Electrical conductivity of Sr$_2$MgMoO$_{6-\delta}$ for solid oxide fuel cell anodes

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A high purity powder of Sr$_2$MgMoO$_{6-\delta}$ (SMM) was synthesized by a solid-state reaction under atmosphere-controlled conditions. The powder was sintered at a relatively low temperature (1200°C) to prepare compacts with high grain boundary density. SMM is a promising anode material for solid oxide fuel cells and hence, the samples were characterized under conditions relevant to this application. The electrical conductivity values of SMM under various oxygen partial pressures ($p_\text{O}_2 = 10^{-15}$–$10^4$ Pa) over the temperature range of 300–850°C were measured by AC impedance spectroscopy. The grain boundary resistivity and bulk resistivity exhibited different oxygen-partial-pressure-dependent behavior. Electron conduction is proposed as the primary mechanism for electrical conductivity in the bulk of the sintered body of SMM under both low and high oxygen partial pressures. Electron conduction and oxygen ion conduction were found to be the primary mechanisms for electrical conductivity at the grain boundary of SMM under low and high oxygen partial pressures, respectively.

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Key-words: Solid oxide fuel cell, Double perovskite, Sr$_2$MgMoO$_{6-\delta}$, Anode material, Electrical conductivity

[Received February 9, 2017; Accepted April 8, 2017]

1. Introduction

Solid oxide fuel cells (SOFCs) can, in principle, directly use hydrocarbon fuels without external fuel reformers to achieve high energy density and low cost electricity production with a fuel that is easier to store and transport than hydrogen gas. Thus, SOFCs are promising as power sources for various mobile applications.¹⁻⁶ The performance of internal reforming SOFCs is governed by the anode material and operating conditions. Nicermet materials are typically used as anodes in conventional SOFCs fed with hydrogen fuel.⁷,⁸ These materials have shown several limitations when hydrocarbon fuels are used directly, such as poor redox stability, low sulfur tolerance, and propensity for coking. When hydrocarbon fuels are directly used, nickel is poisoned by trace amounts of sulfur contamination, e.g. hydrogen sulfide (H₂S), in the fuel.⁹⁻¹⁸ In addition, Ni catalyzes the formation of C–C bonds that cause coking on the surface of the nickel particles.¹⁹ In addition, the nickel particle volume increases due to the oxidation of metallic nickel to NiO by exposure to an oxygen-rich atmosphere resulting in the instability of the electromotive force and finally destruction of the cell.²⁰⁻²⁶

In recent years, much effort has been devoted to the development of ceramic SOFC anodes for direct use of hydrocarbon fuels; some oxide ceramics based on double perovskites exhibit sufficiently good electrode properties and stability while operating on hydrocarbon fuels. Mixed ionic and electronic conductors (MIECs) have been intensely studied under the reducing atmospheres required at the SOFC anode. Gorte et al.²⁷–³⁰ investigated rare-earth-doped ceria impregnated with copper as a possible anode material. For instance, when operating a SOFC with Cu/CeO$_2$/YSZ anodes on H₂ fuel containing sulfur impurities (H₂S) at 800°C it was found that H₂S levels up to 450 ppm had no effect on anode performance.³⁰ Tao et al.³⁰–³² reported that La$_{0.75}$Sr$_{0.25}$Co$_{0.8}$Mn$_{0.2}$O$_{3-\delta}$ exhibited high performance (e.g. 0.3 W/cm² at 950°C and no significant degradation during operation at 925°C for 4 h) when operating with CH₄ fuel. B-site ordered double-perovskite materials with the general formula A₂BB’O$_{6-\delta}$ (A = Sr, B = Mg, Mn, Co, Ni, or La; B’ = Mo) have recently been proposed as anode materials with high electronic and ionic conductivity as well as electrocatalytic activity under the reducing conditions of the anode.³³⁻⁴⁹ These materials have superior resistance to sulfur poisoning and prevent carbon deposition, which improves the direct electrochemical oxidation of hydrocarbon fuels on the anode of the SOFCs. Among these materials, Sr$_2$MgMoO$_{6-\delta}$ (SMM) has attracted considerable attention as a promising anode material for hydrocarbon-fueled SOFCs as excellent performance has been demonstrated.³⁴⁻³⁷,³⁹⁻⁴⁷ For instance, Huang et al.³⁵ reported that the SMM anode showed a power density of 0.44 W/cm² in CH₄ at 800°C and only 1% degradation in the output was observed in 5 ppm H₂S/H₂ fuel.

