— Article —

Conduction Property of PbWO_4 - and PbMoO_4 -based Oxide Ion Conductors in Lower Oxygen Partial Pressures

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Electric conductivities of PbWO_4 - and PbMoO_4 -based oxide ion conductors have been measured in the reducing atmospheres to investigate the transport properties and to evaluate the applicability to the solid electrolytes of fuel cells. Although almost all the solid solutions showed conductivity enhancements due to appearance of n -type electronic conduction with decreasing P_{O_2} down to 10^{-12} atm, pure oxide ion conduction was maintained in the measured P_{O_2} range of $\sim 10^{-18}$ atm at 900°C only for $\text{Pb}_{1-x}\text{La}_x\text{WO}_{4+x/2}$ system. For the tungstate and molybdate mixed crystal systems, furthermore, electronic contribution appears at higher P_{O_2} with increasing molybdenum content. Comparing the two types of substitutions, *i.e.* $\text{Pb}_{1-x}\text{La}_x\text{MO}_{4+x/2}$ and $\text{Pb}_{1-x}\text{La}_{2x/3}\text{MO}_4$ systems ($\text{M} = \text{W}, \text{Mo}$ and mixed one), the former system tended to keep oxide ions in lattice rather than the latter, whereas the former contains excess oxide ions at the interstitial sites. At the end of this paper, test fuel cells have been constructed using $\text{Pb}_{1-x}\text{La}_x\text{WO}_{4+x/2}$ solid electrolyte and operated at 500°C employing wet CH_4 gas as the fuel.

Key Words : Oxide Ion Conductor, Scheelite-type Oxide, Conductivity, Low Oxygen Pressure

1 Introduction

When the lanthanum ions are partly substituted for lead ions in scheelite-type structured PbWO_4 , high oxide ion conduction appears at elevated temperatures.^{1,2)} Typically two types of substituted systems have been investigated, *i.e.* $\text{Pb}_{1-x}\text{La}_x\text{WO}_{4+x/2}$ with oxide ion interstitials and $\text{Pb}_{1-x}\text{La}_{2x/3}\text{WO}_4$ with cation vacancies. These defect structures were confirmed by powder density measurements²⁾ and neutron diffraction experiments.³⁾ Similar solid solutions based on PbMoO_4 also exhibit high oxide ion conduction and the defect structures are essentially the same as those in the PbWO_4 -based systems.⁴⁾ As the ionic conductivity of $\text{Pb}_{1-x}\text{La}_x\text{WO}_{4+x/2}$ ($x = 0.1$) retained 10^{-2} Scm^{-1} at 700°C and 10^{-3} Scm^{-1} even at 500°C ¹⁾, the conductor seems a good candidate for the solid electrolyte of intermediate temperature solid oxide fuel cells (IT-SOFCs). We have so far focused on the defect structure and oxide ion conduction mechanisms of these systems apart from the practical applications.¹⁻¹²⁾ One of the major reasons is that these solid solutions consist of lead, tungsten and molybdenum ions which would be easily reduced at the anode side when hydrogen gas is used as the fuel. Nevertheless these compounds might work as electrolytes under milder conditions such as in CH_4 or exhaust gases for power generation or energy recovery. The stabilities and conduction properties of these materials have not been investigated under reducing conditions. In this paper, we measured the oxygen partial pressure dependence of electric conductivity for these compounds to evaluate the stability and transport properties at elevated temperatures.

