SOME CHARACTERISTICS FOR FABRICATION OF LaGaO$_3$-BASED ELECTROLYTE

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ABSTRACT

We measured the electron and hole conductivity of La$_{0.9}$Sr$_{0.1}$Ga$_{0.8}$Mg$_{0.2}$O$_{3.5}$ by ion blocking method. In a region of $p$(O$_2$)>10$^5$ atm, the hole conduction is dominant and proportional to $p$(O$_2$)$^{1/4}$ at 873, 1073 and 1273 K. On the other hand, in a region of $p$(O$_2$)<10$^{-10}$ atm, the electron conduction was observed to be independent of $p$(O$_2$); this is probably due to experimental unsoundness. The transference number of hole is 0.012 at 1273 K at $p$(O$_2$)=0.21 atm, and decreases with decreasing temperature. The optimum thickness was calculated from oxygen permeability and Joule loss, and was found to decrease with decreasing temperature; it is about 10 $\mu$m at 873 K under a current flow of 0.5 Acm$^{-1}$.

INTRODUCTION

Recently, LaGaO$_3$-based oxide-ion conductors have been found by Ishihara et al[1]. This material has a perovskite structure, and with appropriate dopants such as Sr or Mg, shows higher ionic conductivity than that of YSZ. Particularly, La$_{0.8}$Sr$_{0.2}$Ga$_{0.8}$Mg$_{0.2}$O$_{3.6}$(LSGM8282) has the highest oxide ionic conductivity among the family of compounds. Ishihara et al has reported[2] that the total electrical conductivity of La$_{1-x}$Sr$_x$Ga$_{1-y}$Mg$_y$O$_{3-x/2}$ slightly increases with increasing oxygen partial pressure ($p$(O$_2$)) from 10$^{-5}$ to 1atm. Since the ionic conductivity can be expected to be independent of $p$(O$_2$), this may indicate a contribution from the hole conductivity. For utilization of LaGaO$_3$-based electrolytes in SOFCs, it is desirable to obtain detail data of the electronic conductivity as functions of $p$(O$_2$) and temperature. These are required for evaluating the optimum thickness or judging whether or not a single layer of electrolyte can be used without significant oxygen permeation. As far as we know, no direct measurement has been reported on such electron and hole conductivity of LaGaO$_3$-based electrolyte.

In the present investigation, we measured the electron and hole conductivity by an ion blocking method. By using the measured data, we calculated the energy conversion efficiency of electrolytes for SOFCs as a function of $p$(O$_2$), and obtained the optimum thickness of electrolytes.
EXPERIMENTAL

Materials

Electrolytes with a composition of \( \text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3.0} \) (hereafter we refer it as LSGM9182) were used for electrical measurements.

Calculated amounts of powders of \( \text{La}_2\text{O}_3 \) (Wako, 99.99%), \( \text{Ga}_2\text{O}_3 \) (Wako, 99.99%), \( \text{SrCO}_3 \) (Rare Metalic, 99.9%) and \( \text{MgO} \) (Rare Metalic, 99.9%) were mixed and grounded in a zirconia ball-mill with ethanol for 24 h, and calcined at 1173 K for 10 h in air. A single phase of LSGM9182 was not confirmed by a powder X-ray diffraction (XRD) analysis, so that the calcined powder was ground again in a zirconia ball-mill with ethanol for 24 h, and pressed into disks with a one-axis pelletizer. The disks were sintered at 1773 K for 5 h in air. After that, they turned into brownish red. XRD pattern revealed that the pellets consisted of a single phase of cubic perovskite. A density over 99% was measured by Archimedes method.

Electrochemical Measurements

The total electrical conductivity, \( \sigma_t \), was measured by an AC impedance method. The frequency control was done with a frequency response analyzer (NF5090, NF Electric Instrument). Surfaces of the sintered disks were polished with diamond paste of grain size 1/4 \( \mu \)m. As electrodes, Pt paste was painted in 10 mm diameter on the both faces, and fired at 1323 K for 30 min. Pt-meshes were pushed onto the Pt-electrodes as current collectors.