The synthesis of SMM powder has been under investigation since 2006. In several studies, the SMM powders were prepared using a sol–gel technique with ethylenediaminetetraacetic acid as the chelating agent, and (NH₄)$_6$Mo$_7$O$_{24}$·4H₂O, Sr(NO₃)$_2$ or SrCO$_3$, and Mg(NO₃)$_2$·6H₂O or MgO as the sources of Mo, Sr, and Mg, respectively.³¹⁻³₅,³₇⁻₃₉,⁴₀⁻⁵₀ The sol–gel method is not suitable for mass production because it requires an expensive material, (NH₄)$_6$Mo$_7$O$_{24}$·4H₂O, and the synthesis process is complex. Bernuy-Lopez et al.³⁹ synthesized SMM powder by a solid-state reaction using SrCO$_3$, MgO, and MoO$_3$ as starting materials. A disadvantage of this method is that it is difficult to produce fine powder using a high temperature firing processes, and their prepared powder included some SrMoO$_4$ impurities. However, Kinoshita et al.⁵¹ successfully synthesized fine high-purity SMM powder by a solid-state reaction consisting of a simple three-step calcination process in a controlled atmosphere.
using common and inexpensive materials. Hence, it is now economically feasible to use SMM powder as a SOFC anode material.

The total conductivity of SMM has been measured in many previous studies; however, a detailed analysis of its conduction properties (e.g. the conductivity behavior over a wide range of temperatures and oxygen partial pressures, and the effect of the microstructure of the sintered body) has not yet been undertaken. Huang et al. characterized SMM over a wide temperature range in different atmospheres; total conductivities of 4.26–8.60 S/cm and activation energies of 0.096–0.197 eV were obtained at 800°C in 97% CH₄/3% H₂O, H₂ at 97% O₂/3% H₂O, H₂/5 ppm H₂S, CH₄, and 97% CH₄/3% H₂O. Marrero-López et al. prepared compacts by sintering SMM powder synthesized from a modified freeze-dried precursor and obtained activation energies of 0.270 and 1.43 eV for the total conduction in wet 5% H₂/Ar and air, respectively. They also obtained different activation energies of 0.195 and 0.255 eV for measurements performed in 5% H₂/Ar on discs prepared by sintering in 5% H₂/Ar and air, respectively. In this study, an activation energy of 1.12 eV was obtained from measurements in air using a disc sintered in air. Xie et al. prepared a disc sintered in air using a disc sintered in air. It was confirmed by X-ray diffraction (XRD) analysis that the sintered body after preparation of the platinum electrode maintained a single-phase SMM structure.

The electrical conductivity was measured using an alternative impedance method applying an AC signal of 250 mV over the frequency range of 1 MHz to 1 mHz and temperature range of 300–850°C. After confirming the presence or absence of the current did not affect the impedance value and the shapes of the Nyquist and Bode plots, DC current (current density = 5 mA/cm²) was passed to reduce noise. The temperature was varied with a heating rate of 5 °C/min between consecutive measurements. The oxygen partial pressure during the measurements was varied by changing the flow gas mixtures and was measured using a commercial oxygen sensor (RF-400, Toray Engineering Co., Ltd., Japan). Gas mixtures of humidified (3% at 25°C) 5% H₂/Ar, humidified (3% at 25°C) 1% H₂/He, 10% CO/CO₂, 97 ppm CO/CO₂, N₂, and air corresponded to oxygen partial pressures at 800°C of 10⁻¹⁵, 10⁻¹³.₅, 10⁻¹¹, 10⁻⁹, 10⁻⁷, 10⁻⁵, 10⁻³, and 10⁻¹ Pa, respectively. After changing the oxygen partial pressure and temperature, the specimen was held under steady conditions for several tens of hours and impedance spectra were acquired every hour after the equilibration period in order to ensure complete equilibration of the sample. The electrical conductivity was calculated from Eq. (1), where \( \sigma \), \( A \), \( t \), and \( R \) are the electrical conductivity, cross-section of the sintered body (i.e. electrode area), thickness of the sintered body, and the measured resistivity, respectively.

\[
\sigma = \frac{A}{tR}
\]

3. Results

The XRD results of the synthesized SMM powder is shown in Fig. 1. Previous works based on XRD analysis reported that the SMM structure at room temperature was initially reported to be tetragonal (space group I₄/m), monoclinic (space group P2₁/n), or triclinic (space group I/-1). By using neutron diffraction, Troncoso et al. determined the structure as tetragonal (space group I₄/m). In the present work, Rietveld refinements for SMM at room temperature were performed adopting the tetragonal structure of the sintered PdO sample, and the conductivity was repeatedly measured. Microstructure of the sintered body was confirmed by SEM analysis.