2 Experimental

Two types of oxide ion conductors are prepared for the tungstate and molybdate systems by a conventional solid state reaction method starting from PbO , La_2O_3 , H_2WO_4 and MoO_3 reagents; one is $\text{Pb}_{1-x}\text{La}_x\text{MO}_{4+x/2}$ ($\text{M} = \text{W}$ or Mo) with excess oxide ions in the lattice, and another is $\text{Pb}_{1-x}\text{La}_{2x/3}\text{MO}_4$ ($\text{M} = \text{W}$ or Mo) with cation deficiency.¹⁻⁴⁾ Stoichiometric amount of the starting materials were mixed in an agate mortar with a small amount ethanol and sintered at 700°C for 10 h. The samples were thereafter ground in an alumina mortar, pressed into pellets with the pressure 200 MPa, and finally sintered again at 900°C for 10 h. The samples with tungstate and molybdate mixed systems, $\text{Pb}_{1-x}\text{La}_x\text{W}_{1-y}\text{Mo}_y\text{O}_{4+x/2}$ and $\text{Pb}_{1-x}\text{La}_{2x/3}\text{W}_{1-y}\text{Mo}_y\text{O}_4$, were also prepared through the similar route. The crystal phases of the obtained samples were confirmed by powder X-ray diffraction using $\text{CuK}\alpha$ radiation (Rigaku Ultima IV).

Electric conductivities of the PbWO_4 - and PbMoO_4 -based solid solutions were measured under the controlled P_{O_2} condition by ac two-probe method using an impedance analyzer (HP 4192A). To expedite the equilibration and to compare the reduction behavior, the measurements were carried out mainly at 900°C . Pt paste was applied on the surface of cylindrical samples, which were then fired at 800°C for 2 h to form electrodes. The required oxygen partial pressure down to $P_{\text{O}_2} = 10^{-18}$ atm was obtained by controlling the oxygen content of flowing nitrogen gas (50 ml min^{-1}) using an oxygen pump constructed with a YSZ tube. Oxygen partial pressure was determined from the EMF of a YSZ sensor set around the sample. The details of the apparatus are de-

scribed in the previous literature.¹³⁾

The fuel cells were constructed using $\text{Pb}_{1-x}\text{La}_x\text{WO}_{4+x/2}$ as an electrolyte. Cathode ($\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$) and anode materials (mixtures of NiO and WO_3 with electrolyte additives) were painted on the different side of thin plates of electrolyte (~ 0.25 mm in thickness) to achieve the active areas of 0.5 cm^2 followed by baking at 800°C for 2 h. Pt and Au meshes were fixed on the anode and cathode surfaces as current collectors by Pt and Au pastes, respectively, and two types of test cells were constructed. For the two-chamber configuration, wet CH_3 and O_2 gases as a fuel and an oxidant, respectively were flown into each chamber. For the single chamber fuel cell, the cell was suspended in the center of alumina tube ($\phi 24$), into which CH_4 and O_2 gases were introduced with the rate 150 and 75 ml min^{-1} , respectively. For both types of the cells, I - V characteristics were measured using a galvanostat (Hokuto Denko, HA-151).

3 Results and Discussion

Figure 1 shows the oxygen partial pressure dependence of electric conductivity for $\text{Pb}_{1-x}\text{La}_x\text{WO}_{4+x/2}$ and $\text{Pb}_{1-x}\text{La}_{2x/3}\text{WO}_4$ ($x=0.1\sim 0.3$) measured at 900°C . For $\text{Pb}_{1-x}\text{La}_x\text{WO}_{4+x/2}$ system plotted by closed symbols, all the samples represent the P_{O_2} -independences on the oxygen partial pressure down to $P_{\text{O}_2}\sim 10^{-17}$ atm. Further decreasing P_{O_2} , the measured conductivity became rather scattered and dropped suddenly to the insulating region, presumably due to the sample decomposition. Therefore, oxide ion conduction is supposed to be predominant in

Fig. 1 Oxygen partial pressure dependences of electric conductivity for $\text{Pb}_{1-x}\text{La}_x\text{WO}_{4+x/2}$ (closed symbols) and $\text{Pb}_{1-x}\text{La}_{2x/3}\text{WO}_4$ (open symbols) measured at 900°C . ●, ○: $x=0.1$, ▲, △: $x=0.2$ and ■, □: $x=0.3$. Solid lines: fitted total conductivity, and dashed lines: ionic and electronic components.

