The electrolytic properties and influence of microstructure in $Dy_xCe_{1-x}O_{2-x/2}$ (x=0.10-0.25) solid electrolytes

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Sinterability nanosize powders of $Dy_xCe_{1-x}O_{2-x/2}$ (x=0.10-0.25) have been synthesized via carbonate coprecipitation method. Precursor and calcined powders consisted of round shape nano particles, and the average particle sizes of calcined powders with aforementioned composition were approximately 30 nm. The sintered bodies of $Dy_{0.2}Ce_{0.8}O_{1.9}$ and $Dy_{0.15}Ce_{0.85}O_{1.925}$ were fabricated as representative examples of Dy-doped CeO_2 system using combined method of Spark Plasma Sintering (SPS) and Conventional Sintering (CS). The conductivity of $Dy_{0.2}Ce_{0.8}O_{1.9}$ sintered bodies with average grain size 250 nm which was fabricated by (SPS+CS) was two orders magnitude higher than that of CS specimen with same average grain size. This suggests that microstructural feature is a key for improvement of conducting properties. It is concluded that the combined method was useful for a design of microstructure in Dy-doped CeO_2 systems. In addition, the conductivity in $Dy_{0.15}Ce_{0.85}O_{1.925}$ fabricated by (SPS+CS) method was higher than that of $Dy_{0.2}Ce_{0.8}O_{1.9}$ (SPS+CS) specimen. The conductivity of $Dy_{0.15}Ce_{0.85}O_{1.925}$ (SPS+CS) specimen was comparable to that of $Gd_{0.2}Ce_{0.8}O_{1.9}$ specimen. Therefore, it is expected that nano-structured Dy-doped CeO_2 sintered body will be one of promising solid electrolytes for low temperature operation of solid oxide fuel cells (SOFCs).

Key words: Carbonate coprecipitation, Dy-doped CeO_2, Spark Plasma Sintering, Micro-domain, Conductivity

1. INTRODUCTION

Oxide ion conductors are used in a variety of oxygen sensors, solid oxide electrochemical cells, and solid oxide fuel cells (SOFCs) [1, 2]. In these applications, SOFCs are being especially developed as a clean and efficient power source for generating electricity from a variety of fuels. Doped CeO_2 compounds such as Gd-doped CeO_2 [3-5] and Sm-doped CeO_2 [6-8] are now under active investigations for application as "low" (400°-600 ℃) temperature operation of SOFCs. These electrolytes show high oxide ionic conductivity at high oxygen partial pressure. At low oxygen partial pressures, these materials are partially reduced and develop electrical conductivity during operation of the fuel cell [9]. To overcome this problem and improve the conductivity, a nano-structured doped CeO_2 with high conductivity should be identified. CeO_2 electrolytes doped with rare earth oxide or alkaline earth oxide have been widely investigated. The systematical investigation of relationship among electrical properties, dopant size and dopant concentration in doped CeO_2 was performed. However, the prospective improvements of conductivity in doped CeO_2 were limited using aforementioned approach. In the light of this limitation, the rela-

tionship between conducing property and microstructural feature in doped CeO_2 sintered body should be investigated for development of the high quality electrolyte. It is considered that the conducting property in doped CeO_2 is improved by the design of microstructural feature in sintered body.

To fabricate the homogeneous microstructure, spark plasma sintering (SPS) was used. SPS is a sintering method that enables to quickly densify calcined powders. This sintering method is useful for preparation of nano-structured oxide composites. However, SPS has not been applied to fabricate the dense sintered bodies of rare-earth doped CeO_2 electrolytes. The reason for this is that carbon penetration from the graphite die into the specimen was observed to prevent the densification of the sample. In the present study, the combined method of SPS and conventional sintering (CS) was used to prepare dense dysprosium (Dy) doped CeO_2 with nano-hetero structure. The densification behavior, conducting properties, and microstructure at the atomic level of dense specimens prepared in this manner were examined with a view to finding new ways of improving the conducting properties of Dy-doped CeO_2. The influence of microstructural feature on conductivities in (SPS+CS) specimens was compared with those fabri-

cated by conventional method.

