Low-temperature fabrication and electrical property of 10 mol% Sm₂O₃-doped CeO₂ ceramics

Yarong Wanga,*, Toshiyuki Moria, Ji-Guang Lib, Yoshiyuki Yajimab

aEco-materials Research Center, National Institute for Materials Science, Namiki 1-1, Tsukuba, Ibaraki 305-0044, Japan
bAdvanced Materials Laboratory, National Institute for Materials Science, Namiki 1-1, Tsukuba, Ibaraki 305-0044, Japan

Received 26 March 2003; revised 15 May 2003; accepted 16 June 2003

Abstract

Ten mol% Sm₂O₃-doped CeO₂ solid-solution (20SDC) powders have been synthesized via carbonate coprecipitation using ammonium hydrogen carbonate (AHC) and urea as the precipitants, respectively. Characterizations were achieved by elemental analysis, X-ray diffractometry, differential thermal analysis/thermogravimetry, and FESEM. An amorphous hydroxyl carbonate precursor (Ce,Sm)(OH)₂CO₃·2H₂O having nanosized (~10 nm) spherical particles was formed with AHC, while a mixture of crystalline (Ce,Sm)₂(CO₃)₂(OH)·H₂O and (Ce,Sm)₂O(CO₃)₂·H₂O phases exhibiting irregular particle morphologies was obtained with urea. Both the precursors convert to oxide solid solutions without any phase detected corresponding to Sm₂O₃ during calcination. The oxide powder processed via the AHC method can be sintered to ~99% of the theoretical at a low temperature of 1200 °C, due to the good dispersion and ultrafine size (~15 nm) of the particles, while that from the urea method can only reach ~67.2% dense at the same temperature. Electrical conductivity of the densified ceramic was measured in air in the range 400–700 °C by the DC three-point method, and an activation energy of ~60.5 kJ/mol was derived from the experimental data.

Keywords: Doped-ceria; Ceramics; Synthesis; Coprecipitation; Electrical conductivity

1. Introduction

Ceria (CeO₂) is a fluorite-structured ceramic material (space group Fm₃m) that forms extensive solid solutions with a variety of alien cations. With aliovalent (alkaline-earth or rare-earth) dopants, oxygen vacancies are created in the CeO₂ lattice for charge compensation, and the resultant oxide solid-solutions are valuable for applications as an oxygen buffer in the automotive three-way catalysts, as a promoter for gas phase oxidation/reduction reactions, and as solid electrolytes or anodes in intermediate-temperature solid oxide fuel cells (SOFCs) [1]. The Sm₂O₃/CeO₂ system (SDC) shows the highest electrical conductivity among the doped-ceria materials, since Sm³⁺-doping induces the least distortion of the parent lattice [2].

The traditional ceramic method for fabricating dense SDC electrolytes involves two steps: extensively heat-treating a CeO₂/Sm₂O₃ powder mixture at ~1300 °C to yield a single phase solid-solution and subsequently refining the solid-solution powder at even higher temperatures of ~1700–1800 °C [3,4]. A handful of wet-chemical processing techniques, aimed at promoting cation homogeneity and lowering the sintering temperature, have been reported for SDC during recent years, such as oxalate coprecipitation [5,6] and hydrothermal treatment [7]. The wet-chemically derived powders generally show better reactivity than those via solid-state reaction, but still require a typical sintering temperature of 1400–1600 °C for the material to achieve ~99% of the theoretical. The problem seems to be severe agglomeration and undesirable particle morphologies of the resultant powders.

