Journal of Alloys and Compounds 408–412 (2006) 507–511

Journal of
ALLOYS
AND COMPOUNDS

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Oxide ion conductivity in La(Sr)Ga(Fe,Mg)O_3 and its application for solid oxide fuel cells

Tatsumi Ishihara[a,*], Masaki Ando[b], Makiko Enoki[a], Yusaku Takita[b]

[a] *Department of Applied Chemistry, Faculty of Engineering, Kyushu University, Hakozaki 6-10-1, Higashi-ku, Fukuoka 812-8581, Japan*
[b] *Department of Applied Chemistry, Faculty of Engineering, Oita University, Dannoharu 700, Oita 870-1192, Japan*

Received 30 July 2004; received in revised form 1 December 2004; accepted 15 December 2004
Available online 24 June 2005

Abstract

Oxide ion conductivity in La(Sr)Ga(Fe,Mg)O_3 was investigated in this study and it was found that the oxide ion conductivity increased significantly by doping Fe into Ga site. Although the electrical conductivity monotonically increased with increasing amount of Fe, partial electronic conduction became significant. On the other hand, doping Mg for Ga site simultaneously with Fe is useful for keeping high transport number. By doping Fe for Ga site, perovskite oxide with cubic structure seems to be stabilized and the solid solution limit for Sr for La site is expanded.

Considering the transport number of oxide ion and the electronic conductivity, the optimum composition for oxide ion conductivity in this system is $La_{0.7}Sr_{0.3}Ga_{0.7}Fe_{0.2}Mg_{0.1}O_{3-\delta}$ (LSGFM73721). By using this oxide for electrolyte, large power density of 200 mW/cm^2 can be achieved at 873 K.

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Keywords: Oxide ion conductivity; Solid oxide fuel cell; $LaGaO_3$; Fe dope

1. Introduction

Solid oxide fuel cells (SOFCs) are now attracting much interest as clean power generators with high efficiency [1,2]. For SOFCs, oxide ion conductor is generally used as the electrolyte. In the conventional electrolytes, two types of crystal structure are known as the pure oxide ion conductor. One is well-known fluorite structure oxide, e.g. ZrO_2 and CeO_2 [3]. Another is perovskite oxide [4]. Since the perovskite oxide can accommodate larger amount of vacancies, it is reasonable to expect high oxide ion conductivity. In our previous study, it was found that perovskite oxide of $LaGaO_3$ doped with Sr and Mg for La and Ga site, respectively, exhibits high oxide ion conductivity [5,6] and this $LaGaO_3$-based oxide is now expecting as the electrolyte for intermediate temperature SOFCs [7–11]. However, further increase in ion conductivity is required for achieving the high power density at decreased temperature. In our previous study, it was found that oxide ion conductivity in $LaGaO_3$ doped with Sr and Mg for La and Ga site, respectively, is further increased by doping with transition metal cations, such as Co or Ni [12], and in agreement with the improved oxide ion conductivity, maximum power density of the cell also increases when Co or Ni doped $LaGaO_3$ was used for the electrolyte [13]. However, open circuit potential decrease by hole conduction that appeared by doping with a transition metal [14,15]. In contrast, in case of iron, decrease in transport number of oxide ion is not significant. This may be explained by the chemical stability of iron oxide. In this study, oxide ion conductivity in $LaGaO_3$ doped with Fe and Mg for Ga site was investigated. In addition, power generating characteristics of solid oxide fuel cells using Fe doped $LaGaO_3$ were also studied.

2. Experimental

All specimens used in this study were prepared with the conventional solid-state reaction method. Calculated

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[*] Corresponding author. Fax: +81 92 651 5606.
E-mail address: ishihara@cstf.kyushu-u.ac.jp (T. Ishihara).

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doi:10.1016/j.jallcom.2004.12.086

amounts of commercial La_2O_3 (Wako Chemical, 99.99% purity), $SrCO_3$, MgO (Wako Chemical, 99.9% purity), Ga_2O_3 (High Purity Chemical Co. Ltd., 99.99% purity) and Fe_2O_3 (Wako Chemical, 99.5% purity) were mixed in an Al_2O_3 mortar with a pestle and then precalcined at 1273 K for 6 h. 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 finally sintered at 1773 K for 6 h. X-ray diffraction (XRD) measurement was performed to analyse the purity of the obtained disk by X-ray diffractometer (Rigaku Rint 2000) with Cu Kα line.

