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Characteristics of samaria-doped ceria nanoparticles prepared by spray pyrolysis

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Abstract

Samaria-doped ceria (SDC) nanoparticles were prepared by spray pyrolysis. The means sizes of the samaria-doped ceria nanoparticles were controlled from 21 to 150 nm by changing the calcination temperatures between 700 and 1200 °C. The pellets formed from the SDC particles calcined at temperatures between 700 and 1000 °C had similar grain sizes between 0.75 and 0.82 μm. However, pellet formed from the SDC particles calcined at a temperature of 1200 °C had large grain size of 1.22 μm. The pellet formed from the SDC particles calcined at a temperature of 1000 °C had slightly smaller resistance of grain-boundary than those of the pellets formed from the SDC particles calcined at temperatures between 700 and 900 °C. However, the pellet formed from the SDC particles calcined at a temperature of 1200 °C had low resistance of grain-boundary. The pellet formed from the SDC particles calcined at a temperature of 1200 °C had conductivity of 44.65×10^{-3} S cm^{-1} at a measuring temperature of 700 °C that more twice than those of the pellets formed from the SDC calcined below 1000 °C.

Keywords: A. Powders: gas phase reaction; A. Powders: chemical preparation

1. Introduction

The trivalent rare-earth doped ceria has been extensively studied as electrolytes in low operating temperature solid oxide fuel cells (SOFCs) because of high ionic conductivity at low temperatures [1–4]. Especially, samarium doped ceria have the highest electrical conductivity because of the close ionic radius of Sm^{3+} compared to the radius of Ce^{4+} [5–7].

Samaria-doped ceria electrolyte should have high density and fine grain size at low sintering temperatures. The samaria-doped ceria particles with nanometer size can be densified at much lower temperature because of high surface energy of the nanoparticles, and expected to make it possible to provide fast densification kinetics, finer microstructure and better properties of the sintered materials contrast to the bulk ones [8–11]. Many solution based techniques have been successfully employed for preparation of nanocrystalline Sm-doped CeO_2, such as hydrothermal, mimic alkoxide, micro-emulsion, sol–gel, precipitation, glycine-nitrate combustion, hydrazine, and spray hydrolysis [12–16]. However, the mean sizes and morphologies of the ceria nanoparticels are affected by the preparation processes. The mean sizes and morphologies of the ceria nanoparticles are important factors in controlling the final ceramic microstructure.

In this study, samaria-doped ceria (SDC) particles were prepared by spray pyrolysis. The precursor particles prepared by spray pyrolysis were calcined at temperatures between 700 and 1200 °C. The mean sizes of the SDC nanoparticles are gradually increased with an increase of the calcinations temperatures. The effects of calcination temperatures of samaria-doped ceria particles on the properties of sintered bodies were investigated.

2. Experimental

The details of the preparation procedure and analysis method of SDC particles are given in the schematic diagram as shown in Fig. 1. The precursor particles with hollow structure

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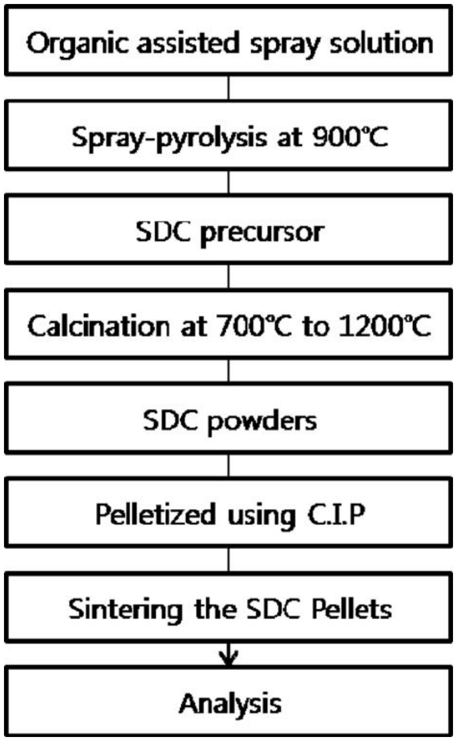


Fig. 1. Schematic diagram of preparation and analysis of SDC pellets.