The properties of a wet-chemically derived oxide powder are known to heavily depend upon the characteristics of its precursor, exhibiting the existence of some sort of 'genetic' relationship. Carbonates may serve as excellent precursors for highly sinterable oxides [8,9] since carbonates, unlike most hydroxides, are non-gelatinous and show much weaker agglomeration after drying. The carbonate coprecipitation method is expected...
to be especially effective for rare-earth doped CeO$_2$, as rare-earths readily form carbonate solid solutions [10], which allows intimate (atomic level) mixing of the cations in the precursor and low-temperature formation of the aimed phase. Carbonate coprecipitation can be performed with a variety of water-soluble carbonate salts as the precipitant, among which ammonium hydrogen carbonate (NH$_4$HCO$_3$ hereafter referred to as AHC) and urea (CO(NH$_2$)$_2$) are preferred, since they do not bring any contaminating alien cations into the system. AHC was reported to be an excellent precipitant for the preparation of ultrafine $\alpha$-Al$_2$O$_3$ powders via chemical precipitation [11,12]. Through reacting aqueous solutions of AHC and alum ($\text{NH}_4\text{Al(SO}_4\text{)}_2\cdot n\text{H}_2\text{O}$), ammonium aluminum carbonate hydroxide (NH$_4$Al(OH)HCO$_3$) is formed under certain conditions, which then converts to $\alpha$-Al$_2$O$_3$ via thermal decomposition at temperatures $\approx$1150 °C [13]. Since the ammonium aluminum carbonate is non-gelatinous, the resultant $\alpha$-Al$_2$O$_3$ powder was shown to have better sinterability than those via hydroxyl precipitation [14]. Nonetheless, AHC has not been reported on the preparation of mixed rare-earth oxides, and the possible application of AHC to synthesizing well-sinterable Sm-doped CeO$_2$ nanopowders still needs investigation. On the other hand, a variety of ceramic powders have been prepared via homogeneous precipitation with urea. Due to the slow hydrolysis of urea (at temperatures $\approx$83 °C), it is possible to exert control over the nucleation and growth process of the particles, and in most cases, the resultant particles are well defined in morphologies (usually submicron-sized). Though single oxides of the rare-earths have been successfully synthesized via this method [15–17], the report on the preparation of mixed rare-earth oxides (such as Sm-doped CeO$_2$) has been very rare. So in this paper we have tried these two carbonate coprecipitation routes to synthesize 10 mol% Sm$_2$O$_3$-doped CeO$_2$ (20SDC) nano-oxides, and the results are compared with each other. Nanocrystalline 20SDC powders, which can be fully densified up to a low temperature of $\approx$1200 °C, have been obtained via the AHC method. Here we report the synthesis, characterization, sintering behavior, and the electrical conductivity of these carbonate-derived 20SDC oxides.

2. Experimental procedure

2.1. Powder synthesis

Cerium nitrate hexahydrate (Ce(NO$_3$)$_3$·6H$_2$O, $>99.99$ pure), samarium nitrate hexahydrate (Sm(NO$_3$)$_3$·6H$_2$O, $>99.99\%$ pure), ammonium hydrogen carbonate (NH$_4$HCO$_3$, ultrahigh purity), and urea (CO(NH$_2$)$_2$, ultrahigh purity) were used as the starting materials (all purchased from Kanto Chemical Co., Inc., Tokyo, Japan). The chemicals were used as received without further purification.

The stock solution of starting salts was made by dissolving the nitrates into distilled water. To ensure that Ce$^{3+}$ and Sm$^{3+}$ cations would be mixed at the stoichiometry of 4:1 molar ratio, cation contents of the mixed solution were assayed by the Inductively Coupled Plasma (ICP) spectrophotometric technique and further adjusted. The final concentration of the stock solution was 0.12 M for Ce$^{3+}$.

In the AHC method, the precursor precipitate was produced by adding dropwise 300 ml of the mixed nitrate solution into 300 ml of a 0.5 M AHC solution kept at 60 °C under mild stirring. After aging at the reaction temperature for 1 h, the resultant suspension was filtered via suction filtration, washed four times with distilled water, rinsed with ethanol (except those for chemical analysis and Differential thermal analysis/thermogravimetry analysis), and dried at room temperature under flowing nitrogen gas for $>24$ h. The dried cake was lightly crushed with a zirconia mortar and pestle, and then calcined at various temperatures for 2 h under flowing oxygen.

