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Sintering characteristics, electrical conductivity and thermal properties of La-doped ceria powders

Eisaku Suda[a,*], Bernard Pacaud[a], Masashi Mori[b]

[a] R&D Department, ANAN KASEI Co. Ltd. 210-51, Ohgata, Anan, Tokushima 774-0022, Japan
[b] Materials Science Research Laboratory, Central Research Institute of Electric Power Industry,
2-6-1 Nagasaka, Yokosuka, Kanagawa 240-0196, Japan

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Abstract

$Ce_{1-x}La_xO_{2-\delta}$ ($0 \leq x \leq 0.4$) powders have been synthesized through a newly devised heat-treatment process in the co-precipitation method, and their sintering characteristics, electrical conductivity and thermal properties have been examined as potential electrolytes in the intermediate-temperature solid oxide fuel cells. Sintering characteristics of the samples have a tendency to decrease with increasing dopant content of La. A relative density ≥94% was obtained after heating at 1500 °C for 2 h for $Ce_{0.9}La_{0.1}O_{1.95}$ and at 1600 °C for 10 h for $Ce_{0.8}La_{0.2}O_{1.9}$. Electrical conductivies at 500 °C and thermal expansion coefficients (50–500 °C) in air for the sintered samples were 3.48×10^{-3} S/cm and $11.5 \times 10^{-6}\,°C^{-1}$ for $Ce_{0.9}La_{0.1}O_{1.95}$, and 3.71×10^{-3} S/cm and $11.7 \times 10^{-6}\,°C^{-1}$ for $Ce_{0.8}La_{0.2}O_{1.9}$.

Keywords: Cerium oxide; SOFC; Electrical conductivity; Co-precipitation method; Electrolyte

1. Introduction

Ceria-based fluorites have been suggested as a candidate electrolyte in intermediate-temperature solid oxide fuel cells (SOFC) in the operating temperature range from 500 to 600 °C by many authors [1]. Although CeO_2-based fluorites show higher oxide-ion conductivity, compared to those of ZrO_2-based ones, the conductivities at the intermediate temperatures are not enough as the electrolyte. Since it is possible to obtain high power density (W/cm^2) and high energy conversion efficiency of the fuel cells by lowering of electrical resistance of the electrolyte, the thickness of the electrolyte is desired to decrease as thin as possible: for example, the thickness is less than 10 μm. The thin electrolyte sheet with thickness of ∼10 μm is hard to handle during SOFC fabrication process. Thus, a development of electrode-supported cells, where the electrode-substrate supports the thin electrolyte layer and provides the mechanical strength of the cell, is necessary.

A co-firing technique of the thick electrode and thin electrolyte is quite appropriate to fabricate electrode-supported cells. However, the highest temperature heat-treatment is necessary for the electrolyte during the fabrication process because the electrolyte in the SOFC must be dense. The heat-treatment at rather a higher temperature often causes chemical reactions among the cell components and loss of porosity in the porous electrode. These lead to a degradation of cell performance. Thus, it is crucially important to devise an appropriate way of fabricating a dense electrolyte layer without the degradation at lower temperatures.

The low-temperature sinterable $Ce_{0.9}Gd_{0.1}O_{1.95}$ powder, which shows the lowest value in the reported sintering temperatures of rare earth metal (RE)-doped ceria powders, has been developed using the newly devised heat-treatment process in the co-precipitation method [2]. In addition, we synthesized the $Ce_{1-x}RE_xO_{2-\delta}$ (RE = Y, Sm, Gd, $0 \leq x \leq 0.2$) powders by the new co-precipitation method, and the

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[*] Corresponding author. Tel.: +81 884 21 7650; fax: +81 884 21 7651.
E-mail address: eisaku.suda@ap.rhodia.com (E. Suda).

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powders showed much higher sintering characteristics, compared to those by the conventional co-precipitation method [3]. The sintering characteristics of these ceria powders were strongly affected by the different dopants. However, details of high sintering mechanisms of the powders remain uncertain.