the region $P_{\text{O}_2} \geq 10^{-17}$ atm, involving that the transport number of oxide ion is unity around the oxidized region.¹⁾ Here, the electric conductivity itself seems not to be simply proportional to the defect concentration. This is presumably because the conduction is due to the mechanism using interstitial and regular oxide ion positions, as discussed in the previous paper.³⁾

For $\text{Pb}_{1-x}\text{La}_{2x/3}\text{WO}_4$ system indicated by open symbols in Fig. 1, electric conductivity increases with decreasing P_{O_2} in the reducing region, suggesting that n -type electronic conduction appears at lower P_{O_2} region. Assuming the total conductivity as the sum of the constant ionic and exponentially varying electronic components with P_{O_2} ,

$$\sigma_{\text{total}} = \sigma_{\text{ion}} + \sigma_{\text{e.o.}} \cdot P_{\text{O}_2}^m, \quad (1)$$

the measured data can well fit the thin solid lines excluding several data points just around the decomposition like $\text{Pb}_{1-x}\text{La}_x\text{WO}_{4+x/2}$. The deduced exponents m as listed in Table 1 are close to $-1/6$, which should be associated with the defect equilibrium, $1/2\text{ O}_2 + \text{V}_\text{O}^{\bullet\bullet} + 2\text{e}' \leftrightarrow \text{O}_\text{O}$, under the constraint of $[\text{e}'] = 2[\text{V}_\text{O}^{\bullet\bullet}]$.¹⁴⁾ A characteristic partial pressure P_t is tentatively introduced from the intersection between the ionic and electronic components, which should be a measure of the transient pressure from ionic to electronic region with decreasing P_{O_2} . The obtained P_t 's are ranging from 10^{-8} to 10^{-12} atm as represented in Table 1, which seems not to show an apparent compositional dependence, indicating that the lanthanum substitution for reducible lead does not simply attribute to the reduction-resistance. The present result that electronic contribution is observed only for $\text{Pb}_{1-x}\text{La}_{2x/3}\text{WO}_4$ system might be simply because the ionic conductivity of $\text{Pb}_{1-x}\text{La}_x\text{WO}_{4+x/2}$ system is enough high to leave the electronic contribution negligible in the measured P_{O_2} range. Nevertheless, it is also possible that $\text{Pb}_{1-x}\text{La}_{2x/3}\text{WO}_4$ system would be easily reduced or release oxide ions to create the conduction electrons ($\text{O}_\text{O} \rightarrow 1/2\text{ O}_2 + \text{V}_\text{O}^{\bullet\bullet} + 2\text{e}'$) in comparison with $\text{Pb}_{1-x}\text{La}_x\text{WO}_{4+x/2}$ system.

To compare the stability between these systems under the reducing atmospheres, powder samples of $\text{Pb}_{1-x}\text{La}_x\text{WO}_{4+x/2}$ and $\text{Pb}_{1-x}\text{La}_{2x/3}\text{WO}_4$ ($x=0.1$) were annealed in $\text{Ar-3\%H}_2$ gas (flow rate: 10 ml min^{-1}) at 900°C for 50 h. While the former remained the color almost white with very small amount of dark spots, the latter turned the color into totally dark gray. X-ray diffraction patterns measured after annealing in the reducing gas are represented in Fig. 2. Although no apparent excess

Table 1 Characteristic parameters obtained from the P_{O_2} dependence of conductivities of PbWO_4 and PbMoO_4 -based oxide ion conductors at 900°C .