2. EXPERIMENTAL

The starting materials used for synthesis of nanosized $Dy_xCe_{1-x}O_{2-x/2}$ ($x=0.10-0.25$) powders were cerium nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$; >99.99% pure, KANTO Chemical Co. Inc., Tokyo, Japan), dysprosium nitrate hexahydrate ($Dy(NO_3)_3 \cdot 6H_2O$; >99.9% pure, Wako Pure Chemical Industries Inc., Osaka, Japan), and ammonium carbonate (($NH_4)_2CO_3$; ultrahigh purity, KANTO Chemical Co. Inc.). The cerium nitrate hexahydrate and dysprosium nitrate hexahydrate powders were dissolved in distilled water, and the solutions were mixed in order to prepare the fixed composition. The molar rations [Dy^{3+}]/ [Ce^{3+}] in mixed solution for synthesis of $Dy_{0.1}Ce_{0.9}O_{1.95}$, $Dy_{0.15}Ce_{0.85}O_{1.925}$, $Dy_{0.2}Ce_{0.8}O_{1.9}$ and $Dy_{0.25}Ce_{0.75}O_{1.875}$ were 6, 8, 10 and 10, respectively. An aqueous solution of ammonium carbonate in distilled water with a concentration of 1.5 M was used as the precipitant. The mixed solution was added into the ammonium carbonate solution kept at 60°C, 65°C, 70°C and 70°C for synthesis of precursor of $Dy_{0.1}Ce_{0.9}O_{1.95}$, $Dy_{0.15}Ce_{0.85}O_{1.925}$, $Dy_{0.2}Ce_{0.8}O_{1.9}$ and $Dy_{0.25}Ce_{0.75}O_{1.875}$, respectively. The mixed solution was gently stirred for 1 h. After repeated washing, the precipitate was dried at room temperature with flowing nitrogen gas and then calcined in flowing oxygen at 700°C for 2 h to yield nanosized powders. For CS, these powders were molded under a pressure of 60 MPa and subjected to a rubber press 200 MPa in order to obtain a green body. CS temperature ranged from 1000° to 1450°C for 4-6 h. In the combined method, a two-step sintering process was performed. The first step uses the SPS that is followed in the second step by CS. For SPS, 2.4-2.8 g of the calcined powders was placed into a 15 mm graphite die and an electric current of 1000 A was applied under a pressure of 60 MPa. The heating rate was 250-500°C/min. The sintering temperature ranged from 1150° to 1200°C. To minimize the penetration of carbon from the graphite die into the specimens, no holding time at the aforementioned sintering temperature was used. The current was simply shut off at the temperature and the pressure was immediately released after the sintering. Following the SPS method, the specimens were sintered at the temperature ranging from 900° to 1200°C for up to 48 h in air.

The crystal phases in the powder and sintered specimens were investigated using X-ray diffraction and selected area electron diffraction analysis, respectively. The bulk density of the sintered body was measured using the Archimedes method. The relative density was calculated from the ratio of the measured bulk density to the theoretical density. The theoretical density was estimated using the lattice constant and the sample composition. The particle sizes in the synthesized powders and the grain sizes in the sintered bodies were observed using scanning electron microscopy (SEM). The average grain size in the sintered body was calculated using linear intercept method measuring more than 200 grains using SEM.

For the electrical conductivity measurement, platinum electrodes were applied to both sides of the sintered bodies at ranging from 900° to 1000°C for 1 h. The conducting properties in the sintered bodies were measured by dc three point measurements at 400°-800°C in air. The accuracy of conductivity in each temperature is ± 0.01 S/cm in log σ.

