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Effects of transition metal addition on sintering and electrical conductivity of La-doped CeO_2 as buffer layer for doped $LaGaO_3$ electrolyte film

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ABSTRACT

Effects of transition metal additives (0.5 at.% Fe, Mn, and Co) on densification, microstructure, crystal structure, and electrical conductivity of $Ce_{0.6}La_{0.4}O_2$ (LDC) were investigated. The power generation property of a single cell using LDC with the transition metal addition as buffer layer was measured. The addition of Co decreased the sintering temperature of LDC to 1373 K and increased the grain size when the sintering was performed at 1623 K. No impurity phase appeared by the addition of transition metals. The total conductivity of the Co-LDC sample sintered at 1373 K was even higher than that of LDC sintered at 1623 K, and Co-LDC sintered at 1623 K exhibited a conductivity of around 0.01 S cm^{-1} at 973 K for the high density and large grain size. The single cell using an LSGM electrolyte film and Co-LDC buffer layers showed an open circuit voltage (~1.1 V) close to the theoretical value and the maximum power density of 974, 353, and 84 mW cm^{-2} at 973, 873, and 773 K, respectively. Thus, Co-LDC is a promising buffer layer for enhanced sintering density and decreasing the ohmic resistance in anode supported SOFCs using LSGM electrolyte films.

1. Introduction

Sr- and Mg-doped $LaGaO_3$ (LSGM) is one of the promising electrolyte materials for intermediate temperature solid oxide fuel cells (IT-SOFCs), because of its higher ionic conductivity than that of Y_2O_3-stabilized ZrO_2 (YSZ) and also its higher oxide ion transport number at a wide range of oxygen partial pressures compared to Gd- or Sm-doped CeO_2 (GDC or SDC) [1]. However, the application of an LSGM electrolyte for SOFCs is limited due to a chemical reaction with NiO at high temperature, which accompanies a decrease in the power density for the formation of a highly resistive secondary phase [2]. La-doped CeO_2 (LDC) is known to be an effective buffer layer material for preventing the detrimental reaction with the LSGM electrolyte [3]. However, an intrinsic property of LDC on sintering density and conductivity appeared to be lower than that of the LSGM electrolyte, which decreased the open circuit voltage (OCV) and increased the ohmic resistance of an anode supported SOFC using an LDC buffer layer and an LSGM electrolyte film [4–6]. Thus, improving the sintering density and conductivity of an LDC buffer layer will play an important role for increasing the efficiency and power generation property of SOFCs with LSGM electrolyte films.

The addition of a transition metal such as Co, Mn, and Fe has been reported to improve the density and conductivity of GDC or SDC. For example, the Co addition decreased the sintering temperature of GDC and increased the ionic conductivity, because of the formation of an amorphous layer of the additive during sintering [7–14]. Furthermore, the transition metal doping on an LSGM electrolyte increased the ionic conductivity with a transport number of oxide ions close to the unity, when the doping was lower than 10 mol% on the Ga-site [15]. Thus, a small amount of transition metal addition is expected to improve the sintering density and conducting property of the LDC layer, which may lead to an increase in the performance of the cell using an LSGM electrolyte film by decreasing ohmic resistance.

In this study, the effects of Co, Mn, and Fe addition on the sintering, microstructure, crystal structure, and electrical conductivity of an LDC buffer layer was investigated for an LSGM electrolyte film prepared by screen printing and co-firing process. The electrochemical performance of SOFCs using an LSGM film and LDC with transition metal additions was studied at intermediate temperatures (773–973 K).

2. Experimental

$La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ (LSGM) and $Ce_{0.6}La_{0.4}O_{2-\delta}$ (LDC) powders were prepared by the solid state reaction method as previously reported [6]. Transition metals of Fe, Mn, and Co were added at 0.5 at.% by ball milling the prepared LDC powder with nitrate-based precursors in ethanol. After drying, the powder mixture were calcined at 1073 K for

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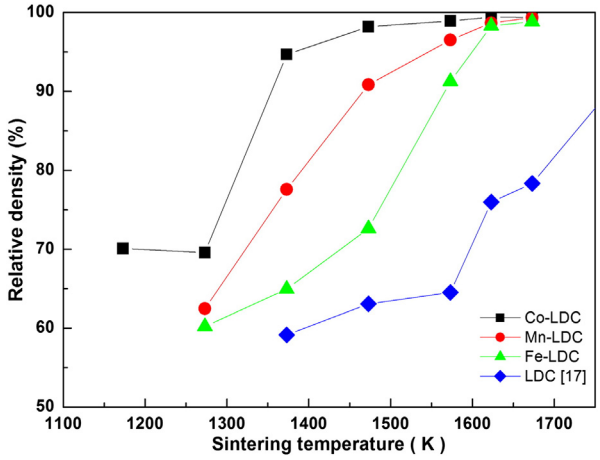

Fig. 1. Dependence of sintering temperature on the relative density of LDC samples with transition metal additions (0.5 at.% Fe, Mn, and Co).

2 h, and then pressed into pellets (20 mm in diameter), followed by sintering in air at 1173–1673 K for 3 h with the heating/cooling rate of 10 K min^{-1}.

The relative density of sintered samples was measured by the Archimedes method. The microstructure was analyzed using a scanning electron microscope (SEM, VE-7800, KEYENCE, Japan). The average grain size was estimated by the linear intercept method over 300 grains in a SEM image. The X-ray diffraction (XRD) patterns were analyzed using Cu *Kα* radiation (Rigaku Rint 2500, Japan). The AC 2-probe conductivity of LDC samples with transition metal additions sintered at 1373 K and 1623 K was measured at 523–1073 K in air using an impedance analyzer (Solartron 1260, Solartron Metrology, UK). The conductivity was measured at a wide P_{O_2} range (10^{-25}–1 atm) by the conventional DC 4-probe method.