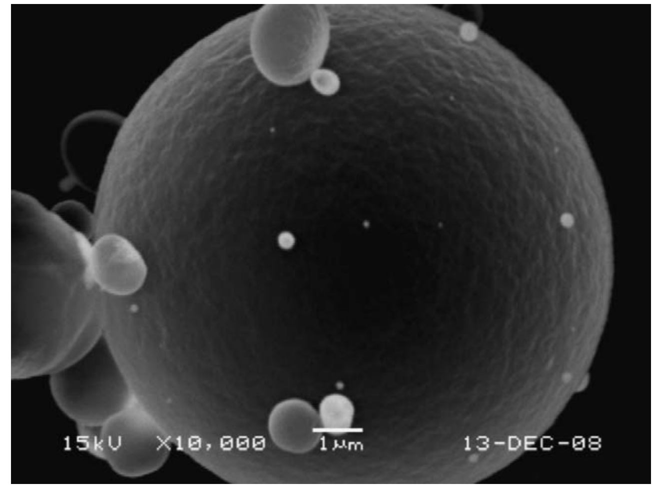


Fig. 2. SEM image of SDC precursor powders prepared by spray pyrolysis.

were prepared by spray pyrolysis from spray solution with ethylene glycol. Ethylene glycol was used as additive to the spray solution to change the morphology of the as-prepared particles obtained by spray pyrolysis. The spray pyrolysis system consists of droplet generator, quartz reactor, and particle collector. A 1.7 MHz ultrasonic spray generator having six vibrators was used to generate a large amount of droplets, which are carried into the high-temperature tubular reactor by a carrier gas. Droplets and particles evaporated, decomposed, and/or crystallized in the quartz reactor. The length and diameter of the quartz reactor are 1200 and 50 mm, respectively. Cerium and samarium nitrates were used as the sources of Ce and Sm components. The concentration of cerium and samarium nitrates was fixed at 0.3 M. The doping concentration of samarium was fixed to 10 mol% of cerium. The flow rate of air used as carrier gas was 20 l/min. The precursor particles obtained by spray pyrolysis were calcined in the box furnace maintained at temperatures between 700 and 1200 °C for 2 h. The calcined particles were pressed into pellets with an uniaxial hydraulic, followed by a cold-isostatic press at 250 MPa. The sintering temperature of the pellet was 1400 °C and the pellets were cooled naturally to room temperature while furnace power was off.

The crystal structures of the calcined SDC particles were studied by X-ray diffraction (XRD, RIGAKU, D/MAX-RB) with Cu Kα radiation ($\lambda = 1.5418$ Å). The morphological characteristics of the particles were investigated using scanning electron microscopy (SEM, JEOL, JSM 6060) and transmission electron microscope (TEM, FEI, TECHNAI 300K). The relative density was evaluated by applying the Archimedes principle. The grain size and microstructure of the pellets were observed by SEM. The ionic conductivity was determined via electrochemical impedance spectroscopy at temperature ranges between 400 and 700 °C in air atmosphere.

3. Results and discussions

The morphology of the precursor powders prepared by spray pyrolysis is shown in Fig. 2. The precursor powders had large size, hollow and thin wall structure. Gas evolution generated by the decomposition of the ethylene glycol caused the particles with hollow and thin wall structures.

Fig. 3 shows the SEM and TEM images of the SDC powders calcined at temperatures between 700 and 1200 °C. The spherical shapes of the precursor powders were maintained after calcinations at temperatures between 700 and 1000 °C. The spherical shape of the precursor powders disappeared at a calcinations temperature of 1200 °C. However, crystal growth of the SDC powders increased with an increase of the calcinations temperature. The mean size of the primary particles measured from the TEM images are shown in Fig. 4. The mean sizes of the primary particles were changed from 21 to 150 nm when the calcinations temperatures were changed from 700 to 1200 °C. The crystal growth of the particles decreased the aggregation degree of the primary particles.