The electronic conductivity was measured by using a polarization cell with an ion blocking electrode which was used by Kawada et al[3]. Fig.1 shows a schematic view of the ion blocking cell. The cell was constructed as follows.

\[
\text{Pt (Oxide ion blocking)} | \text{LSGM9182} | \text{Pt},\text{O}_2 \text{ (reversible)}
\]

The cell was sealed in a flowing gas of 1\%O_2-Ar or O_2 depending on the measuring \( p(O_2) \) range, \( p(O_2)<0.21 \text{ atm} \) or \( p(O_2)=1 \text{ atm} \), respectively. The oxygen partial pressure of the reversible electrode was controlled by flowing O_2-Ar(\( p(O_2)>10^{-4} \text{ atm} \)) or H_2-H_2O-Ar(\( p(O_2)<10^{-10} \text{ atm} \)). The electronic conductivity was measured after a small voltage was applied between the electrodes and a steady state current was obtained. The applied voltage was controlled with a potenio/galvano-stat (2005, Toho-Giken) within 10 mV so as to keep the oxygen potential gradient in the sample small.

RESULTS AND DISCUSSION

Electronic conductivity

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Fig. 2 shows the electronic conductivity of LSGM9182 determined by a polarization cell measurement. In the figure, $p(O_2)$ values of x-axis are defined as the average between inside (blocking side) and ambient (reversible side) atmosphere of the cell. The electronic conductivity shows a linear dependence of $p(O_2)\times$ in a region of $p(O_2)\times>10^5$ at each temperature. It indicates that the hole conduction is dominant in this $p(O_2)$ region. This can be the ultimate cause of a slightly increase of the total conductivity with increasing $p(O_2)$ in the range from $10^5$ to 1 atm reported by Ishihara et al. On the other hand, the observed electron conductivity in a region of $p(O_2)<10^{-10}$ atm is almost independent of $p(O_2)$. If the electron conduction appears in this $p(O_2)$ region, the dependence of $p(O_2)\times$ would be expected. One possible reason for this result may be an inappropriate experimental condition for ion blocking. Oxygen gas can leak into or from the cell, if glass seals are not suitable for this measurement in this $p(O_2)$ region; when glasses are slightly oxide-ion conductive, oxygen gas can permeate as oxide ions in glasses and electrons in platinum. To resolve this problem, further investigation will be needed.

Table 1 shows the hole and the total conductivity at each temperatures in air. The transference number increases with temperature. This is due to the difference in temperature dependence. Fig. 3 shows Arrhenius plots of the total and the hole conductivity. There are two slopes in the total conductivity. The activation energy at high temperature (1023–1273 K) is 0.6 eV, and is 1.1 eV at low temperature (873 K). On the other hand, the activation energy of the hole conduction is 1.2 eV which is independent of temperature, and is higher than that of total conduction.

**Energy Conversion Efficiency as SOFC Electrolyte**

The large hole conduction in the electrolyte for SOFCs gives rise to a significant problem, because oxygen can permeate without generating electricity. By taking the energy loss from oxygen permeation into account, energy conversion efficiency of the electrolyte for a planar SOFC, $\varepsilon_{\text{electrolyte}}$, is defined as follows [4].

The total energy conversion factor of a planar SOFC is defined as follows.

$$
\varepsilon = \frac{J_{\text{ext}}V_{\text{term}}}{J_{O_2}V_{th}} \left( \frac{\Delta E_{\text{electrolyte}} - \Delta E_{\text{electrode}} - \Delta E_{\text{separator}}}{J_{O_2} - J_{O_2} - J_{O_2} + J_{O_2,\text{leak}}} \right) \left( \frac{RT}{4F} \ln \frac{P_{O_2}^1}{P_{O_2}^2} \right)
$$

Here, $J_{\text{ext}}$ and $V_{\text{term}}$ are the current density and the terminal voltage, respectively. $J_{O_2}$ is the total oxygen flux from cathode to anode, and $V_{th}$ is the theoretical voltage calculated from the oxygen partial pressures in cathode and anode, $p_{O_2}^1$ and $p_{O_2}^2$. Calculation from electrolyte can be extracted as follows.
where the first factor $J_{\text{ext}}/J_0^e$ originates from the utilization efficiency of oxygen and the second factor $\Delta E_{\text{electrolyte}}/V_{th}$ is the voltage efficiency inside the electrolyte.