2.2 Electrical conductivity

Porous symmetrical platinum electrodes were deposited on both faces of the sintered disc. A platinum paste was prepared using high purity platinum powder (>99.95%) dispersed in a solution made by dissolving ethyl cellulose in an organic solvent (a mixture of α-terpineol and butyl carbitol acetate). The paste was applied to the sample and then fired at 900°C for 1 h in air. In order to electrically connect the sample to the impedance analyzer (electrochemical work station; SP 150, Biologic SAS), Pt wires were attached to both Pt electrodes with a different platinum paste (some amount of a glass powder (m.p. around 860°C) was added to the pure Pt paste) and then fired at 900°C for 1 h in air. It was confirmed by X-ray diffraction (XRD) analysis that the sintered body after preparation of the platinum electrode maintained a single-phase SMM structure.

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\]
nal $I4/m$ space group ($Rp = 4.85\%$, $Rwp = 6.40\%$, $Rexp = 4.82\%$, $S = 1.33$). All XRD peaks collected in this study were assigned to double perovskite, SMM, in the space group $I4/m$. The lattice parameters were estimated as $a = 5.58981(28)\,\text{Å}$, $c = 7.87850(43)\,\text{Å}$, volume $= 246.172(28)\,\text{Å}^3$, in agreement with previous reports.\(^{40,49}\) Therefore, the synthesized powder is a high purity SMM with a tetragonal crystal structure (space group $I4/m$). The fractured cross section of the sintered body is shown in Fig. 2. Although a small amount of isolated closed pores existed, it was confirmed that the sintered body had a sufficiently high density for conductivity studies.

The impedance spectra obtained at $800^\circ\text{C}$ and various oxygen partial pressures are shown in Fig. 3. Figure 3(a) shows Nyquist plots and Figs. 3(b) and 3(c) show Bode plots. In the Nyquist plots, only one arc was observed for each measurement. In the Bode plots, only one minimum and the stepped impedance of one step increasing with decreasing frequency was observed appeared. The shape of these Bode plots and the single arc of the Nyquist plots mean that all of the observed impedance is due to one predominant reaction. Although there were some differences in the electrochemical reaction resistances of the two Pt electrodes on the sintered SMM samples (because the electrodes were manually produced), the obtained arcs were ideal semicircles without depression. The dependence of the impedance on the thickness of the sintered body is shown in Fig. 4. The position of the high-frequency intercept and the arc diameter (difference between the low-frequency and high-frequency intercepts) linearly increased with the thickness of the sintered body. Therefore, the obtained impedance spectra were not related to the electrochemical reaction on the electrode but rather the electrical conductivity of the SMM, as mentioned by Marrero-López et al.\(^{38}\) As proposed by Adler,\(^{58}\) the arc may correspond to a penetration reaction of electrons or oxygen ions into the crystal grains of the SMM. Thus, the high-frequency and low-frequency intercepts of the arc are associated with the bulk resistance and total resistance (sum of the bulk and grain boundary resistances), respectively. The Bode plots [Figs. 3(b) and 3(c)] moved slightly to the low frequency region as the oxygen partial pressure increased, and were clearly shifted to lower frequencies at an oxygen partial pressure of $10^{13.5}\,\text{Pa}$; the time constant of the grain boundary conduction (which is calculated from Eq. (2)) increased with increasing oxygen partial pressure.

$$\tau = RC$$

where $\tau$, $R$, and $C$ are the time constant, resistance, and capacitance of grain boundary conduction, respectively.

The bulk resistance, total resistance, and grain boundary resistance as functions of the oxygen partial pressure at $800^\circ\text{C}$ are shown in Fig. 5. Despite the fact that the conductivity was measured after the specimen was held at each oxygen partial pressure for a sufficiently long time, the slope of the log ($\sigma$) vs. log ($p_{O2}$) curve was smaller than that expected from the charge carrier concentration due to the oxidation of Mo$^{6+}$ to Mo$^{5+}$ (slope $= -1/6$).\(^{24}\) In particular, the dependence of the bulk resistance on the oxygen partial pressure was extremely small. On the other hand, although the dependence of the grain boundary resistance on the oxygen partial pressure was small when the $p_{O2}$ was in the range of $10^{-15}$ to $10^{-10.0057}\,\text{Pa}$, it increased with further increases in the $p_{O2}$ up to $10^{4.3}\,\text{Pa}$ and approached the expected slope of $-1/6$. 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Figure 6 shows Nyquist and Bode plots of the measured impedances at various temperatures at an oxygen partial pressure of $10^{-13.5}$ Pa. At all temperatures, only one arc was observed. Although the response frequency widened into the low frequency region with decreasing temperature, the shapes of the Bode plots were similar. Arrhenius plots of bulk conductivity, grain boundary conductivity, and total conductivity in a reducing atmosphere of $p_{O_2} = 10^{-13.5}$ Pa are shown in Fig. 7. All conductivity values could be plotted on straight lines. The activation energies of bulk conduction, grain boundary conduction, and total conduction in the reducing atmosphere estimated from the slopes of the Arrhenius plot were 0.0974, 0.390, and 0.363 eV, respectively (Table 1).