	$\text{Pb}_{1-x}\text{La}_{2x/3}\text{WO}_4$			$\text{Pb}_{1-x}\text{La}_x\text{MoO}_{4+x/2}$	$\text{Pb}_{1-x}\text{La}_{2x/3}\text{MoO}_4$
x	0.1	0.2	0.3	0.1	0.1
m	-0.14	-0.15	-0.18	-0.17	-0.19
P_t/atm	4.0×10^{-12}	1.4×10^{-8}	4.4×10^{-12}	4.5×10^{-6}	1.7×10^{-1}

phase is detected for $\text{Pb}_{1-x}\text{La}_x\text{WO}_{4+x/2}$ system, obvious diffraction peaks identified with $\text{Pb}_{0.26}\text{WO}_3$ phase appears in $\text{Pb}_{1-x}\text{La}_{2x/3}\text{WO}_4$ system after annealing, where lead ions are supposed to be partly reduced into metal to evaporate during annealing, remaining the $\text{Pb}_{0.26}\text{WO}_3$ -related phase in addition to the lanthanum-rich scheelite-type structured phase. Therefore, $\text{Pb}_{1-x}\text{La}_x\text{WO}_{4+x/2}$ system hardly be thought reducible in comparison with $\text{Pb}_{1-x}\text{La}_{2x/3}\text{WO}_4$ in lower P_{O_2} condition. This result seems to contradict to the simple assumption that excess oxide ions at interstitial sites would be easily released rather than the regular site oxide ions. Considering that the number of oxide ion interstitials is very small (5 unit cells share only one oxide ion interstitial for $\text{Pb}_{0.9}\text{La}_{0.1}\text{WO}_{4.05}$), the lattice distortion due to the interstitials might not be so large. Moreover, the measured temperature is enough high and oxide ion motion is so activated that the potential difference between the regular

Fig. 2 X-ray diffraction patterns of (a) $\text{Pb}_{0.9}\text{La}_{0.1}\text{WO}_{4.05}$ and (b) $\text{Pb}_{0.9}\text{La}_{0.2/3}\text{WO}_4$ after annealing in the reducing condition at 900°C for 50 h. ICCD card data for (c) $\text{Pb}_{0.26}\text{WO}_3$ (52-178) and (d) PbWO_4 (57-836) are also represented.

Fig. 3 P_{O_2} dependences of electric conductivity for $\text{Pb}_{0.9}\text{La}_{0.1}\text{MoO}_{4.05}$ (●) and $\text{Pb}_{0.9}\text{La}_{0.2/3}\text{MoO}_4$ (○) measured at 900°C . Inset represents the conductivity of $\text{Pb}_{0.9}\text{La}_{0.2/3}\text{WO}_4$ around the reducing region in an enlarged scale.

and interstitial sites would become insignificant. Conversely negatively charged cation-vacancies V_{Pb}'' in $\text{Pb}_{1-x}\text{La}_{2x/3}\text{WO}_4$ system would facilitate the creation of oxide ion vacancy V_{O}'' at the neighboring site to form a Schottky defect-like pair. For further detailed discussion about the stability of oxide ions in these systems, both experimental and calculation studies should be made, *e.g.* equilibrium oxygen partial pressure measurement coupled with coulometric titration¹⁵⁾ or ab-initio calculation of local structure and site energy based on the density functional theory.¹⁶⁾

Figure 3 shows the conductivity variations against P_{O_2} for the molybdate systems; both $\text{Pb}_{1-x}\text{La}_x\text{MoO}_{4+x/2}$ and $\text{Pb}_{1-x}\text{La}_{2x/3}\text{MoO}_4$ ($x=0.1$) exhibit the conductivity enhancement in the reducing atmosphere. Applying the equation (1) to the measured data as thin solid lines, the parameters m and P_t are obtained as Table 1. In contrast to the tungstate system, an increase in electronic conduction is observed even in $\text{Pb}_{1-x}\text{La}_x\text{MoO}_{4+x/2}$ with excess oxide ions, and in addition, P_t occurs at higher oxygen partial pressures in $\text{Pb}_{1-x}\text{La}_{2x/3}\text{MoO}_4$ than in $\text{Pb}_{1-x}\text{La}_{2x/3}\text{WO}_4$ systems. PbMoO_4 -based oxide ion conductors are, therefore, easily reduced or likely to release oxide ions compared with the PbWO_4 -based systems. In view of electronic characteristics, some exponents m in Table 1 are ranging from $-1/6$ to $-1/4$. In the case that a small amount of oxide ion vacancies have been inherently introduced as the Koch-Wagner defects such as those in stabilized zirconias, the slope would provide $-1/4$, because the number of oxide ion vacancy created by the thermal defect equilibrium is much smaller than the initially existing one and the constraint in the defect equilibrium becomes $[V_{\text{O}}''] = \text{constant}$. The electronic part of conductivity for $\text{Pb}_{0.9}\text{La}_{0.2/3}\text{MoO}_4$ is enlarged as the inset in Fig. 3; the measured data can be well fitted with the slope of $-1/4$ and $-1/6$ crossing around $P_{\text{O}_2} \approx 10^{-11}$ atm.