Fig. 5 shows the XRD patterns of the precursor and calcined SDC powders. The precursor powders directly prepared by spray pyrolysis had crystal structure of pure ceria. On the other hand, the XRD pattern of the precursor particles had broad peaks because of short residence time of the particles inside the hot wall reactor as 0.6 s. The peak intensities of XRD patterns increased with an increase of the calcination temperature by crystal growth of the particles. The mean crystallite size of the precursor particles calculated by Scherrer's equation was 8.4 nm. However, the mean crystallite sizes of the calcined SDC particles were changed

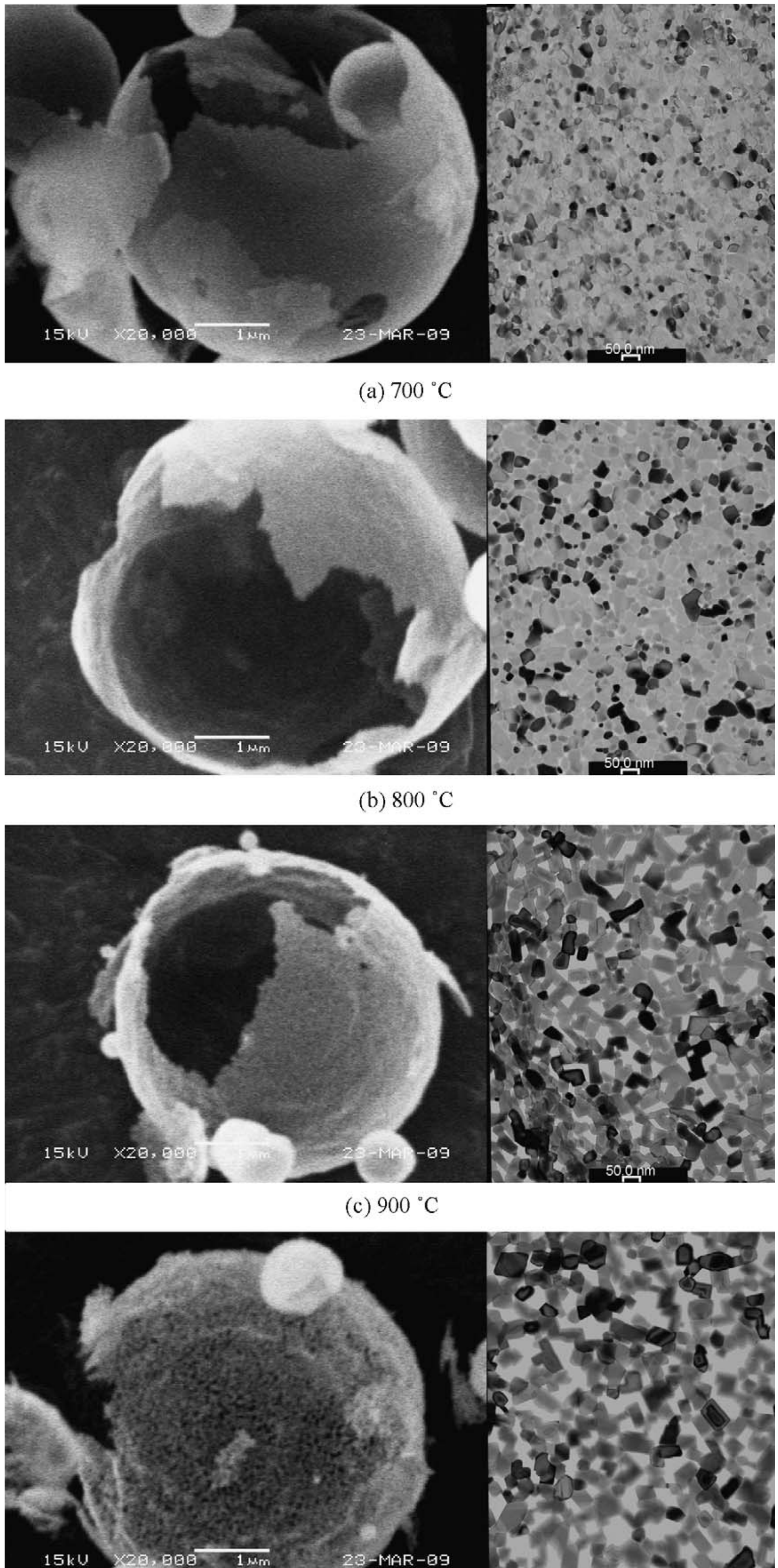
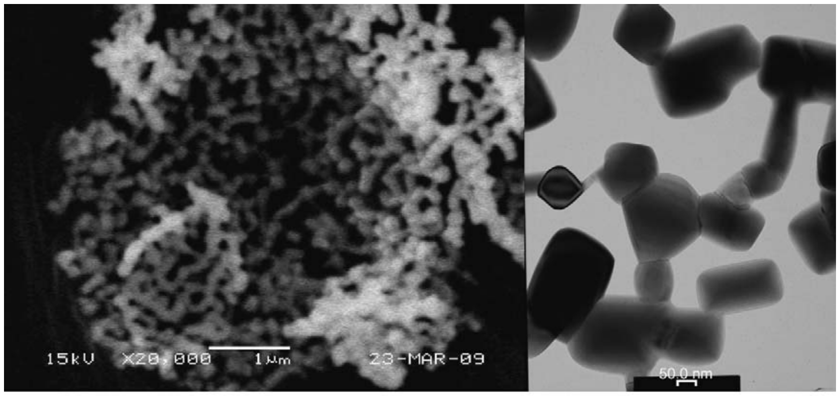


