Lanthanum-doped ceria interlayer between electrolyte and cathode for solid oxide fuel cells

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ABSTRACT

Gadolinia-doped ceria (GDC) is widely used as an interlayer for preventing the formation of SrZrO3 between yttria-stabilized zirconia (YSZ) electrolyte and lanthanum strontium cobalt iron oxides (LSCF) cathode for solid oxide fuel cells (SOFCs). However, the diffusion of Gd ions to YSZ electrolyte results in the decrease in ionic conductivity due to the formation of Gd2(Zr, Ce)O7. In the present work, we focus on lanthanum-doped ceria (LDC) as an interlayer between YSZ electrolyte and LSCF cathode. The ionic conductivity of YSZ/LDC composite was higher than that of YSZ/GDC composite in spite of the lower conductivity of LDC than GDC. The maximum power density for the microtubular SOFC with LDC interlayer was better than that with GDC interlayer. While the ohmic resistance decreased by the change from GDC to LDC interlayers, the polarization resistance for oxygen reduction reaction slightly increased as a result of distribution of relaxation times (DRT) analysis. The chemical compositions of Zr, Ce and La was gradually varied at the interface between YSZ electrolyte and LDC interlayer, which affected the both of ohmic and polarization resistances.

1. Introduction

For solid oxide fuel cells (SOFCs), yttria-stabilized zirconia (YSZ) and lanthanum strontium cobalt iron oxides (LSCF) were widely used as electrolyte and cathode, respectively. It is well known that high-resistive SrZrO3 is formed between YSZ electrolyte and LSCF cathode by high-temperature sintering [1]. Doped ceria interlayer is generally inserted between YSZ and LSCF for preventing the formation of SrZrO3 [2–4]. However, the zirconia-ceria solid solution indicated lower ionic conductivity than YSZ and doped ceria [5]. The formation of the zirconia-ceria solid solution deteriorated anode [6] and cathode [7] performance.

Matsui et al. [8] reported that the formation of Gd2(Zr, Ce)O7 resulted in a significant decrease in the ionic conductivity at the interface between YSZ electrolyte and gadolinia-doped ceria (GDC) interlayer. The interdiffusion of lanthanoid elements also affects the electrical properties. For example, the ionic conductivity of GDC/lanthanum silicate (LS) composite was lower than that of lanthanum-doped ceria (LDC)/LS composite [9] in spite of higher conductivity of GDC than LDC [10]. The ionic conductivity of Gd10Si6O27 was lower than that of La10Si6O27 [11]. The diffusion of Gd ions from GDC to LS was confirmed after co-firing by scanning electron microscopy - energy dispersive X-ray spectroscopy (SEM-EDS) analysis, resulting in the decrease in ionic conductivity of the GDC/LS composite. The chemical compositions of LDC and LS were almost unchanged from those stoichiometric compositions for LDC/LS composite. Somekawa et al. [12] reported that the performance of SOFC with yttria-doped ceria (YDC) interlayer was better than that with GDC interlayer due to the formation of the thinner YSZ/YDC solid solution. In the present work, we focus on LDC as an interlayer between YSZ electrolyte and LSCF cathode. While the ionic conductivity of pyrochlore-type La2Zr2O7 was lower than that of Gd2Zr2O7 [13], the conductivity of La2Ce2O7 was higher than that of Gd2Ce2O7 [14]. The crystal structure and ionic conductivity were investigated for the samples of YSZ/GDC and YSZ/LDC composites after co-firing. The effect of cation interdiffusion on the ohmic and polarization resistances for oxygen reduction reaction was evaluated by impedance measurement and distribution of relaxation times (DRT) analysis for the microtubular SOFCs with GDC and LDC interlayers.

2. Experimental

Commercial powders of (Y2O3)0.08(ZrO2)0.92 (YSZ, Tosoh), Ce0.9Gd0.1O1.95 (GDC, Kusaka Rare Metal) and Ce0.9La0.1O1.95 (LDC, Kusaka Rare Metal) were used as raw materials. The powders of 50 vol.% YSZ/50 vol.% GDC or LDC were mixed using mortars and pestles. The mixed powders were heat-treated at 1400°C for 10 h in...
air. The crystal structures for as-received powders of YSZ, GDC and LDC, and heat-treated powders of YSZ/GDC and YSZ/LDC were evaluated with an X-ray diffractometer (Rigaku SmartLab with Cu-Kα radiation) and Raman spectroscopy (Horiba eXploRA with 532 nm laser) at room temperature in air.

