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Proton and oxide-ionic conduction in Sr- and Zn-doped $LaGaO_3$

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Abstract The ionic conduction behaviors in $La_{0.9}Sr_{0.1}Ga_{0.9}Zn_{0.1}O_{3-\alpha}$ under different atmospheres at 600–1,000 °C were studied by various electrochemical methods including ac impedance, hydrogen and oxygen concentration cells, electrochemical hydrogen and oxygen pumping, etc. The proton conduction in this oxide was investigated for the first time. The hydrogen concentration cell and oxygen concentration cell showed stable electromotive forces close to the theoretical ones calculated from Nernst's equation, indicating that the conduction was almost pure ionic under hydrogen atmosphere or dry oxygen atmosphere. The electrochemical hydrogen pumping rates coincided with the theoretical ones calculated from Faraday's law, confirming that $La_{0.9}Sr_{0.1}Ga_{0.9}Zn_{0.1}O_{3-\alpha}$ is a proton conductor under hydrogen atmosphere. A similar result for electrochemical oxygen pumping was obtained, indicating that it is an oxide-ionic conductor under dry oxygen atmosphere. The ionic conductivity was about 0.06 S cm^{-1} at 1,000 °C.

Introduction

Proton conductors are very important functional materials, which may be applied to electrolytes of fuel cell, hydrogen sensor, water electrolysis, separation and purification of hydrogen, hydrogenation and dehydrogenation of some organic compounds, and synthesis of ammonia at atmospheric pressure, etc. [1, 2].

Since the discovery of high-temperature proton conduction in $SrCeO_3$ based perovskite-type oxides [3], a number of high-temperature proton conduction materials such as doped $BaCeO_3$ [4], $AZrO_3$ (A = Ca, Sr and Ba) [5], $KTaO_3$ [6], $Ln_2Zr_2O_7$ [7], Sr_2TiO_4 [8], $Ba_2SnYO_{5.5}$ [9], and mixed perovskite-type $Ba_3Ca_{1+x}Nb_{2-x}O_9$ [10] have been reported one after another. In our previous studies [11, 12], we discovered that existence of oxygen vacancies to some extent in a sample is absolutely necessary, and that the proton or oxide-ion conductivity increased with the increasing free volume and tolerance factor, t, calculated from equation [13]: $t = (r_A + r_O)/\sqrt{2}(r_B + r_O)$, where r_A, r_B, and r_O are the ionic radius of A-site, B-site, and oxide ion, respectively. The tolerance factor ($t = 0.94$) of perovskite-type $BaCeO_3$ is higher than that ($t = 0.88$) of $SrCeO_3$, coinciding with the change tendency that doped $BaCeO_3$ has usually higher proton or oxide-ionic conductivities than doped $SrCeO_3$. According to the above observations, it may be expected that more excellent proton conductors will be present in some other perovskite-type oxides, which are in possession of a number of oxygen vacancies and higher tolerance factors.

It is well known that $LaGaO_3$-based perovskite-type oxides are excellent oxide-ion conductors. Ishihara reported in 1994 [14] that $LaGaO_3$ doped with Sr and Mg, $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\alpha}$, exhibits higher oxide-ionic conductivity than ZrO_2-based oxides, as well as pure oxide-ionic conduction over a wide range of oxygen partial pressures from 1 to 10^{-20} atm. Hence $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\alpha}$ is regarded as a promising candidate electrolyte for intermediate temperature solid oxide fuel cell. And from then on, almost all researches on $LaGaO_3$-based oxides focused on their oxide-ionic conduction. We think that $LaGaO_3$ has a

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higher tolerance factor ($t = 0.97$) than that in $SrCeO_3$ or $BaCeO_3$, and $LaGaO_3$-based oxides may be expected to exhibit superior proton conduction. And in our recent research, we found that $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\alpha}$ is an excellent proton conductor under hydrogen atmosphere [15].