To evaluate the effect of molybdenum substitution for tungsten site in the scheelite-type structure, conductivity measurements were carried out on tungstate- and molybdate-mixed crystal systems in the reducing conditions. Figure 4 shows the P_{O_2} dependence of electric conductivity measured at 900°C for (a) $\text{Pb}_{1-x}\text{La}_x\text{W}_{1-y}\text{Mo}_y\text{O}_{4+x/2}$ and (b) $\text{Pb}_{1-x}\text{La}_{2x/3}\text{W}_{1-y}\text{Mo}_y\text{O}_4$ systems, where lanthanum contents are fixed as $x=0.1$ to achieve the solid solutions for all the samples. With increasing the molybdenum content, electronic conductivity arises at higher P_{O_2} in both systems. As same as the above procedure, ionic-electronic transient pressures P_t are calculated and plotted versus composition in Fig. 5. As expected, $\text{Pb}_{1-x}\text{La}_{2x/3}\text{W}_{1-y}\text{Mo}_y\text{O}_4$ system (○) exhibits higher P_t than $\text{Pb}_{1-x}\text{La}_x\text{W}_{1-y}\text{Mo}_y\text{O}_{4+x/2}$ (●), or oxide ions in the former system are easily reduced to form conduction electrons. For each system, solid solution becomes more reducible with increasing the molybdenum content, while the obtained data in $\text{Pb}_{1-x}\text{La}_{2x/3}\text{W}_{1-y}\text{Mo}_y\text{O}_4$ system appear to be rather scattered probably due to the larger compositional dependence of ionic component (σ_{ion}).

With decreasing temperature down to 600°C , the oxide-ion-conduction-predominant region is maintained in lower P_{O_2} condition although the absolute value of con-

Fig. 4 Measured electric conductivities of (a) $\text{Pb}_{0.9}\text{La}_{0.1}\text{W}_{1-y}\text{Mo}_y\text{O}_{4.05}$ and (b) $\text{Pb}_{0.9}\text{La}_{0.2/3}\text{W}_{1-y}\text{Mo}_y\text{O}_4$ plotted versus oxygen partial pressure. $\circ$: $y = 0$, $\triangle$: $y = 0.2$, $\square$: $y = 0.4$, ∇ : $y = 0.6$, $\diamond$: $y = 0.8$ and $\bullet$: $y = 1.0$.

Fig. 5 Compositional dependence of transient pressure P_t of $\text{Pb}_{0.9}\text{La}_{0.1}\text{W}_{1-y}\text{Mo}_y\text{O}_{4.05}$ ($\bullet$) and $\text{Pb}_{0.9}\text{La}_{0.2/3}\text{W}_{1-y}\text{Mo}_y\text{O}_4$ ($\circ$).

ductivity should decrease. Figure 6 compares the conductivity of $\text{Pb}_{1-x}\text{La}_x\text{MoO}_{4+x/2}$ ($x = 0.1$) measured at 900 °C ($\bullet$) and 600 °C ($\blacklozenge$). While the transport property seems not to be largely varied with the exponent m remaining -0.17 at 600 °C, P_t develops from 4.5×10^{-6} down to 6.4×10^{-16} atm and the ionic transport number becomes almost unity at ambient pressure with decreasing temperature. Even for $\text{Pb}_{1-x}\text{La}_x\text{WO}_{4+x/2}$ system in which electronic contribution was not detected at 900 °C, relatively lower temperature operation should be preferred for use of the solid electrolyte to avoid electronic conduction.