Figure 8 shows Nyquist and Bode plots of the impedances measured at a high oxygen partial pressure of $10^{4.3}$ Pa. Compared to the values obtained in a reducing atmosphere ($p_{O_2} = 10^{-13.5}$ Pa, Fig. 6), the reaction frequency shifted significantly to the lower frequency region, and the Bode plot became wider. Figure 7 also shows the temperature dependence of the conductivity at the oxygen partial pressure of $10^{4.3}$ Pa. The activation energy of bulk conduction was 0.114 eV, which was similar to that under the reducing atmosphere. In contrast, the activation energy of grain boundary conduction increased by about four times (1.74 eV). As a result, the activation energy of the total conduction increased to 1.73 eV.

4. Discussion

4.1 Microstructure

Average grain size of the specimen was approximately 1–3 μm (Fig. 2) and was small as the value of the high density sintered body suitable for conductivity measurement. Although it is difficult to declare it because the particle size of the sample used were

![Figure 5](image)

Fig. 5. Bulk conductivity, grain boundary conductivity, and total conductivity of a sintered compact measured at 800°C under various oxygen partial pressures.

Table 1. Activation energy values obtained in this study are compared to those published in the literature by Huang et al., Kong et al., Marrero-López et al., and Xie et al.

| Specimen Shape/Sintering Atmosphere | Activation Energy/EV |
|------------------------------------|----------------------|
|                                    | Bulk                 | Grain Boundary | Total          |
|                                    | reducing atmosphere  | air            | reducing atmosphere | air          |
| This work                          | disc/5% H2/Ar        | 0.0973         | 0.390           | 0.363         | 1.73          |
| Huang et al.                       | disc/5% H2/Ar        | 0.084          | 0.197           |               |               |
| Kong et al.                        | disc/air             | 0.0683         | 0.222           |               |               |
| Marrero-López et al.               | disc/air             | 0.270          | 1.43            |               |               |
| Marrero-López et al.               | disc/5% H2/Ar        | 0.195          | 1.12            |               |               |
| Xie et al.                         | disc/air             | 0.226          |                 |               |               |

![Figure 6](image)

(a) Nyquist and (b, c) Bode plots measured at an oxygen partial pressure of $10^{-13.5}$ Pa at various temperatures.

![Figure 7](image)

Fig. 7. Bulk conductivities, grain boundary conductivities, and total conductivities of a sintered compact measured at various temperatures in oxygen partial pressures of $10^{-3}$ or $10^{-13.5}$ Pa.
not shown in all the papers, it is presumed that the crystal grains in previous studies were coarse since the fine powders were sintered at high temperature (for instance: Kong et al.34) sintered a nano-crystalline powder synthesized by a novel sol-gel thermolysis method at 1450°C for 12 h, Marrero-López38,55) sintered submicron sized powder sintered via a freeze-dried precursor route at 1400°C for 3 h, and Xie et al.56) sintered a powder synthesized via a nitrate-citrate route at 1450°C for 10 h to obtain a dense specimen with grain size of 7–15 μm as was confirmed by SEM). That is, it is estimated that the grain boundary density of the sample of this study is higher than that of other samples used in the previous studies.33,34,38,54-56)

4.2 Bulk conduction

The activation energies of bulk conduction in $p_{O_2} = 10^{13.5}$ Pa and $p_{O_2} = 10^{2.3}$ Pa obtained from the slopes of Arrhenius plots (Fig. 7) were 0.0973 and 0.114 eV, respectively. These similar activation energies are much smaller than that of typical oxygen ion conducting ceramics, such as yttria-stabilized zirconia (1.1 eV30,59) and Ce0.9Gd0.1O2-δ (0.78–1 eV60-62), suggesting that the main conduction mechanism is electron conduction. The bulk conductivity was almost independent of oxygen partial pressure; this means that the density and mobility of charge carriers are not dependent on oxygen partial pressure. In other words, when powder synthesis and pellet sintering are performed in a reducing atmosphere, as in this study, pentavalent molybdenum (Mo5+) in the bulk does not oxidize to Mo6+, even when the oxygen partial pressure in the measurement atmosphere increases. Therefore, in the bulk of the SMM sintered body prepared in this manner, the main conduction mechanism is electron conduction regardless of the oxygen partial pressure in the atmosphere, and the density and mobility of the charge carriers are constant.