Sebastian reported that the conductivity of $La_{0.9}Sr_{0.1}Ga_{0.8}Zn_{0.2}O_{3-\alpha}$ was found to be independent of the partial pressure of oxygen in the range of 1–10^{-10} atm, revealing that the conductivity is purely ionic, and it is a pure oxide ionic conductor [16]. However, we think the study on ionic conduction behaviors in Sr- and Zn-doped $LaGaO_3$ is insufficient, especially when there is proton conduction in it, which have not been reported up to the present. In this study, the ionic conduction behaviors, especially the proton conduction in $La_{0.9}Sr_{0.1}Ga_{0.9}Zn_{0.1}O_{3-\alpha}$ (LSGZ1010), were investigated in detail by various electrochemical methods.

Experimental

Ceramic specimens of $La_{0.9}Sr_{0.1}Ga_{0.9}Zn_{0.1}O_{3-\alpha}$ were synthesized using the solid-state reaction method. The required amounts of La_2O_3 (99.0%), $SrCO_3$ (99.0%), Ga_2O_3 (99.5%), and ZnO (99.0%) reagents were fully mixed for 1 h in an agate mortar with ethanol and dried, then calcined at 1,200 °C for 10 h in air. The obtained oxides were ground with ethanol using a planetary ball mill machine in an agate mill container and agate balls at 150 rpm for 5 h and dried by infrared lamp, followed by sieving (100 mesh). The powders were pressed into pellets (diameter: 15 mm, thickness: 2 mm) by a hydrostatic pressure of 2.5×10^2 MPa and sintered at 1,440 °C in air for 10 h. The resulting ceramics were made into thin disks to serve as electrolytes for the electrochemical determinations.

To estimate the contribution of protons and oxide ions to the conduction, the electromotive forces (EMFs) of the following gas concentration cells including hydrogen and oxygen concentration cell were measured:

$$\text{Gas (I), Pt} \mid La_{0.9}Sr_{0.1}Ga_{0.9}Zn_{0.1}O_{3-\alpha} \mid \text{Pt, Gas (II)}$$

The electrical conductivities of the specimen were measured as a function of temperature (600–1,000 °C) by ac impedance method over the frequency range of 1 Hz–3 MHz (Zahner elektrik IM6ex) in different atmospheres.

To examine the proton conduction in the specimen directly, the electrochemical hydrogen pumping through the specimen was examined by sending direct current to the following electrolytic cell:

$$(+)H_2, \text{Pt} \mid La_{0.9}Sr_{0.1}Ga_{0.9}Zn_{0.1}O_{3-\alpha} \mid \text{Pt, dry Ar}(-)$$

$$\text{Anode: } H_2 \rightarrow 2H^+ + 2e^-$$
$$\text{Cathode: } 2H^+ + 2e^- \rightarrow H_2$$

Pure hydrogen (99.999%) at 1 atm was supplied to the anode chamber and dry argon (dried by P_2O_5) was passed through the cathode chamber with flow rate of 30 mL $\min^{-1}$ to carry the generated gas at the cathode to a hydrogen sensor (SG33A, Shanghai), where the concentration of the generated hydrogen gas was detected and the hydrogen evolution rate v in the standard state was calculated using the following equation:

$$v = \frac{273.15 \cdot V_{Ar} \cdot x}{(273.15 + T) \cdot S}$$

where V_{Ar} is the flow rate of carrier gas (Ar), x is the concentration of the hydrogen gas generated in mixed gas of hydrogen and argon, T is the surrounding temperature, and S is the area of the cathode.

To examine oxide-ionic conduction in the specimen directly, electrochemical oxygen pumping through the specimen was also performed by sending direct current to the following electrolytic cell:

$$(+)\text{Dry Ar, Pt} \mid La_{0.9}Sr_{0.1}Ga_{0.9}Zn_{0.1}O_{3-\alpha} \mid \text{Pt, dry } O_2(-)$$

$$\text{Anode: } 2O^{2-} \rightarrow O_2 + 4e^-$$
$$\text{Cathode: } O_2 + 4e^- \rightarrow 2O^{2-}$$

Pure oxygen (dried by P_2O_5) at 1 atm was supplied to the anode chamber and dry argon (dried by P_2O_5) was passed through the cathode chamber with flow rate of 30 mL $\min^{-1}$. The generated oxygen in the anode was measured through an oxygen sensor based on YSZ, and the oxygen evolution rate v in the standard state was also calculated using the above equation, but the x is the concentration of the oxygen gas generated in mixed gas.