In the urea method (urea-based homogeneous precipitation), an aqueous solution containing 0.5 M urea, 1.2 $\times$ $10^{-2}$ M Ce$^{3+}$, and 3 $\times$ $10^{-3}$ M Sm$^{3+}$ was heated to $\approx$90 °C within 1 h and then kept at the temperature for another 2 h to effect precipitation. The resultant suspension was treated as described in the AHC method.

2.2. Powder characterization

Composition of the precursor was determined by chemical analysis. Cation contents were analyzed by the ICP spectrophotometric method with an accuracy of 0.01 wt%; carbon content was assayed on a simultaneous carbon/sulfur determinator with a detection limit of 0.01 wt% (Model CS-444LS, LECO, St Joseph, MI, USA); NH$_4$ content was determined by the Inductively Coupled Plasma titrimetric method with an experimental error of $\pm$0.1 wt%.

Phase identification is performed via X-ray diffractometry (XRD) on a Rigaku RINT 2200HF$^+$ Ultima$^+$ X-ray diffractometer (Rigaku, Tokyo, Japan) operating at 40 kV/40 mA using monochromatized Cu K$\alpha$ radiation. Diffractions are recorded by continued scanning with a speed of 1° 2θ/min. Lattice parameter of the 20SDC solid solution is calculated with the LCR2 program [18]. Crystallite sizes of the calcined powders are calculated by the X-ray line broadening technique from the Scherrer equation.

DTA/TG of the dried precursor is made on a TG-DTA analyzer (EXSTASR6200, SEIKO, Tokyo, Japan) in flowing air with a heating rate of 10 °C/min, using platinum crucible as the sample container and alpha-alumina as the reference. Particle morphology and agglomeration state of the synthesized powders were observed via field-emission
scanning electron microscopy (FESEM) (Model S-5000, Hitachi, Tokyo, Japan). The sample was ultrasonically dispersed into ethanol, and the suspension was spread on the surface of a silicon plate. After drying, the sample was coated with a thin layer of osmium for conductivity.

2.3. Compaction, sintering, microstructure, and electrical conductivity of 20SDC

Powders for sintering were first dry-pressed manually into pellets (~10 MPa) in a tungsten carbide die and then isostatically pressed to 300-MPa pressure. Densification behavior of the powder compacts was monitored in air up to 1500 °C by means of dilatometry performed on a thermal mechanical analyzer (Model TMA 1700, Rigaku, Tokyo, Japan) with a heating rate of 10 °C/min and a cooling rate of 20 °C/min. Density of the powder compact, \( \rho \), at any temperature, was determined from the green density, \( \rho_0 \), and the measured linear shrinkage, \( \Delta L/L_0 \), using the equation

\[
\rho = \frac{\rho_0}{(1 - \Delta L/L_0)^n}
\]

where \( L_0 \) is the initial sample length and \( \Delta L = L_0 - L \), where \( L \) is the instantaneous sample length. The green density of a powder compact was calculated from its weight and geometric dimensions. Relative densities were then obtained by dividing \( \rho \) with the theoretical density of the material. The conventional ramp-and-holding sintering method was also used to densify the 20SDC oxides. In this case, the powder compacts were heated in a tube furnace at 5 °C/min to the selected temperature and then cooled down after being soaked for 4 h.

Microstructure of the sintered body was observed via FESEM after polishing, thermal etching, and Os coating. The average grain size of the sintered material was determined by the linear intercept method.

Electrical conductivity of the densified 20SDC ceramics were measured in air by the DC three-point method in the temperature range 400–700 °C, after applying Pt electrodes to both sides of the sintered body at 1000 °C for 2 h in air. Dimensions of the specimen were ~10 mm in diameter and ~1.5 mm in thickness.