3. RESULTS AND DISCUSSION

Figure 1 shows a particle morphology of (a) $Dy_{0.1}Ce_{0.9}O_{1.95}$ and (b) $Dy_{0.25}Ce_{0.75}O_{1.875}$ powders calcined at 700°C for 2 h as representative examples in the composition of Dy-doped CeO_2 system. The CeO_2 powder doped with Dy^{3+} is observed to be composed of uniformly sized, round shape, and discrete particles. The average particle size was approximately 30 nm. This powder can be sintered to over 95% dense of theoretical density in the temperature range of 1000°-1450°C using CS method. On the other hand, SPS could not make dense Dy-doped CeO_2 sintered bodies over 90% of theoretical one. It is because the carbon powders penetrated the sintered body from the graphite die. The maximum bulk density of SPS specimen was approximately 85% of theoretical one. To make sintered body with high density over 95%, the combined method of SPS and CS was examined.

Figure 2 presents the relationship between the sintering time of CS after SPS and the relative density. The relative density of $Dy_xCe_{1-x}O_{2-x/2}$ ($x=0.10-0.25$) sintered bodies were 82-85% of theoretical density using SPS (1150°-1200°C, no
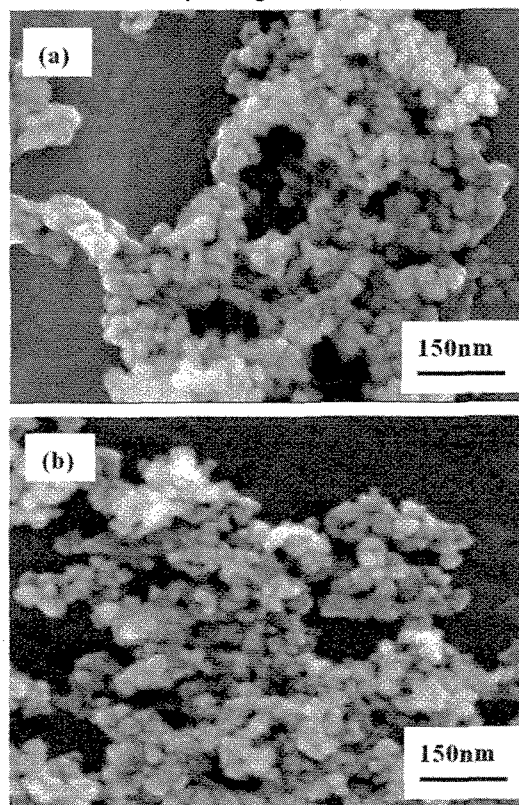

Fig.1 SEM photographs of powders calcined at 700°C for 2h; (a) $Dy_{0.1}Ce_{0.9}O_{1.95}$, (b) $Dy_{0.25}Ce_{0.75}O_{1.875}$.

holding time, 250°-500°C/min of heating rate) process only. However, the relative density of sintered bodies reached approximately 95% of theoretical density using the combined method of SPS and CS. Since there was no successful reports for fabrication of dense doped CeO_2 using SPS method, our data would be first successful report using SPS method.

Figure 3 demonstrates the effect of average grain size on the electrical conductivity and acti-
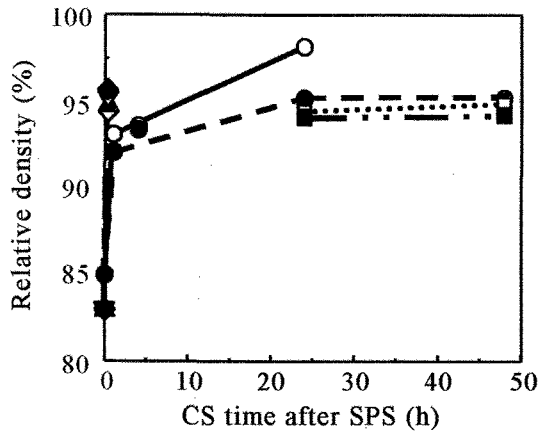