Fig. 3. SEM and TEM images of SDC powders calcined at various temperatures (left side: SEM image; right side: TEM image).



(e) 1200 °C

Fig. 3. (*Continued*).

from 19.0 to 59.7 nm when the calcination temperatures were changed from 700 to 1200 °C.

The SDC particles calcined at various temperatures were ground by hand using agate mortar. The pellets formed from the ground SDC particles were sintered at a temperature of 1400 °C. Fig. 6 shows the SEM images of the sintered SDC pellets. The sintered pellets had dense structures and regular grain sizes irrespective of the calcinations temperatures of the SDC particles. The mean grain sizes and relative densities of the pellets are summarized in Table 1. The pellets formed from the SDC particles calcined at temperatures between 700 and 1000 °C had similar grain sizes between 0.75 and 0.82 μm. However, pellet formed from the SDC particles calcined at a temperature of 1200 °C had large grain size of 1.22 μm. The relative densities of the pellets had similar values irrespective of the calcinations temperatures of the SDC particles.

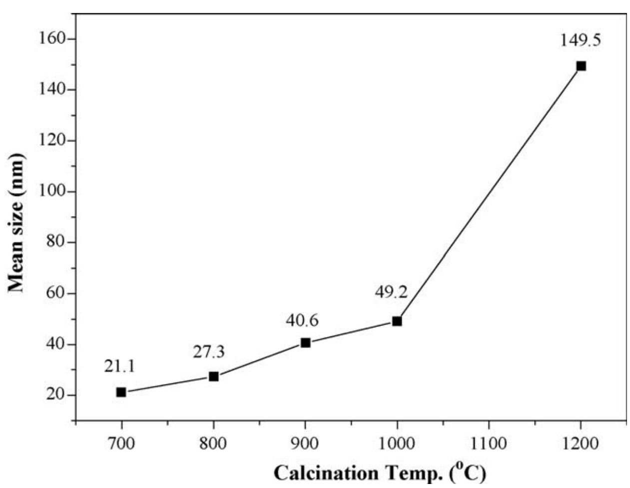


Fig. 4. Mean sizes of SDC powders calcined at various temperatures.