3. Results and discussion

3.1. Powder synthesis and characterization

The following equilibria were expected in the precipitant solution in the AHC method:

\[
\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-
\]

\[
\text{NH}_4\text{HCO}_3 \rightleftharpoons \text{NH}_4^+ + \text{HCO}_3^-
\]

\[
\text{NH}_4^+ + \text{OH}^- \rightleftharpoons \text{NH}_2\text{OH} \rightleftharpoons \text{H}_2\text{O} + \text{NH}_3 \ (g)
\]

\[
\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}
\]

and

\[
\text{H}^+ + \text{HCO}_3^- \rightleftharpoons \text{H}_2\text{CO}_3 \rightleftharpoons \text{H}_2\text{O} + \text{CO}_2 \ (g)
\]

On the other hand, urea is known to undergo hydrolysis in an aqueous solution at temperatures >83 °C to yield ammonium and cyanate ions [19]:

\[
\text{H}_2\text{N} - \text{CO} - \text{NH}_2 \rightleftharpoons \text{NH}_4^+ + \text{OCN}^-
\]

The cyanate ions may undergo further hydrolysis, with the reaction pathways depending on the solution pH:

\[
\text{OCN}^- + 2\text{H}^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3^+ + \text{CO}_2 \ (g)
\]

in a neutral or basic solution

\[
\text{OCN}^- + \text{OH}^- + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3 + \text{CO}_3^{2-}
\]

Apparently the two precipitation systems used in this work contain similar ionic species, although their concentrations may vary between the two methods.

On the other hand, rare-earth (RE) cations are known to undergo weak hydration and slight hydrolysis in water to form complex species [20]:

\[
\text{RE}([\text{H}_2\text{O}]_n)^{3+} + \text{H}_2\text{O} \rightleftharpoons [\text{RE(OH)}(\text{H}_2\text{O})_{n-1}]^{2+} + \text{H}_2\text{O}^+
\]

where \( n \) is the coordination number of the RE\(^{3+}\) cations. The tendency of hydrolysis is dependent on the ionic radius of RE\(^{3+}\), and increases with decreasing ionic size. During precipitation, the complexes formed in Eq. (10) are reacted with carbonate anions and other supporting ionic species generated through Eqs. (2)–(9) to form precipitates, and the final composition should assure that Ce\(^{3+}\) and Sm\(^{3+}\) cations have the lowest solubilities in the solution under the present precipitation conditions.