The theoretical evolution rate of generated hydrogen and oxygen can be calculated by the following equation:

$$V_{th} = \frac{60 \times 22.4 \times I}{n \times F \times S}$$

where I, n, F, and S are the current, the transferred electron number, the Faraday constant, and the area of the electrode, respectively.

In the above experiments, the pO_2 in Ar and H_2 was 10^{-5} and 10^{-20} atm, respectively. And the pH_2O in all gases at room temperature without any drying was 0.03 atm and value of pH_2O in all gases with drying was almost 0 atm.

Results and discussion

The electrical conductivities of $La_{0.9}Sr_{0.1}Ga_{0.9}Zn_{0.1}O_{3-\alpha}$ were obtained from ac impedance measurements. Figure 1 shows the Arrhenius plots of the bulk conductivity of the specimen in H_2, dry air (dried by P_2O_5), ambient air ($pH_2O = 0.03$ atm), and wet air (water saturated at 40 °C,

$pH_2O = 0.073$ atm) atmospheres at 600–1,000 °C. Log (σT) increases basically in linearity with the reciprocal of the temperature. The conductivity differences under various atmosphere are small, and this is similar to Goodenough's report [17]. However, though the conductivity differences are small, Fig. 1 shows that the conductivity in air slightly depends on water vapor partial pressure in air. The conductivities slightly increase in the order: in wet air > in ambient air > in dry air, suggesting that there might be proton conduction in the specimen.

The dependence of the conductivity of LSGZ1010 upon the oxygen partial pressure, pO_2, was also determined. The oxygen partial pressures were adjusted by mixing O_2, air, Ar, and H_2 in proper ratio, the pH_2O in these gases without any drying was 0.03 atm. The typical experimental results are shown in Fig. 2. It is clear that the conductivity is almost independent of pO_2, confirming that LSGZ1010 is almost a pure ionic conductor over the oxygen partial pressure range of $1\text{–}10^{-20}$ atm, which is similar with the early report [16]. So the conductivities under various atmospheres are ionic as shown in Fig. 1; this will be further discussed below. The ionic conductivities are about 0.06 S cm^{-1} at 1,000 °C.

EMF and electrochemical pumping techniques are often used to study electrochemical properties of the specimen, and these two methods have some application in sensor, steam electrolysis, and many another conditions although they have their experimental limitations [18–21]. To study the ionic conduction further, hydrogen concentration cell and the oxygen concentration cell were constructed and their electromotive forces (EMFs) were measured. If the specimen is a proton conductor and pH_2O in both cell compartments is the same, the theoretical value E_{cal} can be obtained from the following Nernst's equation.