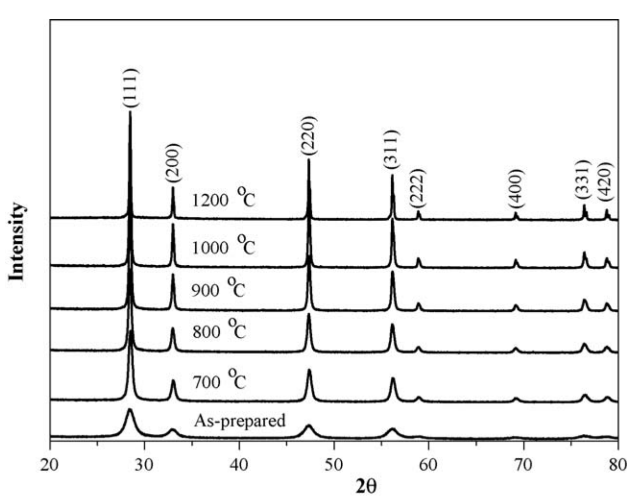
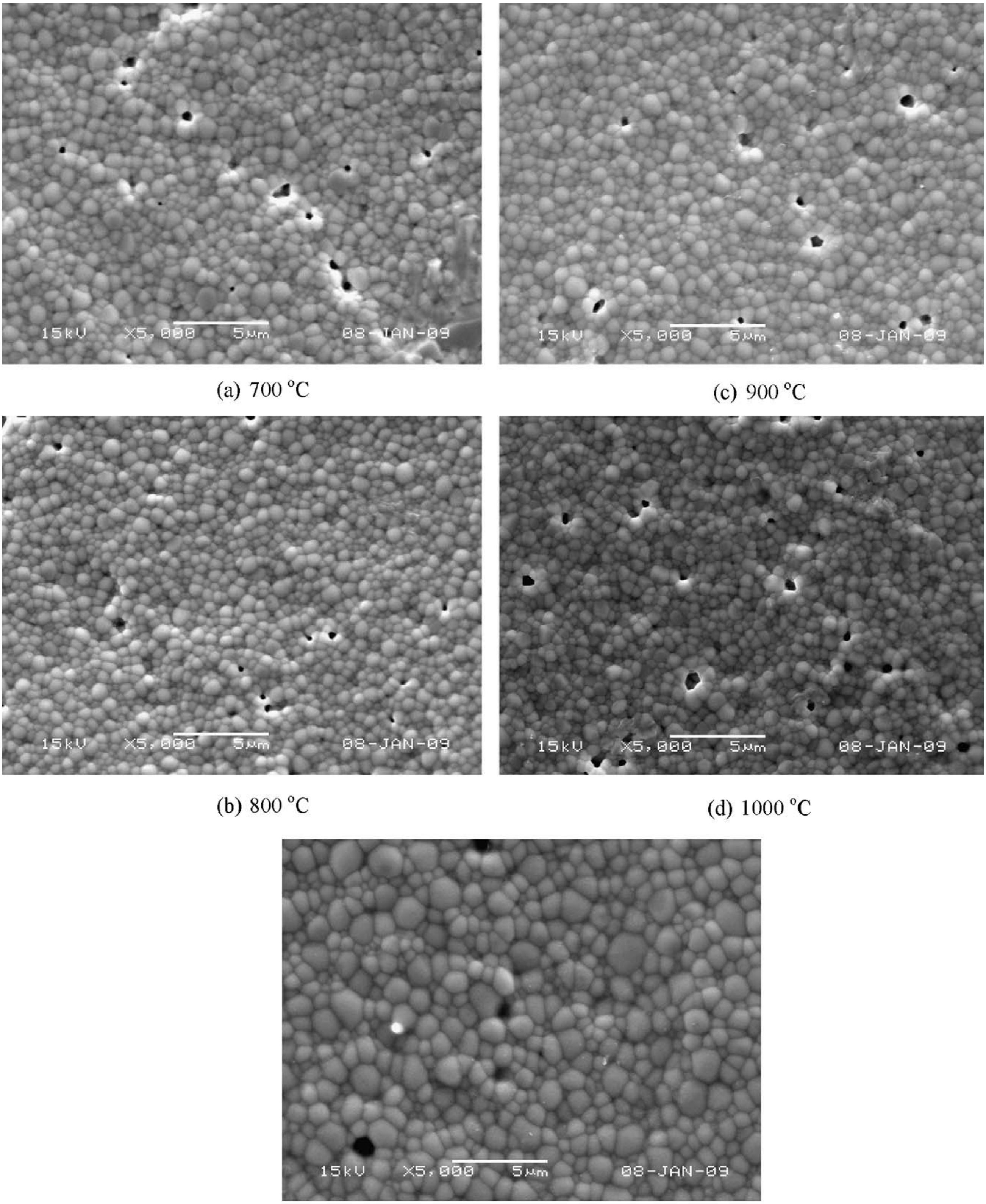