Choudhury \textit{et al.} [5] have reported that $\Delta E_{\text{electrolyte}}, \Delta J_{\text{electrolyte}}$ and $J_{\text{ext}}$ can be written as follows.

\begin{align}
\Delta E_{\text{electrolyte}} &= \frac{RT}{2F} \int_{p_{01}}^{p_{02}} \left( \frac{1}{r} \sigma_e - \sigma_{0^+} \right) \, d\ln p_{O_2} \\
J_{O_2,\text{electrolyte}} &= \frac{rRT}{2FL} \int_{p_{01}}^{p_{02}} \left( \frac{1}{r} \sigma_e - \sigma_{0^+} \right) \, d\ln p_{O_2} \\
J_{\text{ext}} &= \left( 1 + \frac{1}{r} \right) J_0^e
\end{align}

Here, the parameter $r$ is a ratio of the ionic to the electronic current density, which is constant throughout a membrane under a steady state condition. Energy conversion efficiency of the electrolyte was obtained by calculating these equations over the operating oxygen potential range.

In this calculation, the oxide ionic conductivity was assumed to be independent of $p(O_2)$, and the hole conductivity was estimated to fit the experimental data to show a linear dependence of $P(O_2)^{1/4}$. The electron conductivity is assumed to be small because the experimental data shows that the transference number of electron is smaller than that of hole in the $p(O_2)$ range for this calculation. By this assumption, the calculated efficiency depends on the hole conduction. The values of each conductivity which were used in the calculation are shown in Fig.2.

Fig.4 shows the efficiency under different conditions of oxygen potential gradient at 1273K. In the calculation of this figure, $p(O_2)$ of the reducing side is fixed at $10^{-18}$ atm as 3%H$_2$O-H$_2$, and $p(O_2)$ of the oxidant side is selected at 0.21, 1 and 10 atm, respectively. The efficiency is about 93% when air is used as oxidant gas. When a higher $p(O_2)$ was adopted on the oxidant side, the efficiency becomes lower due to increase of the hole conductivity. The maximum value is about 90% at $p(O_2)=10$ atm. There can be an optimum thickness, $L_{opt}$, at which the efficiency takes the maximum. As shown in Fig.4, with increasing $p(O_2)$ of the oxidant gas, $L_{opt}$ shifts to a higher value. The values under 0.5 Acm$^{-2}$ current flow are about a few hundreds $\mu$m.

As shown in Fig.3 and Table 1, decreasing the temperature makes the transference number of hole small. This makes it attractive to use this electrolyte at lower temperatures. The efficiency at different operating temperatures is shown in Fig.5. In the calculation of this figure, $p(O_2)$ of the oxidant side is 0.21 atm at all temperatures, and
The reducing side is 10^{-18}, 10^{-22} and 10^{-26} atm at 1273, 1073 and 873 K, respectively. The efficiency increases with decreasing operating temperature, and the maximum value is about 96% at 873 K. In addition, Fig. 5 shows that the optimum thickness is still within a limit determined by the current technology for fabricating electrolytes in an inexpensive way such as a wet process. This thickness, L_{opt}, of about 10 \mu m for LaGaO_3 at 873K should be compared with a corresponding thickness, 0.1-1 \mu m, for YSZ.

**Future Work**

We have constructed a single SOFC cell by using LSGM9182 (thickness=1mm) as the electrolyte and Pt(10mm\phi) as both the electrodes, and measured the power density. H_2-H_2O gas as fuel and air as oxidant were supplied to the anode side and cathode side, respectively. Gaseous hydrogen was humidified by bubbling in water at 293K. Fig. 6 shows the electrical power density and the terminal voltage as a function of the current density. The maximum power density is 0.23W and 0.083W at 1273 and 1073 K, respectively.

