of ca. 400 mW/cm$^2$ when the electrolyte at 0.35 mm thickness was used. Therefore, decrease in the thickness of electrolyte is effective for increasing the power density.

On the other hand, it is reported that cathodic overpotential as well as the reactivity with electrolyte are strongly affected with Ln site cations of perovskite used for cathode (5). In this study, effects of rare earth cations in Ln site on the power generation characteristics were further investigated to increase the power density at a decreased temperature such as 1073 K. Figure 7 shows the temperature dependence of the maximum power density of cells where Ln$_{0.6}$Sr$_{0.4}$CoO$_3$ (Ln=La, Pr, Nd, Sm, Gd) was used for cathode. The effects of rare earth cations in Ln-site on the maximum power density were observed in the temperature range examined. In particular, the maximum power density of cell becomes higher than 0.4 W/cm$^2$ at 1073 K when Sm$_{0.6}$Sr$_{0.4}$CoO$_3$ or Gd$_{0.6}$Sr$_{0.4}$CoO$_3$ was used for cathode. Kilner et. al reported that SmCoO$_3$ exhibited the high mixed conductivity of oxide ion and hole, and the superior cathodic property of SmCoO$_3$ might result from the large effective electrode area caused by the mixed conductivity (6).

Dependence of the cathodic overpotential on the amount of doped Sr in SmCoO$_3$ was also investigated and the smallest overpotential was obtained at the composition of Sm$_{0.6}$Sr$_{0.4}$CoO$_3$. Figure 8 shows the potential drops due to cathodic, anodic, and electric resistance (IR) as a function of current density at 1073 K when SOFC consists of Sm$_{0.6}$Sr$_{0.4}$CoO$_3$ cathode and Ni anode. Comparing the internal resistance in Fig.4 (b), the overpotential of cathode was decreased by using Sm$_{0.6}$Sr$_{0.4}$CoO$_3$ cathode. Therefore, the terminal voltage is mainly dropped by the IR loss of the cell. Consequently, further increases in the power density are expected by decreasing the thickness of the electrolyte and the contact resistance.
Figure 9 shows the comparison of power generation curves of SOFCs at 1023 K when 16 mol% Y or 12 mol% Yb-stabilized ZrO2 and La0.8Sr0.2Ga0.5Mg0.5O3 were used for electrolyte. The power generation curves of cells with Sm0.6Sr0.4CoO3 cathode are also shown in Fig.9. The open circuit voltage attained the theoretical values, 1.1 V for all cells examined. On the other hand, the maximum power density of cell was greatly affected by the used electrolyte and it attained a value as low as 0.05 and 0.06 W/cm² when Y2O3 or Yb2O3 stabilized ZrO2 was used as the electrolyte, respectively. On the other hand, the power density of the cell with the electrolyte of La0.8Sr0.2Ga0.5Mg0.5O3 is 4 times larger than that of cells with the stabilized ZrO2 electrolytes. The SOFC with the combination of La0.8Sr0.2Ga0.5Mg0.5O3 electrolyte and Sm0.6Sr0.4CoO3 cathode gave the highest power density. Consequently, the LaGaO3 based oxide is one of the promising electrolyte for SOFCs operated in the intermediate temperature. Stability was further investigated and the potential of 0.7 V at 0.2A/cm² was stably sustained over 60 h examined, albeit a decrease in the initial period which may be caused by the migration of anode Ni powder.

CONCLUSION

LaGaO3-based perovskite oxide doped with Sr and Mg is highly stable in reducing and oxidizing atmospheres. Consequently, this new oxide ion conductor is applicable for the electrolyte of SOFC. This study revealed that SOFC where La0.8Sr0.2Ga0.5Mg0.5O3 is used for electrolyte exhibits the high power density in spite of the use of the thick electrolyte plate. Nickel and doped SmCoO3 oxide were suitable as the anode and cathode, respectively, for LaGaO3-based electrolyte. The maximum power density of the SOFC, which consisted of these materials, attained a value as high as 1.3 W/cm² at 1273 K, despite 0.5 mm thickness of electrolyte. Moreover, the power density of the cell was still as high as 0.44 W/cm² even at 1073 K. This power density is about 9 times higher than that of SOFCs where YSZ is used as electrolyte under the same condition. Consequently, it can be concluded that the oxide ionic conductor, LaGaO3-based perovskite type oxide, can be used for the development of SOFCs operated at decreased temperatures.

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Fig. 1 Thermal expansion property of LaGaO$_3$ doped with Sr and Mg in air.

Fig. 2 Oxygen nonstoichiometry of doped LaGaO$_3$ oxide at 1273 K.
Fig. 3 Arrhenius plots of self diffusion coefficient of oxide ion and surface exchange coefficient in La$_{0.9}$Sr$_{0.1}$Ga$_{0.8}$Mg$_{0.2}$O$_3$ estimated with SIMS and the electrical conductivity.

Table 1 Effects of electrode materials on the electrical generation characteristics of SOFCs.

| Anode  | Cathode | O.C.V./V | M.P.D./Wcm$^{-2}$ |
|--------|---------|----------|-------------------|
| Pt     | Pt      | 1.098    | 0.09              |
| Ni     | Pt      | 1.099    | 0.15              |
| Ni     | LSCr    | 1.099    | 0.15              |
| Ni     | LSM     | 1.098    | 0.31              |
| Ni     | LSF     | 1.100    | 0.51              |
| Ni     | LSCo(6:4)| 1.099  | 0.71              |
| Ni     | LSCo(9:1)| 1.052  | 0.93              |
| Ru     | LSCo    | 1.051    | 0.01              |
| Co     | LSCo    | 1.100    | 0.53              |

O.C.V.; open circuit voltage, M.P.D.; maximum power density, LSCr; La$_{0.75}$Sr$_{0.25}$CrO$_3$, LSM; (La$_{0.6}$Sr$_{0.4}$)$_{0.9}$MnO$_3$, LSF; La$_{0.6}$Sr$_{0.4}$FeO$_3$, LSCo; La$_{1-x}$Sr$_x$CoO$_3$, Electrolyte: La$_{0.9}$Sr$_{0.1}$Ga$_{0.8}$Mg$_{0.2}$O$_3$(0.5mm thickness)
Fig. 4 Maximum power density of the cell as a function of operating temperature.

Fig. 5 Details of the voltage drop of the present cell at 1273 K (a) and 1073 K (b). La$_{0.9}$Sr$_{0.1}$CoO$_3$ and Ni are used for cathode and anode, respectively.
Fig. 6 Maximum power density as a function of the thickness of electrolyte at 1073 K.

Fig. 5 Effects of rare earth cations in A site of Co-based oxide cathode on the power generation characteristics. Ni was used as anode.
Fig. 7 Details of voltage drop of the SOFC where Sm$\text{0.6} \text{Sr}_{0.4}\text{CoO}_3$ cathode and Ni anode were applied. The operating temperature is 1073 K.

Fig. 8 Comparison of the power generation characteristics of SOFC where Yb and Y-stabilized ZrO$_2$ and LaGaO$_3$ based oxide were used for electrolyte at 1073 K.

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