Fig. 5. XRD patterns of SDC powders calcined at various temperatures.

The complex impedance spectra of SDC pellets measured at a temperature of 400 °C in air atmosphere are shown in Fig. 7. The impedance spectra represent resistivity of internal grain and grain-boundary from half-circle in two regions. The first half-circle in left side means resistivity of internal grain. The resistivity of internal grains of the pellets had similar values irrespective of the calcination temperatures of the SDC powders. However, the grain-boundary resistivity, the second half-circle in right side, was affected by calcination temperatures of SDC particles. It can be observed, from the data of Table 1, that the grain-boundary resistivity decreased with increasing of grain size from 0.75 to 1.22 μm. The SDC pellets obtained from particles calcined between 700 and 900 °C had small grain size which exhibits a fairly large grain-boundary resistivity. However, the SDC pellet obtained from particles calcined at 1200 °C had the biggest grain size as 1.22 μm, thus smallest percentage of grain-boundary region which result in the smallest grain-boundary resistivity.

The differences in the grain-boundary resistivity of the SDC pellets affect the total conductivity. The resistivity were converted into conductivity value and plotted in Fig. 8. The measured conductivities are summarized in Table 1. The conductivities and activation energies of SDC pellets were affected by the calcination temperatures of the SDC particles. The pellet formed from the SDC particles calcined at a temperature of 1200 °C had higher conductivities than those of the pellets formed from the SDC particles calcined at temperatures below 1000 °C at all measuring temperatures. The pellet formed from the SDC particles calcined at a



(a) 700 °C (c) 900 °C

(b) 800 °C (d) 1000 °C

(e) 1200 °C

Fig. 6. SEM images of SDC pellets formed from the SDC powders calcined at various temperatures.