Since lanthanum ion has the largest ionic radius in the rare earth metals, an effect of the dopant on their sintering characteristics in the $\mathrm{Ce}_{1-x}\mathrm{RE}_x\mathrm{O}_{2-\delta}$ system is very interesting for the new co-precipitation method. In this study, we have synthesized the $\mathrm{Ce}_{1-x}\mathrm{La}_x\mathrm{O}_{2-\delta}$ powders ($0 \leq x \leq 0.4$) by the new co-precipitation in order to clarify the effect of RE dopant on sintering characteristics of doped ceria powders. Additionally, their electrical conductivity and thermal properties have been examined as potential electrolytes in the intermediate-temperature SOFC.

2. Exrerimental

Sample of $\mathrm{Ce}_{1-x}\mathrm{La}_x\mathrm{O}_{2-\delta}$ powders were prepared by the co-precipitation technique as reported previously [2]. After the sample powders were calcined at 700 °C, they were pressed into tablets of 30 mm × 6 mm × 2 mm under a pressure of 200 MPa. These samples were then sintered at selected temperatures with a heating/cooling rate of 5 °C/min in air. Using the fully-sintered samples, sintering characteristics, electrical conductivities, thermogravimetry and differential thermal analysis (TG–DTA) and thermal expansion coefficient (TEC) was measured [4].

3. Results and discussion

3.1. Sintering characteristics

It is concluded that all the powders for $\mathrm{Ce}_{1-x}\mathrm{La}_x\mathrm{O}_{2-\delta}$ ($0 \leq x \leq 0.4$) showed a single fluorite phase with cubic symmetry (space group *Fm*3*m*) after calcining at 700 °C for 5 h, since no peaks for other phases were observed in the XRD patterns. Fig. 1 shows the lattice parameters of the ceria samples after heating at 1400 °C for 2 h, in comparison with those in the $\mathrm{Ce}_{1-x}\mathrm{RE}_x\mathrm{O}_{2-\delta}$ system (RE = Y, Sm, Gd) [3]. The lattice parameters of the fluorites increased with increasing dopant content. This increase in parameters can be explained by the fact that ionic radii of Y^{3+} (115.9 pm), La^{3+} (130 pm), Sm^{3+} (121.9 pm) and Gd^{3+} ion (119.3 pm) are larger than that of Ce^{4+} ion (111 pm) in the fluorite structure [5]. Additionally, in CeO_2 structure, a lower-valence ion-doping results in a charge-compensating by oxygen vacancy formation. Since the formation of oxygen vacancies also reduces Coulombic interaction between cation and anion, the crystal lattice should expand.

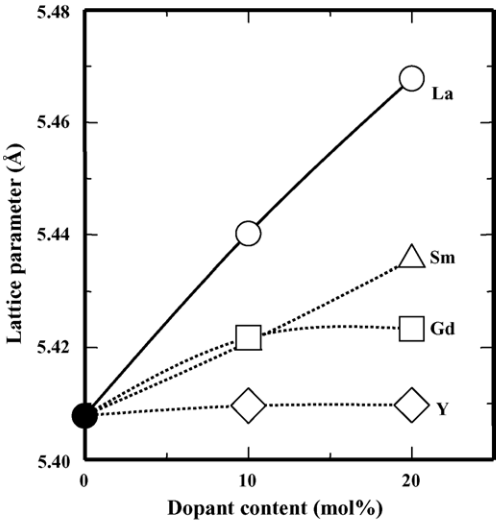

Fig. 1. Lattice parameters of the doped ceria samples after heating at 1400 °C for 2 h as a function of dopant content.

Generally, it is said that an acceptable relative density of electrolyte for SOFC is ≥94%. Thus, in this paper, the sintering temperature, where a relative density of samples reaches 94%, is defined as the fully-sintered temperature. Fig. 2 shows the fully-sintered temperatures in the $\mathrm{Ce}_{1-x}\mathrm{RE}_x\mathrm{O}_{2-\delta}$ system (RE = Y, La, Sm, Gd) as a function of dopant content, where the holding time at the highest temperature was 2 h. A relative density of the $\mathrm{Ce}_{0.8}\mathrm{La}_{0.2}\mathrm{O}_{1.9}$ sample was attained after heating at 1600 °C for 10 h. The sintering of cerium oxides should be proceeded by a bulk diffusion mechanism. Thus, the sintering characteristics in the $\mathrm{Ce}_{1-x}\mathrm{RE}_x\mathrm{O}_{2-\delta}$ system have a tendency to decrease remarkably with increasing ionic radius of dopant content. Note that sintering characteristics for all the doped cerium oxide powders were improved remarkably, when compared to those of the powders obtained by the conventional co-precipitation method.