Test fuel cells were then tentatively constructed using $\text{Pb}_{0.9}\text{La}_{0.1}\text{WO}_{4.05}$ as an electrolyte, $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ as the cathode and the mixtures of $\text{NiO}/\text{WO}_3/\text{Pb}_{1-x}\text{La}_x\text{WO}_{4+x/2}$ (7: 3: 1 in weight) as the anode materials, to evaluate the I - V characteristics at 500 °C by flowing wet CH_4 and O_2 gases as a fuel and oxidant, respectively. Figure 7 shows

Fig. 6 Oxygen partial pressure dependences of electric conductivity for $\text{Pb}_{1-x}\text{La}_x\text{MoO}_{4+x/2}$ ($x = 0.1$) measured at 900 °C ($\bullet$) and 600 °C ($\blacklozenge$).

Fig. 7 Terminal voltage ($\triangle$, $\blacktriangle$) and power density ($\circ$, $\bullet$) curves of the test cells, $\text{NiO} + \text{WO}_3 + \text{electrolyte} / \text{Pb}_{0.9}\text{La}_{0.1}\text{WO}_{4.05} / \text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ using wet CH_4 and O_2 as fuel and oxidant, respectively measured at 500 °C. Open and closed symbols denote the data obtained by two-chamber and single chamber cells, respectively.

I - V curves and power densities of constructed test fuel cells, in which open and closed symbols correspond to the data for two-chamber and single chamber cell configurations, respectively. Despite of a cell with an electrolyte-supporting configuration and without any optimization of electrode materials, small amount of power density ($0.1 \sim 0.2 \text{ mW cm}^{-2}$) could be continuously drawn. Single chamber system exhibits better performance than the two-chamber one while the open circuit voltage is lower. This might be due to that the totally milder condition of the single chamber cell is suitable to the electrolyte and/or electrode in the present test cell sets. Although the obtained power density was three orders of magnitude smaller than other ceria based oxide ion conductors at 500 °C,¹⁷⁾ the present result proves the durability of PbWO_4 -based oxide ion conductors in such reducing conditions. Considering that ionic conductivity of the present oxide system is compatible to the apatite-type^{18,19)} or $\text{La}_2\text{Mo}_2\text{O}_9$ -based oxide ion conductors,^{20,21)} the PbWO_4 -based system might have a potential for the application of the electrolytes for IT-SOFC²²⁾ or energy recovery system²³⁾ using milder reducing gases as the fuel, when the cell configuration and electrode materials are

optimized. The durability under the actual cell operation should be discussed after improving the cell configuration to yield higher power density.

4 Conclusion

Oxygen partial pressure-dependent conductivity measurements were carried out on PbWO_4 - and PbMoO_4 -based oxide ion conductors at 900°C , which revealed that $\text{Pb}_{1-x}\text{La}_x\text{WO}_{4+x/2}$ system retained high oxide ion conduction in the P_{O_2} range down to 10^{-17} atm, while the other systems such as $\text{Pb}_{1-x}\text{La}_{2x/3}\text{WO}_4$, $\text{Pb}_{1-x}\text{La}_x\text{MoO}_{4+x/2}$ and $\text{Pb}_{1-x}\text{La}_{2x/3}\text{MoO}_4$, exhibited typical n -type electronic conduction with the slope of $m = -1/6$ against P_{O_2} in the reducing atmospheres. $\text{Pb}_{1-x}\text{La}_x\text{WO}_{4+x/2}$ system, which possesses oxide ion interstitials, exhibited a higher reduction-resistivity than $\text{Pb}_{1-x}\text{La}_{2x/3}\text{WO}_4$ system with cation vacancies. The similar behavior has been observed for the corresponding molybdates. In the tungstate and molybdate mixed systems, electronic conduction appears easier with increasing molybdenum content. $\text{Pb}_{1-x}\text{La}_x\text{WO}_{4+x/2}$ system can be applicable for the solid electrolyte of intermediate temperature SOFC using CH_4 gas as the fuel.