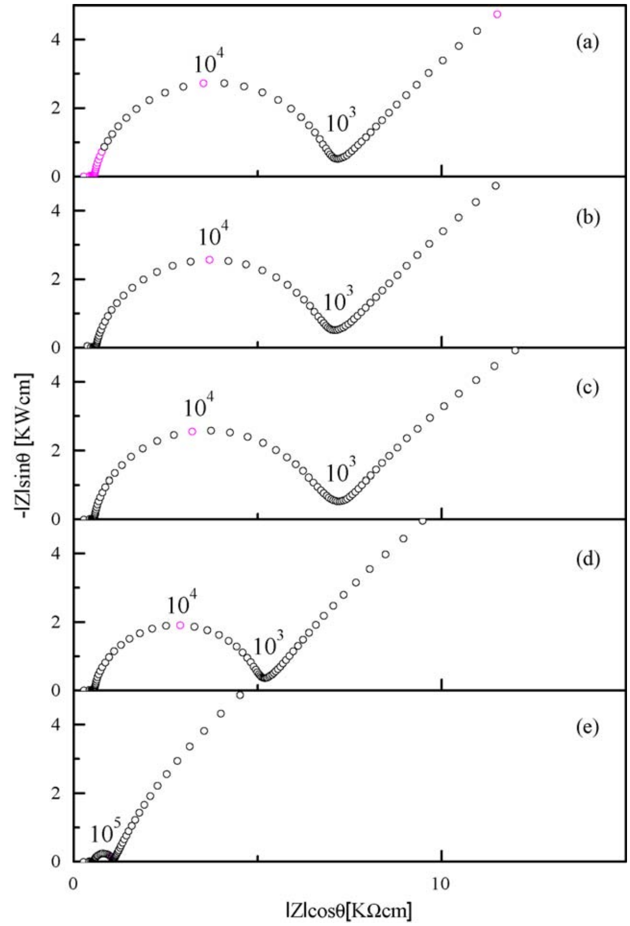


Fig. 7. Complex impedance spectra of SDC pellets formed from the SDC powders calcined at various temperatures: (a) 700 °C, (b) 800 °C, (c) 900 °C, (d) 1000 °C, and (e) 1200 °C.

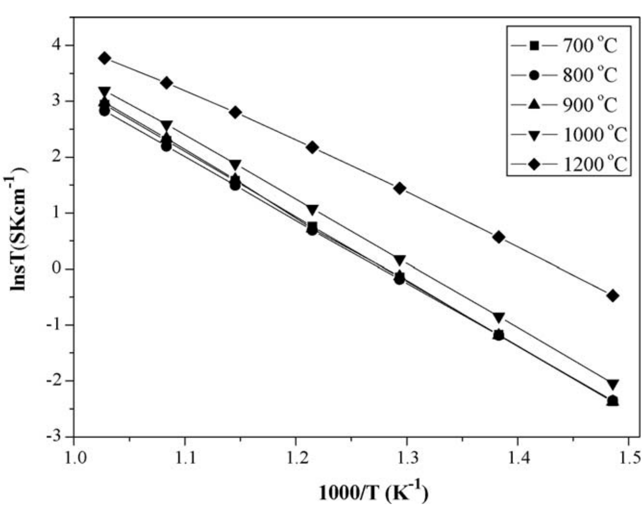


Fig. 8. Arrhenius plots for conductivities of SDC pellets formed from the SDC powders calcined at various temperatures.

temperature of 1200 °C had conductivity of 44.65×10^{-3} S cm^{-1} at a measuring temperature of 700 °C that more twice than those of the pellets formed from the SDC calcined below 1000 °C. The low resistance of grain-boundary of the pellet formed from the SDC particles calcined at a temperature of 1200 °C improved the conductivities of the pellets.

Table 1
Characteristics of SDC pellets formed from the SDC powders calcined at various temperatures.

Calcination temp. (°C)	Grain size (μm)	Relative densities (%)	Conductivity ($\times 10^{-3}$ S cm^{-1}) at 700 °C	Activation energy (eV)
700	0.75	98.9	19.43	0.997 ± 0.001
800	0.72	99.1	17.35	0.973 ± 0.002
900	0.82	97.5	20.19	1.006 ± 0.006
1000	0.76	98.7	24.89	0.986 ± 0.003
1200	1.22	98.9	44.65	0.798 ± 0.001

4. Conclusions

Samaria-doped ceria particles were prepared by spray pyrolysis. The precursor particles with hollow and thin wall structure obtained by spray pyrolysis turned to the nanometer particles after calcinations at temperatures between 700 and 1200 °C. The mean sizes and mean crystallite sizes of the primary SDC particles increased with an increase of the calcinations temperatures. The calcinations temperatures of the SDC particles strongly affected the characteristics of the pellets sintered at a temperature of 1400 °C. The pellet formed from the SDC particles calcined at a temperature of 1200 °C had large grain size and had high conductivity because of low resistance of grain-boundary of the pellet.

Acknowledgement

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