Pellet samples were prepared for ionic conductivity measurement. The powders of as-received YSZ, and mixed YSZ/GDC and YSZ/LDC were uniaxially pressed at 50 MPa in a metallic mold with 30 mm in diameter before cold isostatic pressing at 300 MPa. The obtained pellets were sintered at 1400°C for 10 h in air. The thickness of disk-shaped pellets was ca. 1 mm after sintering. The platinum electrodes with 6 mm in diameter were deposited on the both surfaces by magnetron sputtering (Sanyu Electron SC-701MCY). The ionic conductivity was measured by 4-probe AC method in the temperature range of 500–800°C in air. The ionic conductivities of GDC and LDC were referred to [9] using the samples sintered at 1500°C for 3 h in air.

Anode microtubes were constructed from NiO (Sumitomo metal mining), YSZ, pore former (graphite; Showa Denko UF-G10) and binder (cellulose; Yuken Kogyo) powders. The weight ratio of NiO to YSZ was 60:40. These powders were mixed with a kneading machine by adding an appropriate amount of water over a period of 2 h. The anode microtubes were extruded using a piston cylinder with a metal hold with an outside diameter of 2.4 mm and an inside diameter of 2.0 mm. After extrusion, the tubes were dried overnight at room temperature in air. An electrolyte slurry was prepared by mixing YSZ, binder (polyvinyl butyral; Sekisui Chemical) dispersant (tallow propylene diamine, Kao) and plasticizer (dioctyl adipate; Wako Pure Chemical) into ethanol and toluene solvents for 48 h. The YSZ electrolyte thin-film was formed by dip-coating. The electrolyte thin-film and the anode microtube were co-sintered at 1400°C for 3 h in air. The GDC or LDC interlayer and La0.6Sr0.4O2.9Fe0.8O3-δ (LSCF; Kusaka Rare Metal) cathode were coated in a similar manner. The interlayer and cathode were sintered sequentially at 1300°C for 2 h and at 1050°C for 1 h, respectively, in air. The outside diameter of microtube was 1.8 mm, and the cathode length was 10 mm after sintering. The thicknesses of the anode, electrolyte, interlayer and cathode were ca. 200, 10, 1 and 20 μm, respectively.

Electrochemical properties were evaluated with a potentiostat/galvanostat (Solartron Analytical 1470E) and an impedance analyzer (Solartron Analytical 1455). Silver wires and paste were used as current collectors. A mixture of H2: H2O: N2 = 20:4.76 vol.% was supplied as fuel at a flow rate of 50 mL/min to the anode side, and air was supplied as oxidant at 50 mL/min to the cathode side. The reduction treatment of Ni-YSZ anode was conducted at 700°C for 2 h. Current-voltage (i–V) characteristics were measured from open-circuit voltage (OCV) to 0.4 V at a sweep rate of 5 mV/s. Electrochemical impedance was measured under OCV with an AC amplitude of 10 mV in the frequency range from 100 kHz to 0.1 Hz with 20 steps per logarithmic decade. These measurements were conducted at 700, 650, 600 and 550°C. The distribution of relaxation time (DRT) analysis was performed using Z-Assist software (Toyo Corp.) as described in [15–17]. Before the DRT analysis, it should be confirmed that the real (Z′(ω)) and imaginary (Z″(ω)) impedances are satisfied with the Kramers-Kronig relation [18,19].

\[
Z'(\omega) - Z'(\infty) = \frac{2}{\pi} \int_{-\infty}^{\infty} \frac{x Z''(x) - \omega Z'(\omega)}{x^2 - \omega^2} \, dx \tag{1}
\]

\[
Z''(\omega) = -\frac{2}{\pi} \int_{-\infty}^{\infty} \frac{Z'(x) - Z'(\omega)}{x^2 - \omega^2} \, dx \tag{2}
\]