The electrical conductivity was measured as a function of temperature and oxygen partial pressure by a conventional dc four-probe method with a gas flow system. The oxygen partial pressure was monitored by CaO-stabilized ZrO_2 oxygen sensor that was attached close to the sample in the measurement cell. The transport number of oxide ion was estimated by the electromotive force of the H_2–O_2 gas concentration cell. The oxygen partial pressure in H_2 was adjusted by adding 3 vol% H_2O to H_2.

A single-planar-type fuel cell was always fabricated by using the Fe doped $LaGaO_3$-based oxide electrolyte for the power generating measurement. The disks thus obtained were ground and polished with diamond wheels to 0.5 mm in thickness, and the specimen at this thickness was always used for SOFC application. In our previous study, it was found that $Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$ exhibits a small overpotential at intermediate temperatures. Therefore, $SmCoO_3$-based oxide was always used as the cathode for SOFC. Calculated amounts of Sm_2O_3 (Wako, 99.99% purity), $Sr(CH_3COO)_2$ and $Co(NO_3)_2$ were dissolved in a deionised water and heated to dryness with stirring. The obtained precursors were calcined at 1473 K for 6 h in air. Formation of single-phase of $SmCoO_3$ perovskite oxide was confirmed by XRD analysis. The commercial NiO (Wako, 99.9% purity) without further purification was always used as the precursor of the anode. Before measurement of power generating characteristics, NiO was reduced to Ni in a hydrogen stream at 1273 K. The electrical power generating characteristics of a single SOFC were measured with the four-probe method using humidified hydrogen (3 vol% H_2O) as a fuel and oxygen as an oxidizing agent. The current density was controlled with a glvanostat (Hokuto Denko, HA301). It is also noted that the theoretical electromotive force estimated by the Nernst equation is 1.10 V at 1273 K under the conditions used. Each gas was fed at 100 ml min^{-1}, and molten Pyrex glass was used for sealing the cells. The overpotential of the electrode was measured with a current interrupting method.

3. Results and discussion

In order to optimise the composition for highest oxide ion conductivity, effects of dopants on the electrical conductivity was investigated. Since the highest oxygen permeation rate was achieved on $La_{0.7}Sr_{0.3}Ga_{0.6}Fe_{0.4}O_{3-\delta}$, effects of Mg doped were investigated for this composition [16]. Since the estimated transport number of oxide ion is around 0.5, it is expected that hole conduction may be suppressed by doping Mg for Ga site. In this study, optimisation of composition was investigated by doping 10 mol% Mg for Ga site.

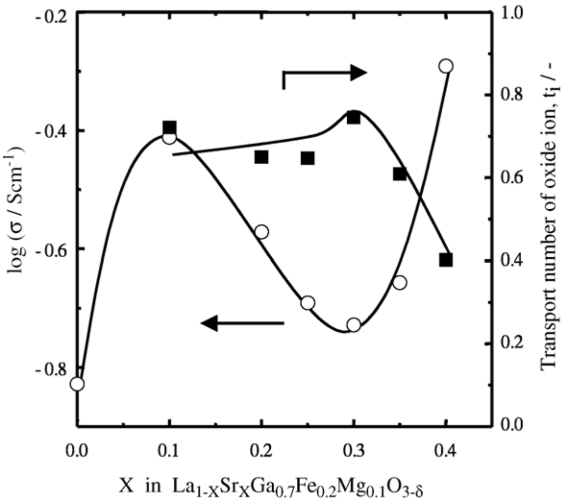

Fig. 1. Conductivity and transport number estimated by H_2–O_2 cell at 873 K as a function of Sr amount in $La_{1-X}Sr_XGa_{0.8}Fe_{0.1}Mg_{0.1}O_{3-\delta}$.

Fig. 1 shows the conductivity and transport number estimated by H_2–O_2 cell at 873 K as a function of Sr amount. In case of La(Sr)Ga(Mg)O_3, limit for solid solution of Sr into La site exist around 20 mol%. However, XRD patterns of all samples prepared in this study are consisted of perovskite phase and no secondary phase was observed up to 40 mol% strontium doped. Therefore, by doping Fe for Ga site, solubility of Sr in La site may expand. This may be explained by the enlarged lattice constant by doping larger sized cation of Fe^{3+} for Ga site. As shown in Fig. 1, it is seen that the dependency of electrical conductivity on Sr amount is complicated. The electrical conductivity first increases then decreases with increasing amount of Sr. Further increase in Sr amount increases the conductivity. The complicated dependency of conductivity on Sr amount may be related with change in valence number of Fe. On the other hand, the estimated transport number of oxide ion slightly increased with increasing amount of Sr and then decreased greatly with Sr amount higher than 30 mol%. Therefore, increase in conductivity at Sr amount higher than 30 mol% may be caused by an increase in hole conductivity. It is seen that conductivity slightly decreased but highest transport number of oxide ion was achieved at 30 mol%. Since the decrease in conductivity is not large, it is considered that the optimum amount for Sr dopant exists at 30 mol%.