It is well-known that sintering characteristics of oxides related to their particle size distribution and specific sur-

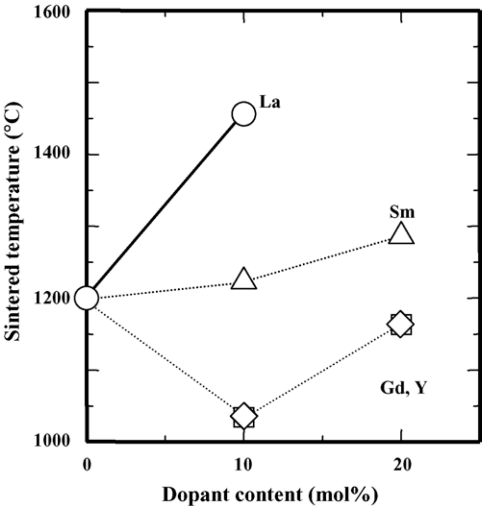

Fig. 2. Fully-sintered temperatures of the doped ceria samples as a function of dopant content.

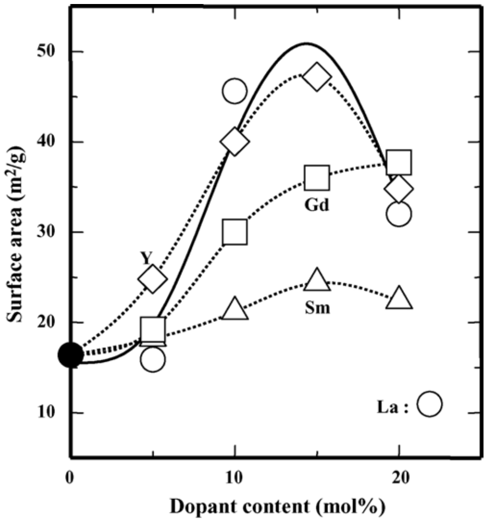

Fig. 3. Specific surface area of the $Ce_{1-x}RE_xO_{2-\delta}$ powders after heating at 700 °C for 5 h as a function of dopant content.

face area. The sample powders by the conventional co-precipitation method showed two peaks (0.5 and 5 μm) in particle size distribution curve [2]. From the results, TEM micrographs, primary particles of this conventional powder are approximately 20 nm [2]. Thus, it is indicated that two peaks in the particle size distribution measurement show the agglomerations of the primary and secondary particles [6]. It could be thought that to be the peak at approximately 0.5 μm for the secondary particles and the one at approximately 5 μm for the tertiary particles.

The values of specific surface area of the $Ce_{1-x}La_xO_{2-\delta}$ powders calcined at 700 °C for 5 h were 16.4 m^2/g for CeO_2, 45.6 m^2/g for $Ce_{0.9}La_{0.1}O_{1.95}$ and 32.0 m^2/g for $Ce_{0.8}La_{0.2}O_{1.9}$ (Fig. 3). The specific surface area for all the samples had a tendency to increase with increasing dopant content. Although the $Ce_{0.9}La_{0.1}O_{1.95}$ powder has large specific surface area in addition to the good distribution for the primary particles, the much lower sintering characteristics were observed, compared to those of the pure CeO_2 and $Ce_{0.9}RE_{0.1}O_{1.95}$ (RE = Y, Sm, Gd) [3]. This indicates that lanthanum oxide is not appropriate as dopant to lower the fully-sintering temperature of ceria powder.