Kramers-Kronig transformation was performed using Lin-KK software (Karlsruhe Institute of Technology) [19]. Either the real or imaginary impedance is then used for the DRT analysis. The real impedance was used for DRT analysis due to less effects of measurement errors and inductive components compared to the imaginary impedance [20]. After DRT analysis, the parameters were refined by CNLS fitting using ZView software (Scribner Associates) with an assumption of an equivalent circuit model with a series connection of inductance (L), resistance (R) and five parallel resistance-capacitance (RC) elements. After the electrochemical evaluation, the cross-sectional microstructures of microtubular SOFCs were observed using a field emission-scanning electron microscopy (FE-SEM; JEOL JSM-6330 F) at an accelerating voltage of 15 kV. The point analysis of chemical composition was performed with an EDS (JEOL Super Mini-cup).

3. Results

Figure 1 shows the X-ray diffraction patterns of YSZ, GDC, LDC, YSZ/GDC and YSZ/LDC measured with CuKα radiation at room temperature in air. All diffraction peaks were assigned as fluorite-type cubic (space group: Fm-3m) structures. While the YSZ peaks were remained for YSZ/GDC and YSZ/LDC composites, no pyrochlore-type peak was detected. The amount of remaining YSZ in YSZ/LDC was slightly larger than that in YSZ/GDC, suggesting the lower chemical reactivity between YSZ and LDC than GDC. The lattice parameters of YSZ, GDC, LDC, YSZ/GDC and YSZ/LDC were shown in Table 1. The lattice parameter of YSZ/GDC or YSZ/LDC was intermediate between YSZ and GDC or LDC, respectively, suggesting the dissolving Gd or La into zirconia-ceria solid solution. Figure 2 shows the Raman spectra of YSZ, GDC, LDC, YSZ/GDC and YSZ/LDC measured with 532 nm laser at room temperature in air. The tetragonal peaks at ca. 150, 250, 320 and 460 cm⁻¹ were confirmed for YSZ. It is well
known that the crystal structure of 8 mol% YSZ is the metastable $t''$ phase, which is defined as a tetragonal phase with the $c/a$ axial ratio of unity [21]. The $F_{2g}$ peak position at ca. 460 cm$^{-1}$ for LDC was slightly shifted to a lower wave number compared to GDC due to the larger lattice parameter. Four peaks were detected for YSZ/GDC and YSZ/LDC composites. The peak at ca. 600 cm$^{-1}$ is ascribed to the oxygen vacancy in the zirconia-ceria solid solution [22]. The relative intensity of this peak for YSZ/LDC was slightly stronger than that for YSZ/GDC, which expected higher ionic conductivity for YSZ/LDC. Figure 3 shows the Arrhenius plots of ionic conductivity for YSZ, GDC, LDC, YSZ/GDC and YSZ/LDC in air. The values of GDC and LDC were referred to [9] using the samples sintered at 1500°C for 3 h in air, since the relative densities of GDC and LDC pellets sintered at 1400°C for 10 h were insufficient for the evaluation of ionic conductivity. Inaba and Tagawa [23] reported that the ionic conductivity of LDC was lower than that of GDC. The ionic conductivity of YSZ measured in the present work well agree with the previous paper [23]. The activation energies of GDC and LDC were smaller than that of YSZ as shown in Table 2. The ionic conductivities of YSZ/GDC and YSZ/LDC composites were 1–2 orders of magnitude lower than those of GDC and LDC. The conductivity of YSZ/LDC was slightly higher than that of YSZ/GDC, related to the peak intensity at ca. 600 cm$^{-1}$ in Raman spectra (Figure 2).

The microtubular SOFCs with Ni-YSZ substrate, YSZ electrolyte, GDC or LDC interlayer and LSCF cathode were manufactured and evaluated. The sintering temperature of GDC and LDC interlayers was 1300°C. Figure 4 shows the current density-voltage

![Figure 1](image1.png)

Figure 1. X-ray diffraction patterns of YSZ, GDC, LDC, YSZ/GDC and YSZ/LDC measured with CuKα radiation at room temperature in air.

![Figure 2](image2.png)

Figure 2. Raman spectra of YSZ, GDC, LDC, YSZ/GDC and YSZ/LDC measured with 532 nm laser at room temperature in air.