Effects of Fe doped amount on oxide ion conductivity were further studied. Fig. 2 shows the electrical conductivity as well as the transport number of oxide ion which is estimated from H_2–O_2 gas concentration cell at 873 K as a function of Fe amount. It is seen that total conductivity increased monotonically with increasing Fe amount.

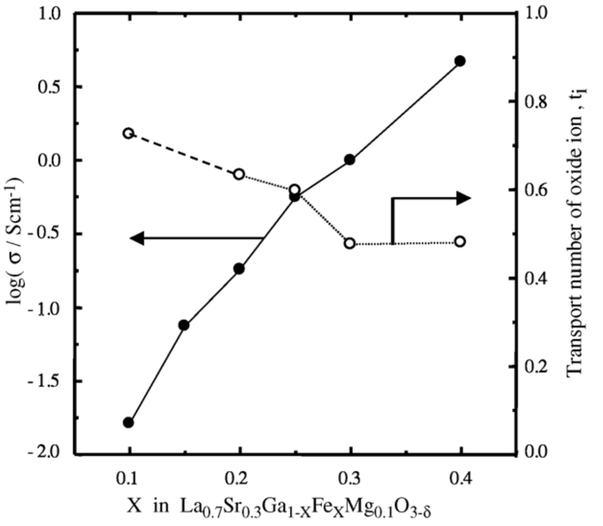

Fig. 2. Electrical conductivity as well as the transport number of oxide ion in $La_{0.7}Sr_{0.3}Ga_{0.9-X}Fe_XMg_{0.1}O_3$ at 873 K as a function of Fe amount.

However, transport number of oxide ion decreased with increasing Fe amount. Therefore, increase in conductivity is not ionic but electronic one. In particular, decrease in ionic transport number is significant at 30 mol%. The oxide ion conductivity can be estimated by multiplying total conductivity by ionic transport number. The estimated oxide ion conductivity is the highest around 20–30 mol% Fe. In this Fe concentration range, electrical conductivity and ionic transport number are higher than $\log(\sigma)$ $(S\,\mathrm{cm}^{-1}) = -0.5$ at 873 K and 0.6, respectively. Therefore, it is considered that the optimised Fe amount for Ga site exist at 20 mol%. Effects of Mg dopant on electrical conductivity were further studied. Electrical conductivity monotonically decreased by increasing the amount of Mg smaller than 15 mol% doped. However, transport number of oxide ion shows the opposite dependency on the Mg amount and it increased with increasing amount of Mg. Considering the conductivity and transport number of oxide ion, it can be said that the optimum amount for Mg doping is 10 mol% for Ga site. As a result, it is considered that the optimum amount for Fe and Mg doped $LaGaO_3$ is $La_{0.7}Sr_{0.3}Ga_{0.7}Fe_{0.2}Mg_{0.1}O_{3-\delta}$, which is denoted as LSGFM in the following part.

Fig. 3 shows the electrical conductivity of LSGFM as a function of oxygen partial pressure. It is seen that the electrical conductivity is independent of oxygen partial pressure over a wide range. However, at high temperature, conductivity slightly increased with increasing P_{O_2}. Therefore, in high P_{O_2} at temperature higher than 1073 K, hole conduction becomes significant. On the other hand, at low temperature, hole conduction is hardly observed, however, electrical conductivity decreased in H_2 atmosphere. At the moment, detailed mechanism of this decrease in conductivity is not clear. Since there is no significant change observed in XRD and the conductivity recovered to the original level by changing O_2 atmosphere, decrease in conductivity may not be caused by decomposition of crystal structure, but by phase change by reduction of Fe. In any case, at 773 K, conductivity of this $La_{0.7}Sr_{0.3}Ga_{0.7}Fe_{0.2}Mg_{0.1}O_3$ oxide is close to $\log(\sigma)$ $(S\,\mathrm{cm}^{-1}) = -1$ and oxide ion conductivity is hardly dependent on oxygen partial pressure suggesting dominant oxide ion conductivity. Therefore, this Fe and Mg doped $LaGaO_3$ is expected as a suitable new oxide ion conductor for the electrolyte for intermediate temperature SOFCs.

