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Densification behavior and electrolytic properties of nano-structured $Dy_xCe_{1-x}O_{2-\delta}$ (x=0.1, 0.15, 0.2 and 0.25) solid electrolytes with high density

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Sinterability round shape nano-size powders of $Dy_xCe_{1-x}O_{2-\delta}$ (x=0.1, 0.15, 0.2 and 0.25) have been synthesized via carbonate co-precipitation method. Precursor and calcined powders consisted of round shape nano-particles, and the average particle sizes of calcined powders with aforementioned composition were approximately 30nm. The sintered bodies of $Dy_{0.20}Ce_{0.80}O_{1.9}$ (20DyDC) and $Dy_{0.15}Ce_{0.85}O_{1.925}$ (15DyDC) 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 20DyDC sintered bodies with average grain size 250nm which was fabricated by (SPS + CS) was two orders of magnitude higher than that of CS specimen with same average grain size (250nm). This suggests that micro-structural feature is a key for improvement of conducting properties. It is concluded that the combined method was useful for a design of microstructure in DyDC systems. In addition, the conductivity in 15DyDC fabricated by (SPS + CS) method was higher than that of 20DyDC fabricated by the combined method. 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.

Key words: Solid electrolytes, Co-precipitation method, Nano-size powder, Spark Plasma Sintering, micro-domain, fuel cell application

1. INTRODUCTION

Oxide ion conductors are used in solid oxide fuel cells (SOFCs).[1-3] SOFCs are being especially developed as a clean and efficient power source for generating electricity from a variety of fuels. For long lifetimes with low temperature (500°-650°C) and efficient operation below 500°C, high oxide ionic conductivity is required for the electrolytes. Yttria stabilized zirconia (YSZ) and scandia stabilized zirconia (SSZ) are common electrolytes used in SOFCs.[1,4] However, its ionic conductivity is still unsatisfactory level for low temperature operation of SOFCs. Accordingly, it is important that a new, high-quality electrolyte with higher oxide ionic conductivity than that of YSZ and SSZ is identified. Di- or trivalent metal oxides such as calcia or rare earth oxide doped CeO_2 possess higher oxide ionic conductivity than aforementioned stabilized zirconia.[5-7] At high oxygen partial pressures, these doped CeO_2 electrolytes show high oxide ionic conductivity. At low oxygen partial pressures, which come about as a result of reactions associated with anodic conditions, the Ce^{4+} ion can be partially reduced to Ce^{3+} ion resulting in an increase in electronic condition – an unsatisfactory condition for fuel cell applications. In this reduction of CeO_2 based oxides, quasi-free electrons are introduced into a fluorite lattice. CeO_2 based oxides exhibit high oxide ionic conductivity in oxidizing atmosphere, whereas they are partially reduced and develop electronic conductivity under anodic conditions in the fuel cell. The stability in both oxidizing and reducing atmosphere is an essential requirement for candidate electrolytes rare earth doped CeO_2 systems. To overcome this problem and improve the conductivity for low temperature operation of SOFCs, a design of nano-structure in doped CeO_2 solid electrolytes is required. It is expected that a new conduction pathway will be appeared in nano-structured solid electrolytes. As a consequence of this, an influence of processing route and microstructural feature on conducting properties should take into account to fabricate the nano-structured doped CeO_2 electrolytes. Recently, gadolinium[8,9] doped CeO_2 electrolytes have attracted much attention from the perspective of SOFCs application. On the other hand, Dy doped CeO_2 has not been developed as a new solid electrolytes in SOFCs. It is because the conductivity in aforementioned material was not so high as compared with Gd doped CeO_2 solid electrolytes. Since Dy doped CeO_2 has a comparable association enthalpy with that of Y doped CeO_2 or Gd doped CeO_2 electrolyte,[10] the authors examined Dy doped CeO_2 solid electrolytes for low temperature operation of SOFCs by means of a design of nano-structure in this material.

To fabricate a nano-structured Dy doped CeO_2, the combined process of spark plasma sintering (SPS) and conventional sintering (CS) was examined. The densification behavior, conducting properties and microstructure 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 micro-structural features on conductivities in (SPS+CS) specimens was compared with those prepared by conventional means.