3.2. Electrical and thermal properties

Fig. 4 shows the oxygen vacancies in the $Ce_{1-x}La_xO_{2-\delta}$ samples in the H_2 atmosphere as a function of temperature when the oxygen vacancies of unfired fluroites are assumed to be zero at 25 °C in the H_2 atmosphere. Generally, the fluorites show non-stoichiomerty of O-site in air. On the other hand, in reducing atmosphere at temperatures greater than approximately 550 °C, non-doped or doped ceria-based oxides show the formation of oxygen vacancies in the fluorite structure and a charge compensation of the Ce^{4+} to the Ce^{3+} ion occurs [7]. Two serious problems remain to be solved as electrolytes in the SOFC:

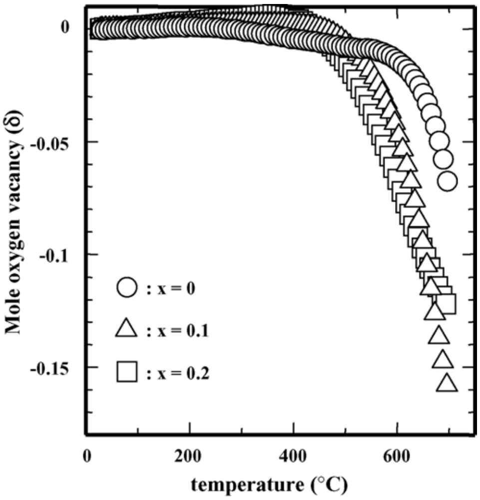

Fig. 4. Oxygen vacancies in the $Ce_{1-x}La_xO_{2-\delta}$ samples in the H_2 atmosphere as a function of temperature.

(1) The reduction of Ce^{4+} into Ce^{3+} ions causes the appearance of electronic conduction.
(2) The ionic radius increase of Ce^{4+} ions (111 pm) into Ce^{3+} ions (128.3 pm) and the formation of oxygen vacancies cause a large isothermal expansion (reduced expansion) of crystal lattice in the structure.

Fig. 5 shows the electrical conductivity of the $Ce_{1-x}La_xO_{2-\delta}$ samples with relative density of approximately 95% as a function of dopant content. The open and closed symbols represent the conductive values in air and in the mixture gas. The oxide-ionic conductivities of the present $Ce_{0.8}La_{0.2}O_{1.9}$ samples in air agree to those reported previously [8,9]. Electrical conductivities at 500 °C were

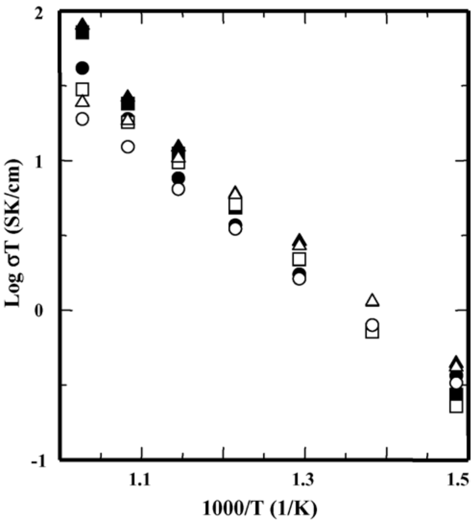

Fig. 5. Arrhenius plots of electrical conductivity of the sintered $Ce_{1-x}La_xO_{2-\delta}$ samples with relative density of approximately 95%. Circles, triangles and squares represent $x = 0.05$, $x = 0.1$ and $x = 0.2$, respectively. Open and closed symbols represent in air and in the reducing atmosphere, respectively.

Table 1
Lattice parameters, theoretical densities, average particle size, specific surface area and linear thermal expansion coefficients of prepared cerium powders calcined at 700 °C for 5 h.