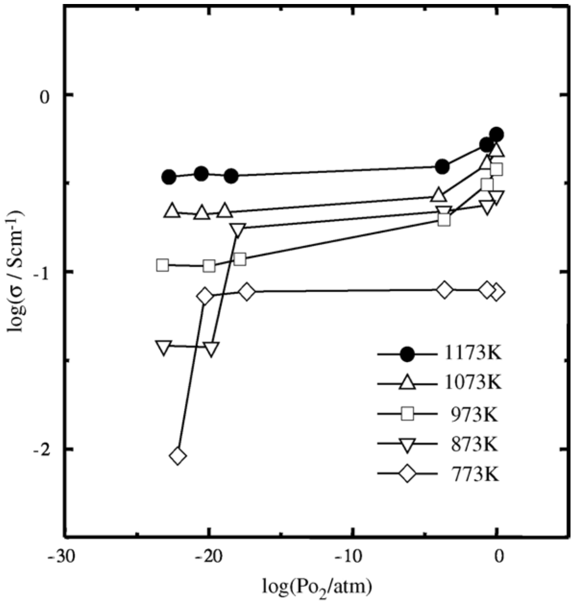

Fig. 3. Electrical conductivity of $La_{0.7}Sr_{0.3}Ga_{0.7}Fe_{0.2}Mg_{0.1}O_{3-\delta}$ as a function of oxygen partial pressure.

Fig. 4 shows the maximum power density of the SOFC using $La_{0.7}Sr_{0.3}Ga_{0.9-X}Fe_XMg_{0.1}O_3$ (0.5 mm) for electrolyte. In agreement with increased oxide ion conductivity

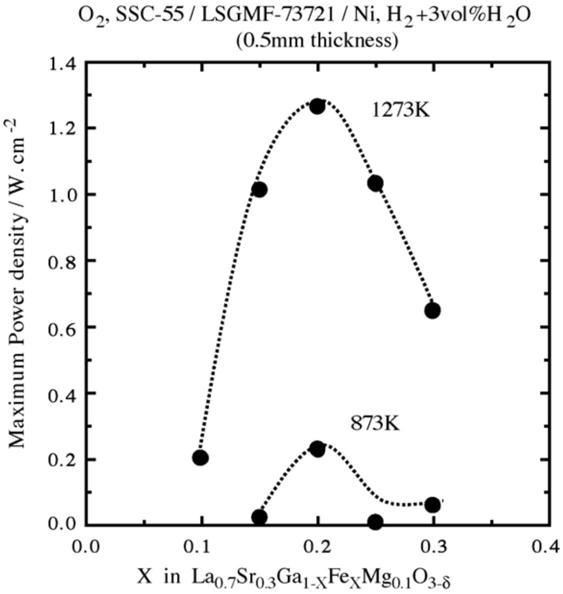

Fig. 4. Maximum power density of the SOFC using $La_{0.7}Sr_{0.3}Ga_{0.9-X}Fe_XMg_{0.1}O_3$ (0.5 mm) for electrolyte as a function of Fe amount.

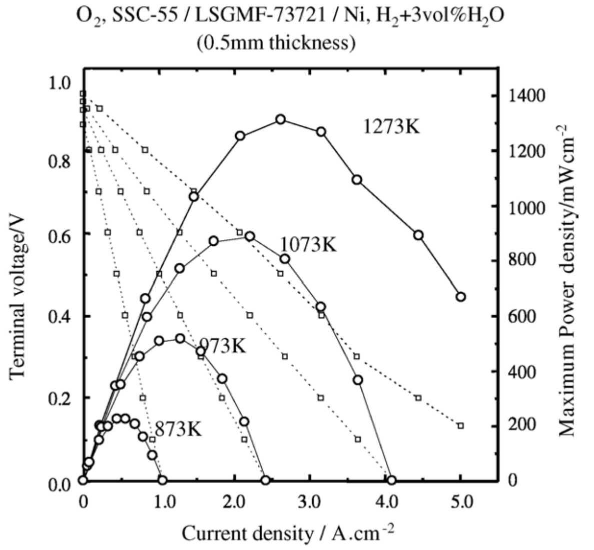

Fig. 5. Power generating curves of the SOFC using $La_{0.7}Sr_{0.3}Ga_{0.7}Fe_{0.2}Mg_{0.1}O_{3-\delta}$ for an electrolyte.