Anode supported single cells were prepared by screen printing the LSGM electrolyte and buffer layers after co-firing at 1623 K for 3 h. Detailed information for fabrication of the single cell was reported elsewhere [16]. The power generation property of the single cells was measured by the conventional 4-probe method at 773–973 K using humidified hydrogen (3 vol.% H_2O, 100 mL min^{-1}) as the fuel and oxygen (100 mL min^{-1}) as the oxidant. Electrochemical impedance analysis was conducted under OCV condition using an impedance analyzer (Solartron 1278/1260, Solartron Metrology, UK).

3. Results and discussion

Fig. 1 shows the dependence of the relative density of LDC samples with 0.5 at.% Fe, Mn, and Co additions on the sintering temperature. The relative density of LDC varies with the kind of additives and increases with an increase in the sintering temperature. The densification was improved by the additives, resulting in decreased sintering temperatures compared to that of LDC without additives. For instance, higher densities (>95%) were achieved in the samples with Co, Mn, and Fe additions after sintering at 1373 K, 1573 K, and 1623 K, respectively, while LDC required a temperature higher than 1773 K to achieve the same density [17].

The effect of transition metal additions on the densification of LDC is evident from the microstructure analysis with SEM observation. Fig. 2 shows the surface morphology of the LDC samples with transition metals sintered at 1373 K and 1623 K for 3 h. A decrease in the porosity and an increase in the grain sizes were observed with an increase in the sintering temperature. After sintering at 1373 K, the Co-LDC sample shows a dense surface, while open pores are observed at the surface of Mn- or Fe-LDC. However, there is no significant difference in the grain sizes of these samples despite the variation in density. Sintering at 1623 K produced dense surfaces in all samples with well-developed grain boundaries. The grain growth is dependent on the kind of transition metal added. For instance, there was an increase in the grain size in Co-LDC (5.7 μm) compared to Fe- (2.0 μm) or Mn-LDC (1.9 μm). Thus, Co addition accelerated the densification of LDC at the lower sintering temperature (1373 K) and grain growth at the elevated temperature (1623 K).

The XRD patterns of LDC samples with the additives sintered at 1623 K revealed the typical cubic fluorite structure (*Fm3m*) of single phase CeO_2 with no impurity. However, peak shifts were observed toward a higher angle, which would be assigned to a partial substitution of the transition metal cations with smaller ionic radii (0.065 nm, 0.053 nm, and 0.075 nm for Fe^{3+}, Mn^{4+}, and Co^{2+}) than Ce^{4+} (0.097 nm) [18]. The amount of transition metals (0.5 at.%) added in this study was smaller than the solubility limits on CeO_2 as reported: ~10–15 mol% of Fe [19], ~30 mol% of Mn [20], and ~0.5 mol% of Co (~1173 K) [21].

Zhang et al. reported that a transition metal addition such as Fe, Mn, and Co enhanced the densification of CeO_2 by a viscous flow mechanism, where the friction for mass transport at inter-particles along with grain boundaries decreased for the formation of a thin amorphous layer of the transition metal during sintering [9,22–25]. Thus, an improvement in the densification of LDC may be related with a similar

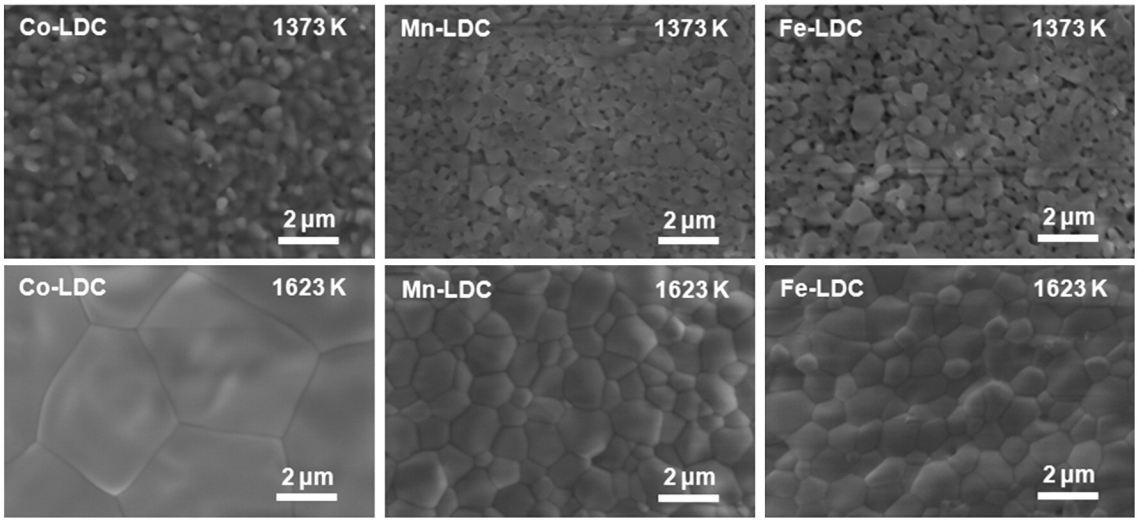

Fig. 2. Surface morphology of LDC samples with transition metal additions after sintering at 1373 K and 1623 K for 3 h.

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