Elemental analysis confirmed that the precursors from the two systems are both stoichiometric (Ce\(^{3+}\):Sm\(^{3+}\) = 4:1) within the accuracy of the analysis method (0.01 wt%). The precursors contain considerable amounts of carbon but nearly no NH\(_2\) and NO\(_3\) (below the detection limits), indicating that the latter two species are non-precipitating and the precursors are primarily carbonates. We previously reported that ammonium rare-earth double carbonates ([(NH\(_4\))\(_x\)Ce\(_{0.25}\)Sm\(_{0.75}\)CO\(_3\))\(_{1.875+x/2}\) · yH\(_2\)O, \( x \leq 1 \) and \( y \leq 2 \)) are produced with ammonium carbonate (hereafter referred to as AC, (NH\(_4\))\(_2\)CO\(_3\)) [8,21] under conditions similar to those used in the AHC method. The discrepancies in precursor compositions may arise from the different solution pH (~9.5 for the AC method, and ~7.0 for the AHC method, and ~5.5 for the urea method), NH\(_4\)\(^+\) concentration (the highest for the AC method), and CO\(_3^{2-}\) concentration (the highest for the AC method, as high solution pH favors CO\(_3^{2-}\)).
Fig. 1 shows XRD patterns of the powders prepared with AHC. The as-synthesized precursor is essentially amorphous to X-rays. Elemental analysis on this unknown precursor yields ~43.9 wt% of Ce\(^{3+}\), 11.8 wt% of Sm\(^{3+}\), and ~4.7 wt% of C. Assuming that all the carbon are from CO\(_3\)\(^{2-}\), such a result conforms to a Ce\(^{3+}\):Sm\(^{3+}\):CO\(_3\)\(^{2-}\) molar ratio of 0.8:0.2:1.0. Considering molecular electrical neutrality, composition of this precursor may be expressed as Ce\(_{0.8}\)Sm\(_{0.2}\)(OH)CO\(_3\)·2H\(_2\)O, where the molecular water was determined from the weight contents of the analyzed elements in the formulae. Crystallization of the powder occurs at a minimum temperature of 300 °C upon calcination, and major diffraction peaks corresponding to the fluorite-structure of CeO\(_2\) (JCPDS: 34-394) appeared. Apparently, oxidation of Ce\(^{3+}\) cations to Ce\(^{4+}\) has occurred up to 300 °C during calcination (cerium has a valence of 3 + in the starting salt solution and in the dried precursors). Continuous refinements in peak shapes and intensities were observed along with an increase in the calcination temperature, indicating crystallite growth. Crystalline phase corresponding to Sm\(_2\)O\(_3\) was not found at any calcination temperature, suggesting an intimate mixing of Ce\(^{3+}\) and Sm\(^{3+}\) cations in the precursor. Indeed, lanthanides readily form carbonate or hydroxyl carbonate solid-solutions among each other [10], due to their similar chemical properties. The lattice parameter of the 20SDC oxide calcined at 1000 °C was determined to be \(a = 0.54340 \pm 0.00002\) nm, using a computer program based on the Rietveld method. Apparently, Sm\(^{3+}\) doping induces an expansion in the unit cell of CeO\(_2\) (\(a = 0.541134(12)\) nm). Assuming that the Sm\(^{3+}\) cations are homogeneously distributed in the CeO\(_2\) lattice and...
occupy the Ce$^{3+}$ sites to form a solid-solution of Ce$_{0.8}$Sm$_{0.2}$O$_{1.9}$. X-ray density of the 20SDC solid-solution, $d_{th}$, was calculated to be 7.146 g/cm$^3$ according to the following equation

$$d_{th} = 4[(1 - x)M_{Ce} + xM_{Sm} + (2 - x/2)M_O]/a^3N_A$$  

(11)

where $x = 0.2$, $a$ is the lattice constant of the solid solution at room temperature; $N_A$, the Avogadro constant; $M$ denotes the atomic weight.

Fig. 2 shows XRD patterns of the precursor synthesized with urea and its calcination products. Unlike its counterpart, the precursor is highly crystalline, and was indexed to a mixture of (Ce,Sm)$_2$(CO$_3$)$_2$(OH)$_2$·H$_2$O (JCPDS: 46-0369) and (Ce,Sm)$_2$O(CO$_3$)$_2$·H$_2$O (JCPDS: 43-0602) phases. The formation of this phase mixture is due to the partial hydrolysis of the already less hydrolyzable Ce$^{3+}$ and Sm$^{3+}$ cations (due to their larger ionic size) under the low solution pH (~5.5) of the precipitation system (acidic condition retards hydrolysis further). The hydroxyl carbonate was formed via the reaction between the hydrolyzed species and CO$_3^{2-}$ anions

$$2[(Ce,Sm)(OH)(H_2O)_{n-1}]^{2+} + 2CO_3^{2-}$$
$$\rightarrow (Ce,Sm)_2(OH)_2(CO_3)_2\cdot H_2O + (2n - 3)H_2O$$  

(12)

while the oxycarbonate phase was formed via the reaction of non-hydrolyzed cations with CO$_3^{2-}$:

$$2[(Ce,Sm)(H_2O)_n]^{3+} + 3CO_3^{2-}$$
$$\rightarrow (Ce,Sm)_2O(CO_3)_2\cdot H_2O + CO_2 + (2n - 1)H_2O$$  

(13)

Eq. (13) only presents the mass balance of the process. The production of the oxy-ion by the decomposition of carbonate anion is more likely than the usual dehydration reaction $2OH^- \rightarrow O^{2-}$ [15]. Crystalline Ce$_2$O(CO$_3$)$_2$·H$_2$O

![Fig. 2. XRD patterns of the precursor synthesized with urea and its calcination products.](image-url)
phase was similarly obtained from cerium nitrate solution at the presence of urea [15]. Besides, compared with the AHC method, in which the precursor is largely amorphous, the high reaction temperature in the urea method is responsible for the crystallization of the precursor.