4.3 Grain boundary conduction

The shift of the Bode plot to the low frequency region as the oxygen partial pressure increased, as shown in Figs. 3(b) and 3(c), suggests that two conduction mechanisms with different time constants coexisted and the contribution of the reaction with a slower time constant increased with increasing oxygen partial pressure. The shape of the Nyquist and Bode plots did not change with temperature when the oxygen partial pressure is constant [Figs. 6(a)–6(c) and 8(a)–8(c)], supporting the hypothesis that the mechanism for grain boundary conduction at constant oxygen partial pressure is the same for all temperatures. That is, dominant conduction mechanism is different between high oxygen partial pressure and low oxygen partial pressure and does not change with temperature. The fact that each Arrhenius plot is a straight line and the activation energy obtained from its slope is different (0.390 eV at $p_{O_2} = 10^{-11.5}$ Pa, 1.74 eV at $p_{O_2} = 10^{4.3}$ Pa) also supports this hypothesis.

In the oxygen partial pressure range of $p_{O_2} = 10^{-15}$–$10^{-0.0057}$ Pa, the dependence of the grain boundary conductivity on $p_{O_2}$ was small and the slope of the log (σ) vs. log ($p_{O_2}$) plot was $-5.9 \times 10^{-2}$. The small oxygen partial pressure dependence indicates two possibilities; the molybdenum at the grain boundary does not oxidize despite the specimen being held for a long time under high oxygen partial pressure, or the charge carriers (electrons or holes) for electron conduction with a small time constant remain, even after molybdenum is oxidized. In any case, considering the small activation energy, electron conduction is the main mechanism of grain boundary conduction in the oxygen partial pressure range of $p_{O_2} = 10^{-15}$–$10^{-0.0057}$ Pa.

In contrast, by further increasing the oxygen partial pressure, the $p_{O_2}$ dependence became larger and the slope approached $-1/6$ with increasing $p_{O_2}$ up to $10^4$ Pa, which is the expected value relating to a decrease in the charge carrier concentration due to molybdenum oxidation from Mo5+ to Mo6+.24) That is, molybdenum at the grain boundary was well oxidized at the sufficiently high $p_{O_2}$ and the charge carrier concentration reduced significantly. Considering the large activation energy, oxygen ion conduction is the dominant mechanism of grain boundary conduction in the large oxygen partial pressure around $p_{O_2} = 10^{4.3}$ Pa.

4.4 Total conduction

The activation energies for total conduction when the $p_{O_2}$ was $10^{-13.5}$ and $10^{2.3}$ Pa were 0.363 and 1.73 eV, respectively. These are similar to the activation energy for grain boundary conduction, and their corresponding conductivity values are close to those for grain boundary conduction. Therefore, the rate-determining process of total conduction is thought to be grain boundary conduction.

The conductivity and activation energy values for total conduction obtained by Huang et al.33,34) Kong et al.55) Marrero-López et al.38,55) Xie et al.56) and those from this study, are summarized in Table 1. The activation energy for total conduction calculated in this study was greater than the values presented in these previous studies (0.084–0.255 eV). This larger activation energy is presumed to be due to the large contribution of grain boundary conduction (which has high activation energy) to the total conduction because the grain boundary density in the specimens studied here is estimated higher. It is proposed that the different activation energy values for total conduction observed in these studies are attributable to differences in the grain boundary density.
density in the specimens. As shown in Fig. 9, the conductivity sharply decreased with increasing activation energy. That is, the total conductivity of the SMM sintered body decreased due to increasing grain boundary density.

5. Conclusions

The contributions of the bulk and grain boundary conductivities of Sr2MgMoO6−δ on the total conductivity properties were discussed for the first time. In a reducing atmosphere, the predominant mechanism of bulk conduction and grain boundary conduction was found to be electronic conduction. Under high oxygen partial pressure (e.g., air), the dominant conduction mechanisms in the bulk and grain boundary were electronic conduction and oxygen ion conduction, respectively. The activation energies of electronic conduction in the bulk and grain boundaries were 0.0973 and 0.390 eV, respectively. The activation energy of oxygen ion conduction at the grain boundary was 1.74 eV. The activation energies and contributions to the total conductivity depended on the grain boundary density in the SMM sintered body.

Acknowledgements
This work was supported by a Study Grant from the JSPS KAKENHI (grant No. 15K06691).

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