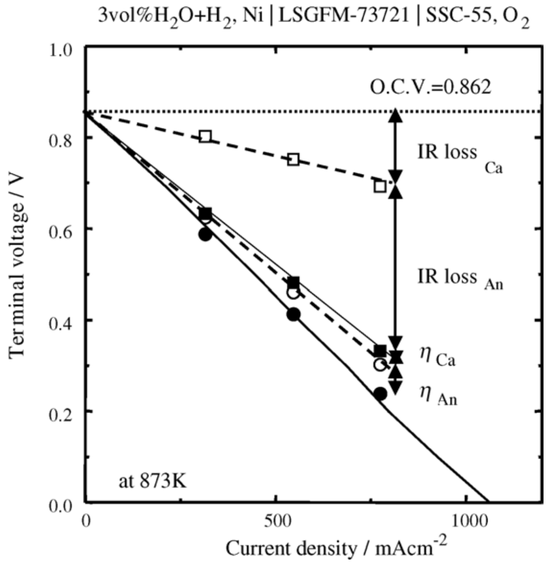

Fig. 6. Details of the internal resistance of the cell that used $La_{0.7}Sr_{0.3}Ga_{0.7}Fe_{0.2}Mg_{0.1}O_{3-\delta}$ as an electrolyte at 873 K.

(Fig. 4), maximum power density at 1273 and 873 K increased with increasing amount of Fe and the highest power density was achieved at 20 mol% Fe, at which oxide ion conductivity estimating by transport number of oxide ion and total electrical conductivity becomes the highest. Therefore, in agreement with the electrical conductivity measurement results, it is considered that the optimum composition is $La_{0.7}Sr_{0.3}Ga_{0.7}Fe_{0.2}Mg_{0.1}O_3$.

Fig. 5 shows the *I–V* and *I–P* curves of the SOFC that used $La_{0.7}Sr_{0.3}Ga_{0.7}Fe_{0.2}Mg_{0.1}O_{3-\delta}$ as an electrolyte. Although open circuit potential is slightly smaller than theoretical value, large maximum power density of 900 mW/cm^2 was achieved at 1073 K and even at 873 K, the maximum power density of the cell is close to 200 mW/cm^2 in spite of 0.5 mm thickness of electrolyte. Although electronic hole conduction is also recognized, it can be said that LSGFM can be used as electrolyte of SOFC operating at intermediate temperature. Comparing with the cell using $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.125}Co_{0.085}O_3$ (LSGMC) for electrolyte, it is obvious that the open circuit potential is smaller on LSGFM cell, however, much higher power density can be achieved by using $La_{0.7}Sr_{0.3}Ga_{0.7}Fe_{0.2}Mg_{0.1}O_3$ for electrolyte. Therefore, although the open circuit potential become slightly decreased, $La_{0.7}Sr_{0.3}Ga_{0.7}Fe_{0.2}Mg_{0.1}O_3$ is highly interesting as the electrolyte for low temperature operation.

Fig. 6 shows the details of the internal resistance of the cell at 873 K. It is seen that main reason for potential drop is IR loss. In particular, IR loss at anode side was quite large. Considering the electrical conductivity shown in Fig. 3, observed IR loss in LSGFM cell is much larger. This is explained by conductivity drop at reducing atmosphere. Therefore, by preventing the reduction at anode side, the SOFC using LSGFM could be further improved. On the other hand, electrode overpotential became quite small on both anode and cathode. Therefore, doping Fe for electrolyte is also effective for decreasing electrode overpotential. This study reveals that the doping Fe for Ga site is effective for increasing oxide ion conductivity and the large power density was achieved at low temperature by using LSGFM for electrolyte.

4. Conclusions

Effects of Fe into Ga site of La(Sr)Ga(Mg,Fe)O_3 on oxide ion conductivity were studied and it was found that oxide ion conductivity is increased significantly by doping Fe for Ga site. Considering the transport number of oxide ion and conductivity, the optimum composition for oxide ion conductivity is $La_{0.7}Sr_{0.3}Ga_{0.7}Fe_{0.2}Mg_{0.1}O_3$. Although transport number of oxide ion is slightly small (ca. 0.8), high power density was achieved by using LSGFM for electrolyte. The maximum power density of 200 mW/cm^2 was obtained at 873 K in spite of 0.5 mm thickness. Therefore, although transport number of oxide ion is smaller at high temperature, LSGFM is a promising electrolyte for SOFC at reduced temperature range because of the high electrical conductivity. In order to achieve the high power density, active catalyst for electrode reaction is essentially required. This is now under investigation.

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