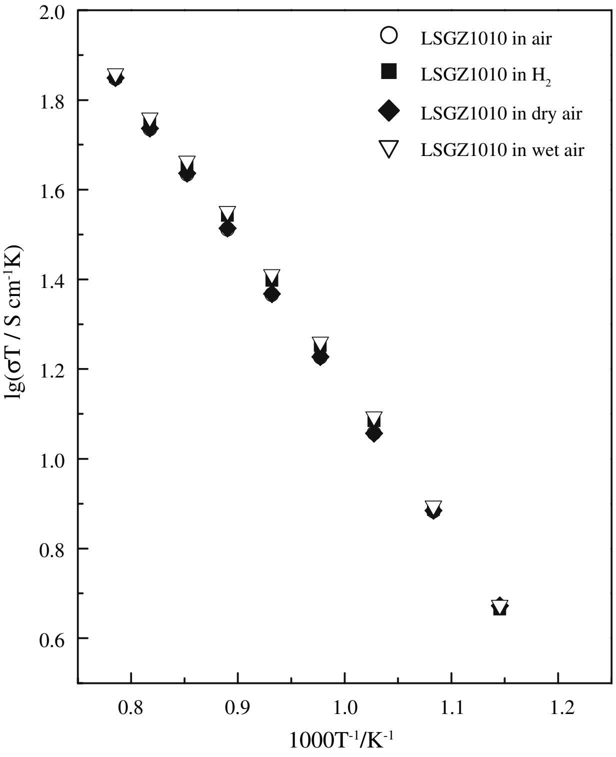

Fig. 1 Arrhenius plots of $La_{0.9}Sr_{0.1}Ga_{0.9}Zn_{0.1}O_{3-\alpha}$

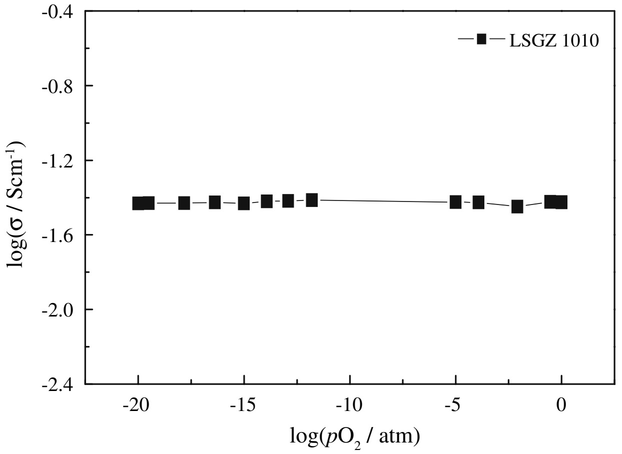

Fig. 2 Dependence of the conductivity of LSGZ1010 upon oxygen partial pressure at 900 °C

$$E_{\mathrm{cal}} = \frac{RT}{2F} \ln \frac{pH_2(\mathrm{I})}{pH_2(\mathrm{II})}$$

where $pH_2(\mathrm{I})$ and $pH_2(\mathrm{II})$ are pressures of hydrogen in anode and cathode compartments, respectively; while R, T, and F have their usual meanings.

If the specimen is an oxide-ionic conductor and pH_2O in both cell compartments is the same, the theoretical value E_{cal} can be obtained from the following Nernst's equation.

$$E_{\mathrm{cal}} = \frac{RT}{4F} \ln \frac{pO_2(\mathrm{II})}{pO_2(\mathrm{I})} = \frac{RT}{2F} \ln \frac{pH_2(\mathrm{I})}{pH_2(\mathrm{II})}$$

where $pO_2(\mathrm{II})$ and $pO_2(\mathrm{I})$ are pressure of oxygen in cathode and anode compartments, respectively.

Both E_{cal} equations have the same form, meaning that the observed EMF of the hydrogen concentration cell gives the sum of the proton and oxide-ionic conductions.

Figures 3 and 4 are the measured results of electromotive forces (EMFs) of the hydrogen concentration cell and the oxygen concentration cell, respectively. The dash-line expresses the theoretical EMF, E_{cal}, and the solid symbol stands for the observed EMF, E_{obs}, at each temperature. As shown in these two figures, the experimental values of EMF are quite close to the theoretical ones. The ionic transport number, t_{i}, which is determined from $E_{\mathrm{obs}}/E_{\mathrm{cal}}(=t_{\mathrm{i}})$, is almost unity at temperatures from 600 to 1,000 °C under hydrogen atmosphere or dry oxygen atmosphere, indicating that LSGZ1010 is a pure ionic conductor.