Fig.2 Relationship between CS time after SPS and relative density; $Dy_{0.15}Ce_{0.85}O_{1.925}$ (◆ :1450 °C , ▽ :1350°C , ▲ :1250°C , ◇ :1200°C , □ :1150°C , ■ :1100°C), $Dy_{0.2}Ce_{0.8}O_{1.9}$ (○:1150°C, ●:1100°C).
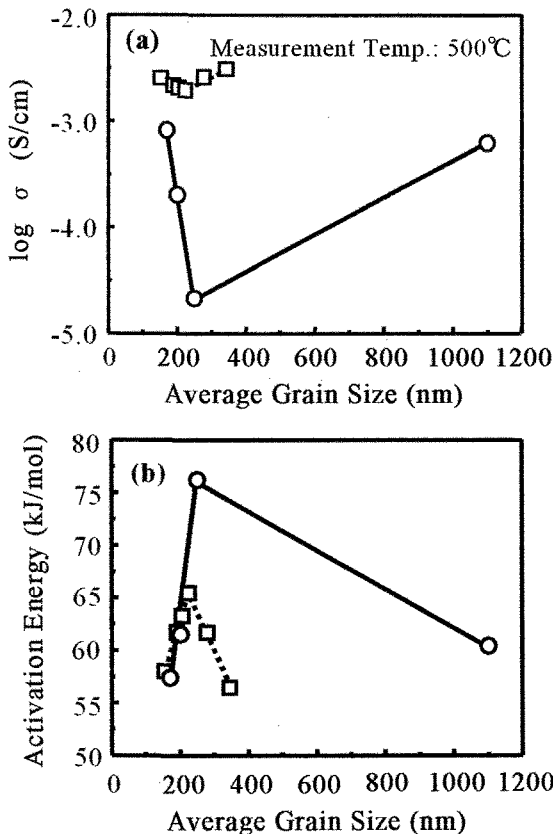

Fig.3 Effect of average grain size on the electrical conductivity (a) and activation energy (b); □ : $Dy_{0.2}Ce_{0.8}O_{1.9}$ (SPS+CS) specimens, ○: $Dy_{0.2}Ce_{0.8}O_{1.9}$ CS specimens.
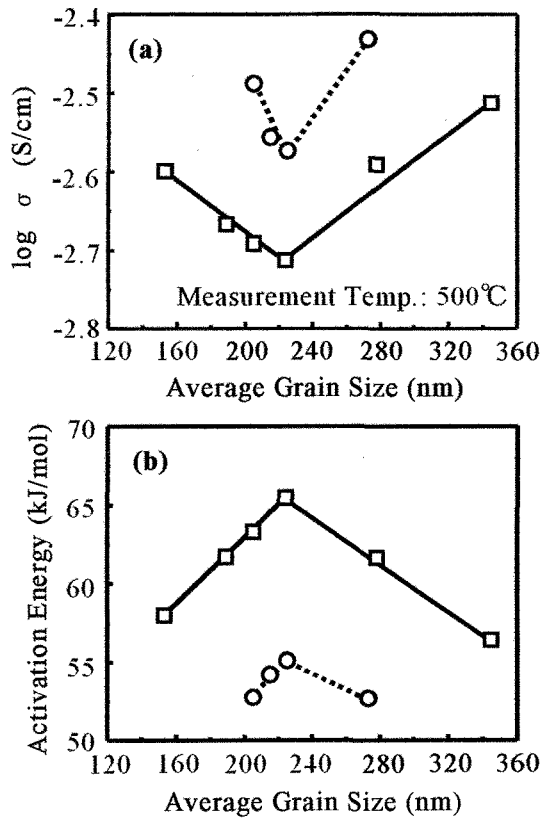

Fig.4 Effect of average grain size on the electrical conductivity (a) and activation energy (b); □ : $Dy_{0.2}Ce_{0.8}O_{1.9}$ (SPS+CS) specimens, ○ : $Dy_{0.15}Ce_{0.85}O_{1.925}$ (SPS+CS) specimens.