![Figure 3](image3.png)

Figure 3. Arrhenius plots of ionic conductivity for YSZ, GDC, LDC, YSZ/GDC and YSZ/LDC in air. The values of GDC and LDC were referred to Ref. [9].

| Sample          | Lattice Parameter (nm) |
|-----------------|------------------------|
| YSZ             | 0.51335(4)             |
| GDC             | 0.54132(2)             |
| LDC             | 0.53402(4)             |
| YSZ/GDC         | 0.52847(9)             |
| YSZ/LDC         | 0.53085(2)             |

Table 1. Lattice Parameters of YSZ, GDC, LDC, YSZ/GDC and YSZ/LDC.

| Sample          | Activation Energy (eV) |
|-----------------|------------------------|
| YSZ             | 1.034 ± 0.012          |
| GDC             | 0.6579 ± 0.0106        |
| LDC             | 0.6749 ± 0.0052        |
| YSZ/GDC         | 1.213 ± 0.003          |
| YSZ/LDC         | 1.225 ± 0.001          |

Table 2. Activation energies of ionic conductivity for YSZ, GDC, LDC, YSZ/GDC and YSZ/LDC in air.
and power density characteristics at 550, 600, 650 and 700°C. The theoretical electromotive forces (EMFs) at 600 and 700°C are 1.066 and 1.041 V, respectively, in the fuel of 20%H₂–4%H₂O and the oxidant of air. The OCVs were almost the same as the EMFs. The maximum power densities for the LDC interlayer were 0.26 and 0.73 W/cm² at 600 and 700°C, respectively, which were larger than those for GDC interlayer of 0.24 and 0.68 W/cm² at 600 and 700°C, respectively. Figure 5 shows the impedance spectra measured under OCV at 550, 600, 650 and 700°C. The ohmic and total resistances for the LDC interlayer were smaller than those for the GDC interlayer, which agreed with the cell performance in Figure 4. However, several polarization processes were overlapped in the Nyquist plots (Figure 5). Before DRT analysis, Kramers-Kronig validation was performed as shown in Figure 6. Residuals between measured and Kramers-Kronig transformed impedances were within 0.4% as well as the previous paper [16]. A usage of either the real or imaginary impedance is acceptable for DRT analysis. The DRT spectra were obtained for separating each polarization process using the real impedance as shown in Figure 7. Five DRT peaks were detected for the microtubular SOFCs. The DRT peaks at 20–1000 kHz (P₁) are ascribed to ionic conduction process in the mixed ionic-electronic conductor in the cathode, the peaks at 0.3–20 kHz (P₂) and P₂ are ascribed to fuel oxidation process in the anode, and the peaks at 1–40 Hz (P₃) are ascribed

Figure 4. Current density–voltage and power density characteristics for the microtubular SOFCs with (a) GDC and (b) LDC interlayers.

Figure 5. Impedance spectra measured under OCV for the microtubular SOFCs with (a) GDC and (b) LDC interlayers.

Figure 6. Residuals between measured and Kramers-Kronig transformed impedances for the microtubular SOFCs with (a) GDC and (b) LDC interlayers.
to gas diffusion process in the anode substrate [17-24–30]. In the present work, we focus on the peaks at 40–300 Hz \( P_{c3} \), which are ascribed to oxygen surface exchange and diffusion processes in the cathode. Although the time constants (\( \tau \)) were dependent on temperature, the \( \tau \) of each process was almost unchanged between GDC and LDC interlayers at the same temperature. Figure 8 shows the temperature dependence of area specific resistances of ohmic \( (R_o) \) and polarization for oxygen reduction reaction \( (R_{p2}) \). The \( R_o \) for LDC interlayer were smaller than that for GDC, which agreed with the ionic conductivity of YSZ/LDC and YSZ/GDC in Figure 3. However, the \( R_{p2} \) for LDC interlayer were larger than that for GDC, suggesting the LDC interlayer has a disincentive factor for oxygen reduction reaction.