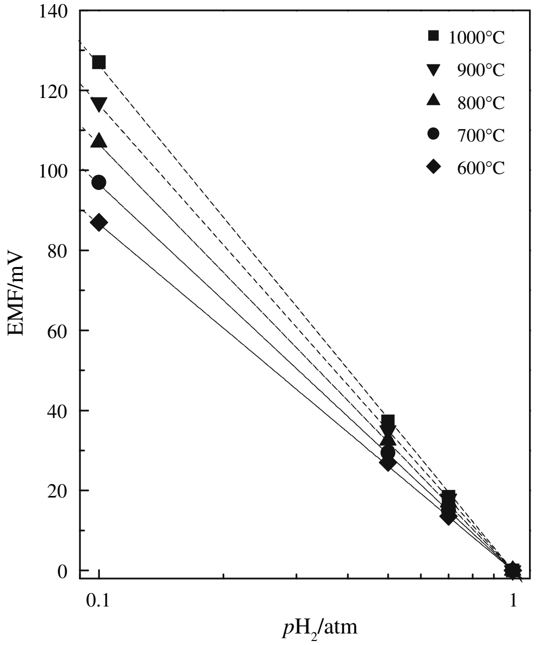

Fig. 3 EMFs of the hydrogen concentration cell: H_2(99.999%), Pt | LSGZ1010 | Pt, H_2--Ar(pH_2)

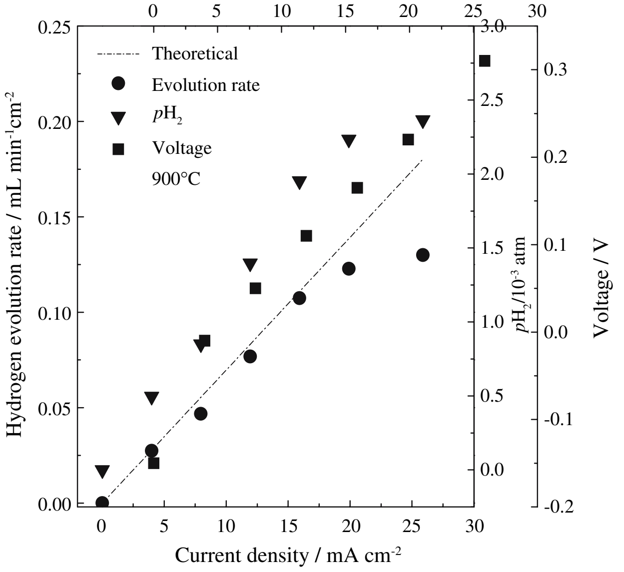

Fig. 5 The result of electrochemical hydrogen pumping of LSGZ1010. (+)H_2(99.999%), Pt | $La_{0.9}Sr_{0.1}Ga_{0.9}Zn_{0.1}O_{3-\alpha}$ | Pt, dry Ar(−)

For confirming the proton conduction in LSGZ1010 directly, the experiment of the electrochemical hydrogen pumping using LSGZ1010 as solid electrolytes was carried out. As shown in Fig. 5, the dependence of hydrogen evolution rate on electrolytic current obeys Faraday's law when the current density is less than 20 mA cm^{-2}, indicating that the charge carriers in the specimen are almost pure protons under hydrogen atmosphere. And as shown in Fig. 6, the experimental reproducibility of electrochemical hydrogen pumping at 900 °C proves that clearly again. Thus, the conductivity under H_2 atmosphere can be considered as proton conductivity. On the other

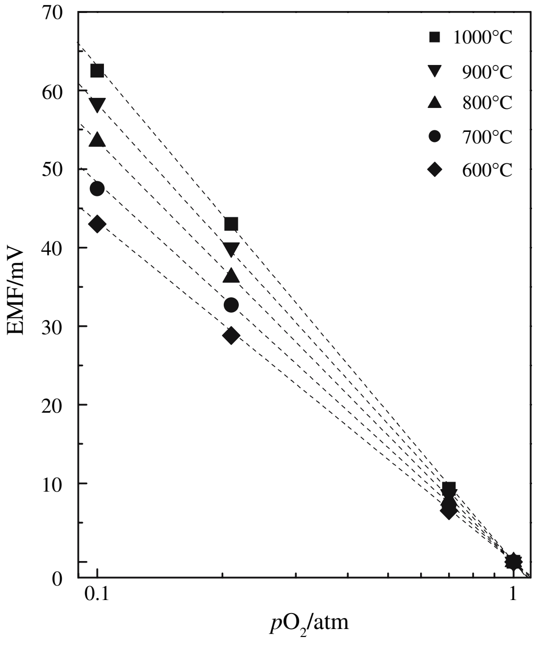

Fig. 4 EMFs of the oxygen concentration cell: Dry O_2, Pt | LSGZ 1010 | Pt, dry O_2--Ar(pO_2)