2. EXPERIMENTAL

Preparation of powder and sintered body - The starting materials used for Dy doped CeO_2 synthesis were commercial available nitrate and ammonium carbonate powders. The cerium nitrate and dysprosium nitrate powders were dissolved into distilled water, and the solutions were mixed in order to prepare the fixed composition of $Dy_xCe_{1-x}O_{2-}$ ($0.15 \leq x \leq 0.25$). An aqueous solution of ammonium carbonate in distilled water with a concentration of 1.5M was used as the precipitant. The mixed solution was added into the ammonium carbonate solution kept at 70°C whilst being gently stirred. After repeated washing, the precipitate was dried at room temperature in nitrogen gas flow and then calcined in flowing oxygen at 700°C for 2 hours to yield Dy doped CeO_2 powders. For CS, these powders were molded under a pressure of $500 kg/cm^2$ and subjected to a rubber press at $2 t/cm^2$ ($1t = 10^3 kg$) to obtain a green body. CS temperature ranged from 1,000° to 1,450°C for 6 to 18 hours. In the combined process, two step sintering process was performed. The first step uses the SPS which is followed in the second step by CS. For SPS, the specimen was heated up to 900°C for 8 minutes. The heating rate was 500°C/min over 900°C. The sintering temperature ranged from 1,000° to 1,200°C. To minimize the penetration of carbon from the graphite-die into the specimens and reduction of specimen, no holding time at the aforementioned sintering temperature was used. Following the SPS process, the specimens were sintered at the temperature ranging from 1,000° to 1,200°C for up to 48 hours in air.

Sample characterization - 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 the linear intercept method measuring more than 200 grains using SEM.[11] The crystal phases in the sintered specimens were investigated using a selected area electron diffraction analysis. The micro-structural features in the grain were investigated using transmission electron microscopy (TEM). TEM observation was performed with gun voltages of 200keV.

Measurement of electrical properties – Electrical conductivity of the sintered specimens was measured by dc three-point measurements at 400°-650°C in air. A platinum electrode was applied to both sides of the sintered bodies at 1,000°C for 1hour in air. The activation energy was calculated using the data of conductivity at the temperature ranging from 400° to 650°C.

3. RESULTS AND DISCUSSION

Figure 1 (a) and (b) show the morphology of powders of $Dy_{0.15}Ce_{0.85}O_{1.925}$ (15DyDC) and $Dy_{0.2}Ce_{0.8}O_{1.9}$ (20DyDC) as representative examples in the composition of Dy doped CeO_2 system, respectively. These figures indicate that round shape particles interconnect with each other to make networks. It is concluded that the agglomeration of particles is not strong.

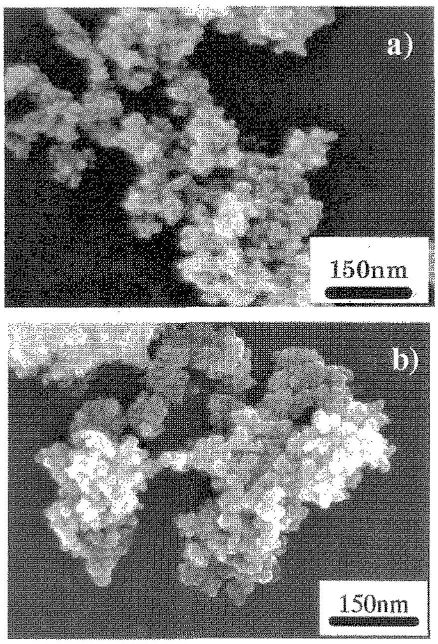


Figure 1 Particle morphologies of a) $Dy_{0.2}Ce_{0.8}O_{1.9}$ powder and b) $Dy_{0.15}Ce_{0.75}O_{1.925}$ powder, calcination temperature: 700°C.

The calcined powders were observed to be composed of uniformly sized and round shaped particles. The average particle sizes of both powders were 15 to 30nm. This powder can be sintered to over 95% dense of theoretical density in the temperature range of 1,050° to 1,450°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 and reduced Dy doped CeO_2 specimens in the SPS process. It is concluded that these phenomenon lowered the bulk density of the specimen. The maximum bulk density of SPS specimen was approximately 85% of theoretical one. To make sintered body with high density over 95%, the combined process of SPS and CS was examined.

Figure 2 presents relationship between electrolytic properties and Dy content in Dy doped CeO_2 specimens which were sintered at 1450°C using conventional sintering method.

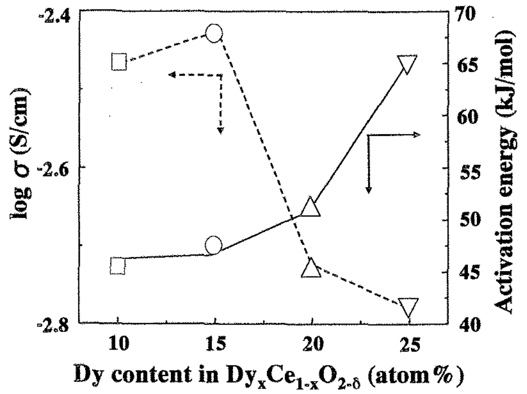


Figure 2 Relationship between electrolytic properties and Dy content in $Dy_xCe_{1-x}O_{2-\delta}$ which was fabricated using CS method, measurement temperature of conductivity: 500°C.