After the electrochemical evaluation, the cross-sectional microstructures were observed with FE-SEM as shown in Figure 9, and the chemical composition was analyzed with EDS as shown in Table 3. Although the GDC and LDC interlayers had porous structures, they completely prevented the contact of YSZ electrolyte with LSCF cathode. The backscattered electron images suggested that the dense solid solution with ca. 200 nm in thickness was formed at the interface between YSZ electrolyte and GDC or LDC interlayer. As a result of EDS analysis, the cation interdiffusion of Zr, Y, Ce, Gd and La was confirmed for GDC and LDC interlayers. The ratios of Ce/(Zr+Ce) were gradually increased from YSZ electrolyte to GDC or LDC interlayer sides. While the ratios of \( Y/(Zr+Y) \) were almost unchanged from the stoichiometric composition of YSZ at all positions, the ratios of Gd/(Ce+Gd) and La/(Ce+La) increased at the positions close to the YSZ electrolyte. It suggested the possibility of \( Gd_2(Ce,Zr)_2O_7 \) and \( La_2(Ce,Zr)_2O_7 \) formation near the positions 2 and 7. As the result of Figure 3, the conductivity of \( Gd_2(Ce,Zr)_2O_7 \) was lower than that of \( La_2(Ce,Zr)_2O_7 \), which enhanced the ohmic resistance for GDC interlayer. On the other hand, no cations of Ce, Gd and La were detected at the positions 1 and 6 in YSZ electrolyte. However, the cations of Zr and Y were detected at the positions 5 and 10 in GDC and LDC interlayers, respectively. The most active area for oxygen reduction reaction might be the triple phase boundary among GDC or LDC interlayer, LSCF cathode and gas phase. The polarization resistance for LDC interlayer was larger than that for GDC interlayer. The \( La_2Zr_2O_7 \)-rich phase with lower ionic conductivity than \( Gd_2Zr_2O_7 \) phase was possibly formed at the surface of LDC by the diffusion of Zr cations from YSZ electrolyte, which deteriorated the surface exchange and/or diffusion coefficients for oxygen reduction reaction. It is concluded that the cation interdiffusion between electrolyte and interlayer affects not only the ohmic but also the polarization resistances for oxygen reduction reaction on the cathode.

4. Conclusion

In the present work, the LDC interlayer between YSZ electrolyte and LSCF cathode was compared
with the GDC interlayer for microtubular SOFCs. The crystal structure was fluorite-type cubic (space group; Fm-3m) for YSZ/GDC and YSZ/LDC composites heat-treated at 1400°C for 10 h in air. The ionic conductivity of YSZ/LDC composite was slightly higher than that of YSZ/GDC in spite of lower conductivity of LDC than GDC. The cation interdiffusion of Zr, Y, Ce, Gd and La was confirmed by SEM-EDS analysis at the interface between YSZ electrolyte and GDC or LDC interlayer. The La$_2$Zr$_2$O$_7$-rich phase with lower ionic conductivity than Gd$_2$Zr$_2$O$_7$-rich phase was formed at the surface of LDC by the diffusion of Zr cations from YSZ electrolyte, resulting in the increase in the polarization resistance for oxygen reduction reaction for LDC interlayer as a result of DRT analysis. The maximum

Figure 9. Cross-sectional backscattered electron images of the microtubular SOFCs with (a) GDC and (b) LDC interlayers after the electrochemical evaluation.
power density was successfully improved by the change in GDC to LDC interlayers due to the decrease in the ohmic resistance.

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Disclosure statement
There are no conflicts to declare.

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Table 3. Chemical composition at the positions 1–5 in Figure 8(a) and at the positions 6–10 in Figure 8(b) evaluated by EDS point analysis.

| Position | Zr  | Y   | Ce  | Gd  | La  | Ce/(Zr+Ce) | Y/(Zr+Y) | Gd/(Ce+Gd) | La/(Ce+La) |
|----------|-----|-----|-----|-----|-----|------------|----------|------------|------------|
| GDC      | 2   | 14.1%| 0.8%| 0.2%| 0%  | 0%         | 0%       | 0%         | 0%         |
| LDC      | 6   | 5.2% | 22.6%| 11.7%| 4%  | 0.0%       | 0%       | 0%         | 0%         |

Figure 8(a) and 8(b) illustrate the chemical compositions at various positions.
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