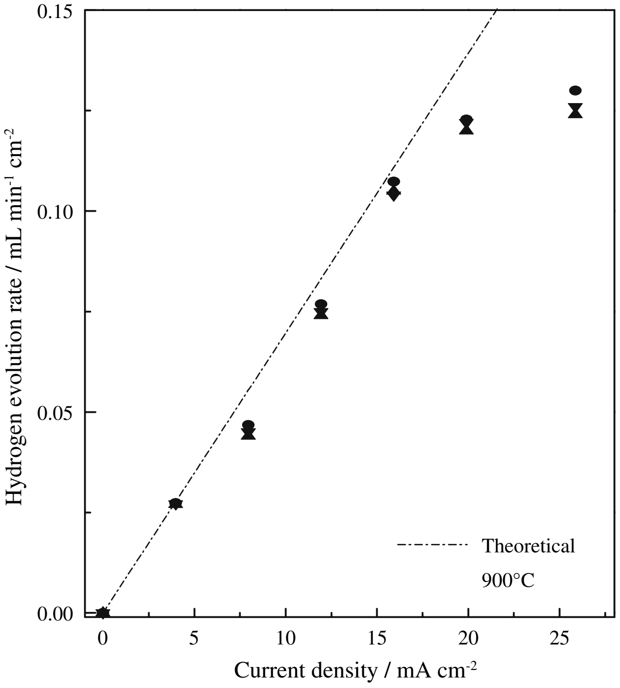

Fig. 6 The experimental reproducibility of electrochemical hydrogen pumping at 900 °C

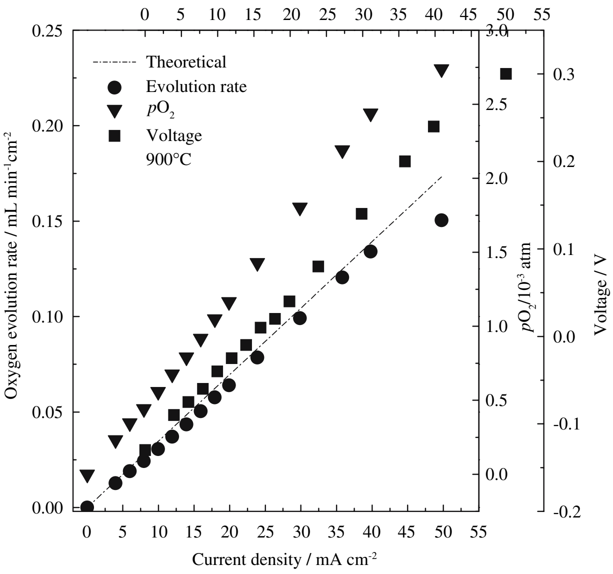

Fig. 7 The result of electrochemical oxygen pumping (+)Dry Ar, Pt | $La_{0.9}Sr_{0.1}Ga_{0.9}Zn_{0.1}O_{3-\alpha}$ | Pt, dry O_2(−)

hand, as shown in Fig. 5, when the current density is higher than 20 mA cm^{-2}, the measured hydrogen evolution rate deviates from the theoretical value, and the reason is not clear. It may be related to the polarization of electrode and the increasing electronic conductivity due to membrane reduction under higher current density.

A similar result (Fig. 7) was observed in the electrochemical oxygen pumping test, confirming that the charge carriers are almost pure oxide ions under dry oxygen atmosphere and that the conductivity in dry air atmosphere as shown in Fig. 1 is oxide ionic.

The above results confirmed that the specimen is a superior proton conductor in hydrogen atmosphere and a superior oxide-ionic conductor in dry oxygen atmosphere, suggesting that the conductivities in ambient air and wet air as shown in Fig. 1 might be mixed ionic (proton + oxide-ion) ones. As described above, the conductivities slightly increase in the order: in wet air > in ambient air > in dry air, because the increase of water vapor concentration in the atmosphere may lead to the increase in concentration of proton (in the form of $OH_o^{\bullet}$) in the specimen.

The conduction behaviors in the various atmospheres may be explained by the following defect reactions.