After the measurement for about 48 h, the microstructure was observed by SEM/EDX. Two particular problems appear in this observation. The first problem is that a new phase appeared at the grain boundaries which exist near the cathodic electrode, as shown in Fig. 7. The height of the phase decreases away from the electrode area. The second problem is that Pt or Zr is observed in the grain boundaries as an impurity by line scanning of EDX, as shown fig. 7. We cannot judge that the impurity is Pt or Zr because Pt and Zr have almost the same main energy spectrum under EDX measurement. We have thus measured the distribution of Pt and Zr by SIMS(CAMECA ims5f). Fig. 8 shows the scanning image of GaO', ZrO' and Pt', and reveals that the impurity in grain boundary is Pt. Pt diffusion will be a serious problem because we use Pt as the electrode for many kinds of electrical measurements. Since this phenomena were observed only in this measurement, the high current dencity and its related properties may be the reason for this platinum migration out of the electrode though grain boundaries. In any case, we need to pay more attention to use Pt as the electrode, and to investigate the diffusion between Pt and LSGM.

**CONCLUSION**

The present investigation has clarified that LaGaO_3-based electrolyte appropriate electrical properties as low temperature SOFC electrolyte. Since the inter diffusion between LaGaO_3-based electrolyte and cathode materials (LaCaO_3-based and LaMnO_3-based mix-conductor) has been recently found to occur significantly[6], it is hoped to examine possible change in electrical properties after the significant inter diffusion.

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Table 1  Temperature dependence of the total conductivity, the hole conductivity and the transference number of hole in air.

| Temperature / K | $\sigma_t$ / Scm$^{-1}$ | $\sigma_h$ / Scm$^{-1}$ | $\tau_h$ ($\sigma_h/\sigma_t$) |
|----------------|-----------------------|-----------------------|------------------|
| 1273           | 0.31                  | 0.0036                | 0.012            |
| 1073           | 0.13                  | 0.00074               | 0.006            |
| 873            | 0.021                 | 0.000072              | 0.003            |

Fig. 1  Schematic view of the ion blocking cell. (reference as [3])
Fig. 2 The total and the electronic conductivity as a function of $p(\text{O}_2)$. Plots are experimental data. Solid lines are the total conductivity in air. Dotted lines are the hole conductivity with a $p(\text{O}_2)^{1/4}$ dependence, and broken lines are the electron conductivity which is assumed to be with a $p(\text{O}_2)^{1/4}$ dependence. These three kind of lines are used for a calculation of the efficiency.

Fig. 3 Arrhenius plot of the total and the hole conductivity in air.
Fig. 4 Dependence of energy conversion factor, $\varepsilon$, on electrolyte thickness, $L$, and external current density, $J_{\text{ext}}$, at 1273 K under a different oxygen potential gradient. $p(\text{O}_2)$ of reducing side are fixed $10^{-18}$ atm, and $p(\text{O}_2)$ of oxidant side are different values which are 0.21, 1 and 10 atm.

Fig. 5 Dependence of $\varepsilon$ on $L$ and $J_{\text{ext}}$ at different temperature. $p(\text{O}_2)$ of the oxidant side are fixed of 0.21 atm, and $p(\text{O}_2)$ of the reducing side are defined by $\text{H}_2$-3$\%\text{H}_2\text{O}$ as $10^{-18}$, $10^{-22}$ and $10^{-26}$ atm at 1273, 1073 and 873 K, respectively.
Fig. 6 The power density and the terminal voltage of a cell (Pt/LSGM9182 (1mm thick)/Pt) as a function of the current density.

Fig. 7 Microstructure and line scan image of the surface which is near to the cathodic electrode area after the power density measurement.
Fig. 8  Secondary ion images of the surface of LSGM9182 which is near to the cathodic electrode area after the power density measurement. White dots show the place where secondary ion was detected.