Conductivity increased with decreasing dopant Dy content as shown in Fig.2. Conductivity reached the maximum value at 15 atom% of Dy in the composition of $Dy_xCe_{1-x}O_{2-\delta}$. The tendency of conductivity corresponded to that of activation energy in Fig.2. To conclude of an influence of microstructure on electrolytic properties in Dy doped CeO_2, the densification behavior and electrolytic properties of $Dy_{0.2}Ce_{0.8}O_{1.9}$ and $Dy_{0.15}Ce_{0.85}O_{1.925}$ was examined.

Figure 3 shows the relative density as a function of the sintering time of CS after SPS. The relative density of $Dy_{0.2}Ce_{0.8}O_{1.9}$ sintered body was approximately 85% of theoretical density using SPS (1200°C, no holding time) process only. However, the relative density of sintered bodies reached 95% of theoretical density using the combined process of SPS and CS. The tendency of sintering behavior of 15DyDC specimens was the same in combined process of (SPS+CS) method. The relative density of aforementioned specimens reached 95% of theoretical density using the present combined process.

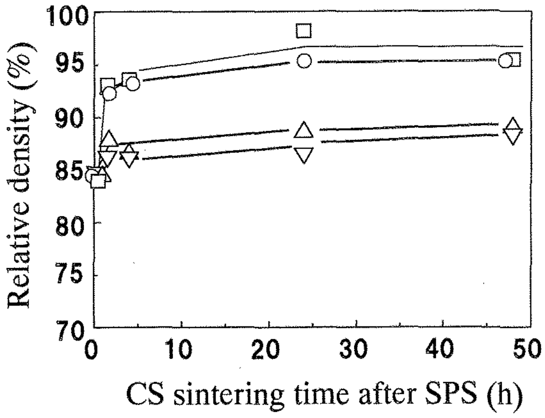


Figure 3 Relative density as a function of sintering time of CS after SPS, the relative density of specimen obtained by SPS: 85% of theoretical density. CS temperature; ▽: 1000°C, △: 1050°C, ○: 1100°C, □: 1150°C.

Figure 4 demonstrates relationship between electrolytic properties and average grain size of 20DyDC sintered bodies.

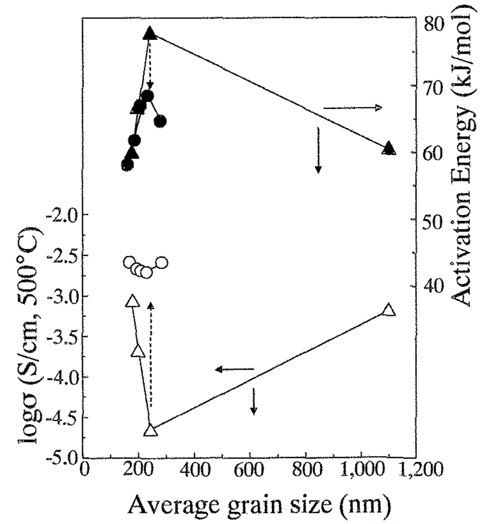


Figure 4 Relationship between electrolytic properties and average grain size of $Dy_{0.2}Ce_{0.8}O_{1.9}$ sintered bodies. Conductivity vs. average grain size;○: (SPS+CS) specimen, △: CS specimen. Activation energy vs. average grain size;●: (SPS+CS) specimen, ▲: CS specimen.

The conductivity in the specimens which were obtained by CS showed the curvature in the grain size dependence of conductivity. The conductivity decreased with decreasing grain size and reached the lowest value at an average grain size of 237nm. This tendency would be attributable to the space charge layer around the grain boundary in the sintered body. In contrast, the conductivity increased with decreasing grain size under 237nm. This suggested that the space charge layer with high resistivity is minimized around the grain boundary in this region. Since the change of conductivity is large when the grains are below 237nm then we suggest it is not all attributable to space charge changes. Other micro-structural features within the grain are also beginning to have an influence. Both change of the space charge layer width around grain boundary and the micro-structural features within the grain would lead to improvements in the conductivity that is observed in the sintered bodies. To improve the electrolytic properties, the combined process of SPS and CS was performed. As shown in Fig.4, the conductivity of $Dy_{0.2}Ce_{0.8}O_{1.9}$ with average grain size of 237nm was drastically improved by the present combined process. This tells us that an important factor for enhancement of conductivity is not only grain size. The important would be micro-structural feature in the specimen.