References

- 1) T. Esaka, T. Mina-ai, and H. Iwahara, *Denki Kagaku (Electrochemistry)*, **59**, 343 (1991).
- 2) T. Esaka, T. Mina-ai, and H. Iwahara, *Solid State Ionics*, **57**, 319 (1992).
- 3) S. Takai, S. Touda, K. Oikawa, K. Mori, S. Torii, T. Kamiyama, and T. Esaka, *Solid State Ionics*, **148**, 123 (2002).
- 4) S. Takai, T. Furusho, K. Oikawa, T. Kamiyama, and T. Esaka, *Joint International Meeting ECS and ECSJ, S1-Fifth International Symposium on Ionic and Mixed Conducting Ceramics*, 1701 (2004).
- 5) T. Esaka, R. Tachibana, and S. Takai, *Solid State Ionics*, **92**, 129 (1996).
- 6) S. Takai, K. Sugiura, and T. Esaka, *Mater. Res. Bull.*, **34**, 193 (1999).
- 7) T. Esaka, *Solid State Ionics*, **136**, 1 (2000).
- 8) S. Takai, Y. Karita, T. Nakanishi, and T. Esaka, *Solid State Ionics*, **138**, 161 (2000).
- 9) S. Takai, T. Nakanishi, T. Tojo, H. Kawaji, T. Atake, and T. Esaka, *J. Therm. Anal. Calorimetry*, **69**, 805 (2002).
- 10) S. Takai, T. Nakanishi, K. Oikawa, S. Torii, A. Hoshikawa, T. Kamiyama, and T. Esaka, *Solid State Ionics*, **170**, 297 (2004).
- 11) S. Takai, T. Adachi, and T. Esaka, *Mater. Res. Bull.*, **41**, 2088 (2006).
- 12) T. Esaka, *Electrochemistry*, **78**, 16 (2010).
- 13) S. Takai, K. Tabuchi, H. Okada, and T. Esaka, *J. Ceram. Soc. Jpn.*, **118**, 895 (2010).
- 14) W. D. Kingery, H. K. Bowen, and D. R. Uhlmann, *Introduction to Ceramics, 2nd ed.*, John Wiley & Sons, (1976).
- 15) C. Wagner, *Prog. Solid State Chem.*, **6**, 1 (1971).
- 16) G. Ghosh and G. B. Olson, *Acta Materialia*, **55**, 3281 (2007).
- 17) A. Tomita, S. Teranishi, M. Nagao, T. Hibino, and M. Sano, *J. Electrochem. Soc.*, **153**, A956 (2006).
- 18) J. E. H. Sansom, D. Richings, and P. R. Slater, *Solid State Ionics*, **139**, 205 (2001).
- 19) L. Leon-Reina, E. R. Losilla, M. Martinez-Lara, S. Bruque, and M. A. G. Aranda, *J. Mater. Chem.*, **14**, 1142 (2004).
- 20) P. Lacorre, F. Goutenoire, O. Bohnke, R. Retoux, and Y. Laligant, *Nature*, **404**, 856 (2000).
- 21) F. Goutenoire, O. Isnard, E. Suard, O. Bohnke, Y. Laligant, R. Retoux, and P. Lacorre, *J. Mater. Chem.*, **11**, 119 (2001).
- 22) B. C. H. Steele and A. Heinzl, *Nature*, **414**, 345 (2001).
- 23) M. Nagao, M. Yano, K. Okamoto, A. Tomita, Y. Uchiyama, N. Uchiyama, and T. Hibino, *Fuel Cells*, **8**, 322 (2008).