The substitution of Sr^{2+} for La^{3+} site and Zn^{2+} for Ga^{3+} site provides oxide-ion vacancies. As shown by reaction (1), in dry air, the diffusion of oxide-ion vacancies may cause oxide-ionic conduction.

$$V_o^{\bullet\bullet} + \frac{1}{2}O_2 \rightleftharpoons O_o^x + 2h^{\bullet} \qquad (1)$$

In hydrogen atmosphere, proton is incorporated into the structure in the form of $OH_o^{\bullet}$ by reaction (2):

$$H_2 + 2O_o^x + 2h^{\bullet} \rightarrow 2OH_o^{\bullet} \qquad (2)$$

In water vapor-containing air, the defect reactions may be expressed as reactions (3) and (4):

$$H_2O(g) + 2O_o^x + 2h^{\bullet} \rightleftharpoons 2OH_o^{\bullet} + \frac{1}{2}O_2 \qquad (3)$$

$$H_2O(g) + 2O_o^x + V_o^{\bullet\bullet} \rightleftharpoons 2OH_o^{\bullet} \qquad (4)$$

From reaction (1), we can know that oxide ionic conduction may take place in the specimen in water vapor containing air, which is similar to the case in dry air. From reactions (3) and (4), it is clear that protons are incorporated into the structure by absorption of water, resulting in proton conduction in the specimen. Thus the specimen may exhibit a mixed conduction of oxide ion and proton in ambient air and wet air atmospheres.

Compared with $La_{0.9}Sr_{0.1}Ga_{0.9}Mg_{0.1}O_{3-\alpha}$, $La_{0.9}Sr_{0.1}Ga_{0.9}Zn_{0.1}O_{3-\alpha}$ shows lower electrical conductivity under the same condition. The mechanism responsible for the difference in ionic conduction behavior of both gallates is very complex. This difference may be relevant to electron configuration, effective nuclear charge, and basicity of dopant ion. Zn^{2+} and Mg^{2+} have almost same ionic radius and different electron configurations: $3s^23p^63d^{10}$ and $2s^22p^6$. It may be that Zn^{2+} ion has larger effective nuclear charge Z^* ($Z^* = Z - \sigma$, Z: nuclear charge, σ: shielding constant) and ionic potential ϕ ($\phi = Z^*/r$) than Mg^{2+}. This leads to larger static gravitation between Zn^{2+} and O^{2-} and decrease in conductivity of O^{2-}. In addition, the higher basicity of constituent cation in solid oxide electrolyte may help to improve the protonic conduction in the oxides. It is well known that zinc element is an amphoteric element and has less basicity, resulting in the lower protonic conductivity of $La_{0.9}Sr_{0.1}Ga_{0.9}Zn_{0.1}O_{3-\alpha}$ than $La_{0.9}Sr_{0.1}Ga_{0.9}Mg_{0.1}O_{3-\alpha}$ [1].

Conclusions

The proton conduction in $La_{0.9}Sr_{0.1}Ga_{0.9}Zn_{0.1}O_{3-\alpha}$ ceramics was found for the first time under hydrogen atmosphere at temperatures from 600 to 1,000 °C. The rate of electrochemical hydrogen pumping through the specimen coincided with the theoretical rate calculated from Faraday's law, confirming directly that the specimen has excellent proton conduction under hydrogen atmosphere. The conductivity is almost independent of pO_2 in various atmospheres, confirming that $La_{0.9}Sr_{0.1}Ga_{0.9}Zn_{0.1}O_{3-\alpha}$ is almost a pure ionic (protonic + oxide-ionic) conductor over the oxygen partial pressure range of 1–10^{-20} atm. And the results of electrochemical oxygen pumping confirmed that it is a pure oxide ionic conductor under dry oxygen atmosphere. The above results indicated that $La_{0.9}Sr_{0.1}Ga_{0.9}Zn_{0.1}O_{3-\alpha}$ is a mixed proton and oxide ionic conductor, but the ionic conduction is different under different atmospheres and depends on the pH_2, pH_2O or pO_2 value in the atmospheres.

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