vation energy in the $Dy_{0.2}Ce_{0.8}O_{1.9}$ sintered bodies that were obtained by CS and combined method of SPS and CS. The conductivity in the $Dy_{0.2}Ce_{0.8}O_{1.9}$ specimens obtained by CS showed the curvature in the grain size dependence of conductivity (Fig.3 (a)). The conductivity decreased with decreasing grain size and reached the lowest value at an average grain size of 240 nm and the conductivity increased with decrease of grain size under 240 nm. The activation energy in the $Dy_{0.2}Ce_{0.8}O_{1.9}$ specimens fabricated using CS has a clear maximum in the graph showing the relationship between average grain size and activation energy. The maximum point is equal to the minimum point of conductivity (Fig.3 (b)).

As Fig.3 indicates, the conductivity in the $Dy_{0.2}Ce_{0.8}O_{1.9}$ (SPS+CS) specimens was much higher than that of $Dy_{0.2}Ce_{0.8}O_{1.9}$ specimens fabricated by CS, and the conductivity in (SPS+CS) specimens was two orders of magnitude larger than that of CS specimens at 230 nm of average grain size. The activation energy in $Dy_{0.2}Ce_{0.8}O_{1.9}$ (SPS+CS) specimens was much lower than that of $Dy_{0.2}Ce_{0.8}O_{1.9}$ specimens fabricated by CS. In addition, $Dy_{0.15}Ce_{0.85}O_{1.925}$ (SPS+CS) specimens show better electrolytic properties as compared with $Dy_{0.2}Ce_{0.8}O_{1.9}$ (SPS+CS) specimens (Fig. 4). This suggests that the present combined method can improve the microstructure in doped CeO_2 solid electrolytes. And the optimization of composition is important for development of
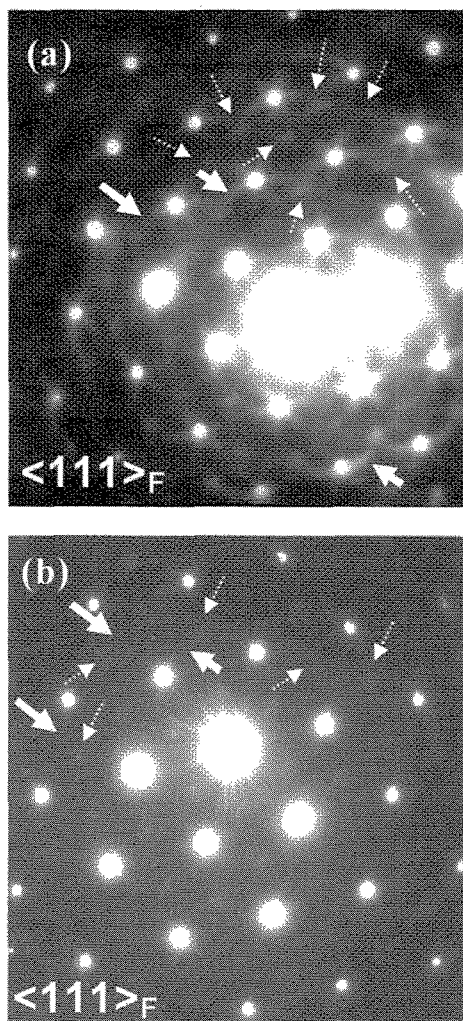
Fig.5 Selected area electron diffraction patterns (SAEDPs) recorded from (a) $Dy_{0.2}Ce_{0.8}O_{1.9}$ CS specimen and (b) $Dy_{0.15}Ce_{0.85}O_{1.925}$ (SPS+CS) specimen. Dashed line arrow indicates extra reflection. Solid line arrow indicates diffuse scattering.

Dy-doped CeO_2 solid electrolytes.