Figure 5 presents comparison of conductivity of 20DyDC and 15DyDC sintered bodies which were fabricated by the combined process of (SPS+CS).

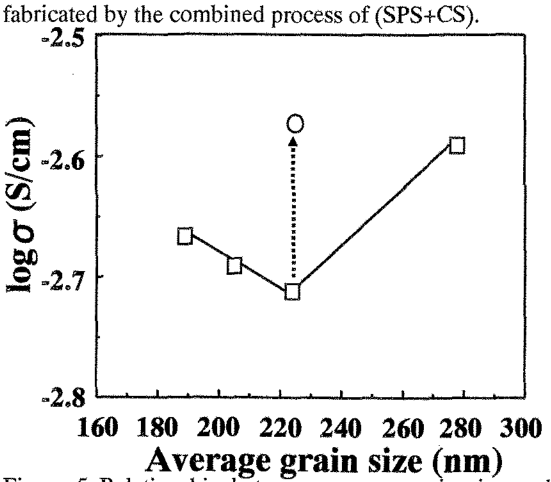
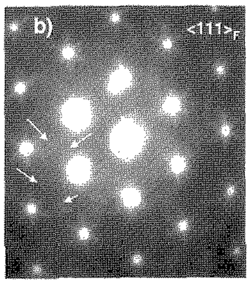


Figure 5 Relationship between average grain size and conductivity of ☐ : $Dy_{0.2}Ce_{0.8}O_{1.9}$ (SPS+CS) specimens, ○ : $Dy_{0.15}Ce_{0.825}O_{1.925}$ (SPS+CS) specimens, measurement temperature of conductivity : 500°C.

This indicates that the conductivity of Dy doped CeO_2 (SPS+CS) specimens with nano-grain size can be improved by a selection of optimum composition in Dy doped CeO_2 system on the basis of the results of Fig.2. It is expected that Dy doped CeO_2 (SPS+CS) specimens will be one of promising solid electrolytes for low temperature operation of fuel cells.

To conclude the influence of microstructure on conducting properties in Dy doped CeO_2 sintered bodies, the selected area electron diffraction patterns recorded from 20DyDC CS specimen with large grain size (1.1μm) and 20DyDC (SPS+CS) specimen with small grain size (280nm) were displayed in **Fig.6**. The diffuse scattering around extra reflection was observed in both patterns. The extra reflection was indexed on distorted pyrochlore structure by comparison between observed pattern and calculated pattern (Fig.6c). This tells us that Dy doped CeO_2 has micro-domain with distorted pyrochlore structure within the grain. It is concluded that the electrolytic properties is influenced by size of micro-domain. The micro-domain size would be minimized by the present combined process of (SPS+CS). It is expected that detail image analysis will clarify the structure of micro-domain. The carefull analysis will contribute to the development of Dy doped CeO_2 system.



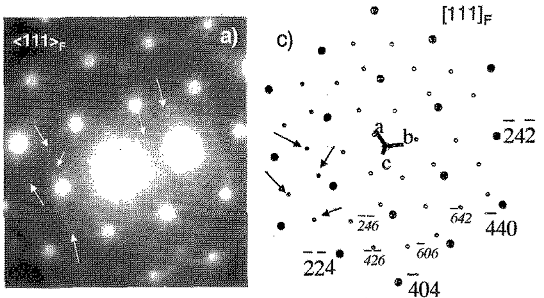


Figure 6 Selected area electron diffraction patterns recorded from a) $Dy_{0.2}Ce_{0.8}O_{1.9}$ CS specimen (1.1μm), b) $Dy_{0.2}Ce_{0.8}O_{1.9}$ (SPS+CS) specimen (280nm), and c) calculated combination pattern of $[111]_P$ and $[111]_F$. P indicates pyrochlore structure, F indicates fluorite structure, arrow indicates pyrochlore structure in fluorite structure.

SUMMARY

The combined process of (SPS+CS) was examined for development of Dy doped CeO_2 solid electrolytes for fuel cell applications. The electrolytic properties were improved using the present combined process of (SPS+CS). It is concluded that the size of micro-domain with distorted pyrochlore structure in Dy doped CeO_2 is minimized in the grain by the present combined process. It is expected that the careful observation will clarify the micro-structural features in (SPS+CS) specimens with high conductivity.

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