Sample	a (Å)	Theoretical density (g/cm^3)	Average particle size (μm)	Specific surface area (m^2/g)	Electrical conductivity at 500 °C (SK/cm)		TEC ($\times 10^{-6}$ °C^{-1}) 50–500 °C	
					In air	In reducing	In air	In H_2
CeO_2	5.4078(6)	7.231	0.21	16.4	1.01×10^{-4}	–	11.2	10.9
$Ce_{0.95}La_{0.05}O_{1.975}$	5.4250(4)	7.148	0.41	15.9	1.62	1.73	11.8	11.0
$Ce_{0.9}La_{0.1}O_{1.95}$	5.4400(1)	7.051	0.30	45.6	2.69	2.87	11.5	11.3
$Ce_{0.8}La_{0.2}O_{1.9}$	5.4678(4)	6.915	0.47	32.0	2.19	2.18	11.7	13.3
$Ce_{0.6}La_{0.4}O_{1.8}$	5.5405(9)	6.593	0.52	28.8	–	–	–	–

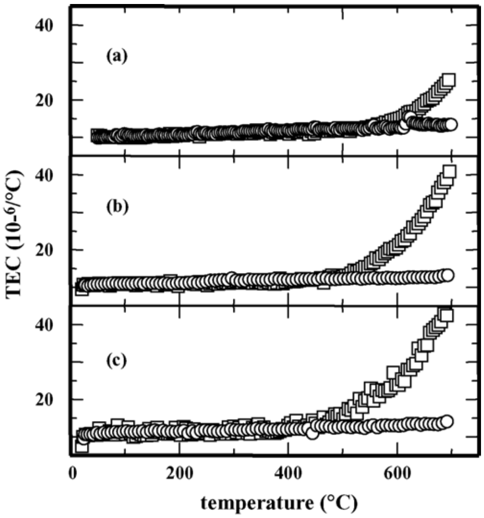

Fig. 6. Differential coefficient of thermal expansion–temperature curve of the sintered $Ce_{1-x}La_xO_{2-\delta}$ samples. Open circles and open squares represent TECs in air and in the H_2 atmosphere, respectively. (a) CeO_2, (b) $Ce_{0.9}La_{0.1}O_{1.95}$ and (c) $Ce_{0.8}La_{0.2}O_{1.9}$.

3.48×10^{-3} S/cm for $Ce_{0.9}La_{0.1}O_{1.95}$, and 3.71×10^{-3} S/cm for $Ce_{0.8}La_{0.2}O_{1.9}$. The electrical conductivity of all the samples in the temperature range from 400 to 550 °C were represented by the function $\sigma T \propto \exp(-E/k_BT)$, where σ is the electrical conductivity, T the absolute temperature, E the activation energy for electrical conduction and k_B is the Boltzmann constant. Since the linearity of the increased conductivity was observed for the samples, their conduction should be due to oxide-ions in this temperature range.

Fig. 6 shows the differential coefficient of thermal expansion-temperature curve of $Ce_{1-x}Gd_xO_{2-\delta}$, where the TECs are calculated using thermal expansion slops between 2.5 °C above and 2.5 °C below a give temperature. In air, all the samples showed a linear temperature dependence. On the other hand, TEC in H_2 atmosphere increased remarkably at 450–600 °C. This increase in the reducing atmosphere corresponds the reduced expansion. It is observed that the reduced expansion temperature decreases with increasing dopant in the H_2 atmosphere, due to the formed oxygen vacancies and in a charge-compensating by reducing of Ce^{4+} to Ce^{3+} ions [10]. The reduced expansion of the $Ce_{1-x}La_xO_{2-\delta}$ samples started at the lowest temperature in the $Ce_{1-x}RE_xO_{2-\delta}$ system (RE = Y, La, Sm, Gd). For the $Ce_{1-x}La_xO_{2-\delta}$ powders, the lattice parameters, characteristics of particle, electrical conductivity and linear TEC in the present study are summarized in Table 1.

4. Conclusion

The La-doped ceria powders have been synthesized through a newly devised heat-treatment process in the coprecipitation method. It is clear that the effect of dopant on sintering characteristics of doped CeO_2 for the new coprecipitation. The sintering characteristics of these powders show the lowest value in the $Ce_{1-x}RE_xO_{2-\delta}$ system (RE = Y, La, Sm, Gd). Among the $Ce_{1-x}RE_xO_{2-\delta}$ fluorites, $Ce_{1-x}La_xO_{2-\delta}$ fluorites ($0 \leq x \leq 0.2$) showed the lowest performance of electrical and thermal properties as electrolytes in the intermediate-temperature SOFC.

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