To conclude the influence of microstructure on conducting properties in Dy-doped CeO_2 sintered bodies, the selected area electron diffraction patterns (SAEDPs) recorded from $Dy_{0.2}Ce_{0.8}O_{1.9}$ CS specimen with large grain size (1.1 μ m) and $Dy_{0.15}Ce_{0.85}O_{1.925}$ (SPS+CS) specimen with small grain size (270 nm) were compared in Fig.5. In the background of both SAEDPs, diffuse scattering around extra reflection was observed. This indicates that micro-domain with ordered structure of oxygen vacancy exists in the fluorite lattice. The position of extra reflection spots indicates that the micro-domain consists of distorted pyrochlore structure. Since the micro-domain with distorted pyrochlore structure is quite small, it is concluded that X-ray diffraction analysis cannot detect this microstructural feature in doped CeO_2. Moreover, the intensity of extra reflection and diffuse scattering in SAEDPs recorded from (SPS+CS) specimen was smaller than those of CS specimen. This suggests that the

micro-domain size in (SPS+CS) specimen is minimized using the present combined process.

4. SUMMARY

The influence of microstructural features on conducting properties in Dy-doped CeO_2 solid electrolytes was examined. Nano-sized $Dy_xCe_{1-x}O_{2-x/2}$ (x=0.10-0.25) powders were synthesized using carbonate coprecipitation method. Dense sintered bodies were obtained using the combined method of SPS and CS. The present study would be first report for fabrication of dense doped CeO_2 using SPS method. The micro-domain size in specimens minimized using the present method, and the conductivity of sintered bodies were improved. Therefore, it is found that the design of nano structure is important for improvement of conducting properties in doped CeO_2 electrolytes for SOFC application.

5. Reference

[1] N. Q. Minh, "Ceramic Fuel-cells", *J. Am. Ceram. Soc.*, **76**(3), 563-588 (1993).

[2] B. C. H. Steel, "Materials for fuel-cell technologies", *Nature*, **414**(15), 345-352 (2001).

[3] T. Zhang, Z. Zeng, H. Hing, P. Hing, J. Kilner, "Effect of alumina addition on the electrical and mechanical properties of $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ ceramics", *Mater. Lett.*, **57**, 124-129(2002).

[4] T. Mori, J. Drennan, Y. Wang, G. Auchterlonie and J.-G. Li, "Influence of nano-structural features on the electrolytic properties of Gd doped CeO_2 solid electrolytes", *J. Ceram. Soc. Jpn.*, **112**(5), S642-S648 (2004).

[5] Y. Wang, T. Mori, J. Drennan, J.-G. Li and Y. Yajima, "Low temperature synthesis of 10 mol% Gd_2O_3-doped CeO_2 ceramics and its characterization", *J. Ceram. Soc. Jpn.*, **112**(5), S41-S45 (2004).

[6] T.Mori, T. Ikegami and H. Yamamura, "Application of a crystallographic index for improvement of the electrolytic properties of CeO_2 - Sm_2O_3 system", *J. Electrochemical Society*, **146**(12), 4380-4385 (1999).

[7] T. Mori, J. Drennan, J.-H. Lee, J.-G. Li and T. Ikegami, "Oxide ionic conductivity and microstructure of Sm or La doped CeO_2 based system", *Solid State Ionics*, **154-155**, 461-466 (2002).

[8] T. Mori, Y. Wang, J. Drennan, G. Auchterlonie, J.-G. Li and T. Ikegami, "Influence of particle morphology on nano-structural feature and conducting property in Sm-doped CeO_2 sintered body", *Solid State Ionics*, **175**, 641-649 (2004).

[9] H. Hayashi, M. Kanoh, C. J. Quan, H. Inaba, S. Wang, M. Dokiya and H. Tagawa, "Thermal expansion of Gd-doped ceria and reduced ceria", *Solid State Ionics*, **132**, 227-233 (2000).