The phase mixture obtained with urea decomposes into oxide at temperature $\approx 300^\circ\text{C}$. Again, any phase corresponding to samarium oxide was not detected with XRD at any calcination temperature up to 1000 $^\circ\text{C}$, suggesting the existence of Sm$^{3+}$ in the form of solid solution. No appreciable difference was observed in the lattice parameters of the powders prepared by the two methods and calcined at the same temperature of 1000 $^\circ\text{C}$.

Thermal behaviors of the two precursor powders have been investigated by DTA/TG, and the results were compared in Fig. 3. Both the precursors decompose to oxide via two distinct stages (Fig. 3b), producing two corresponding endothermic peaks on the DTA curve (Fig. 3a). For the powder synthesized with AHC, the calculated weight loss for complete decomposition of $(\text{Ce},\text{Sm})(\text{OH})\text{CO}_3\cdot2\text{H}_2\text{O}$ ($\approx 32.4\%$) is close to the value revealed by TG ($\approx 33.13\%$). The weight loss at temperatures below $\approx 300^\circ\text{C}$ and the endotherm peaking at $\approx 120^\circ\text{C}$ is mainly due to dehydration (the loss of crystal water) and dehydroxylization (the decomposition of OH groups) of the basic carbonate to form oxycarbonate intermediates. Rare-earth carbonates were known to decompose via oxycarbonate intermediate phases [22]. According to the weight loss ($\approx 16.3\%$), the intermediate composition of the powder at $\approx 300^\circ\text{C}$ was calculated to be $(\text{Ce},\text{Sm})_2\text{O}(\text{CO}_3)_2$. The second stage of decomposition with an endothermic peak centering at $\approx 324^\circ\text{C}$ corresponds to the further decomposition of $(\text{Ce},\text{Sm})_2\text{O}(\text{CO}_3)_2$ to form oxide solid solution. The precursor powder by the urea method shows a very similar thermal behavior, though the endothermic peak corresponding to the second stage of decomposition is slightly lower ($\approx 285^\circ\text{C}$).

Fig. 4 shows crystallite sizes of the solid solution oxides prepared by the two methods, as a function of calcination temperature. The powder from AHC exhibits better reactivity and shows a higher rate of crystallite growth.

Fig. 5 shows particle morphologies of the powders produced by the AHC method. The precursor (Fig. 5a) is mainly composed of spherical primary particles sizing up to $\approx 10$ nm. Agglomeration is obvious, but the agglomerates have quite open structures, which are in sharp contrast to those obtained via hydroxyl coprecipitation. The primary particles assume a nearly spherical morphology up to $\approx 700^\circ\text{C}$ (Fig. 5b) during calcination, and become faceted at $900^\circ\text{C}$ (Fig. 5c) due to the crystallite growth (Fig. 4) and the increased crystallinity (Fig. 1).

Fig. 6 exhibits particle morphologies of the powders synthesized by the urea method. The precursor (Fig. 6a) is mainly made up of irregularly shaped particles, and the primary crystallites tend to assume a platelet-like morphology. The flower-shaped particles are obviously formed via multiple crystallite growth from a single nucleus. The particle morphology is highly stable against calcination, and keeps essentially unchanged up to $\approx 900^\circ\text{C}$ (Fig. 6b and c). As mentioned earlier, urea has been used to synthesize a variety of single oxides of the rare earths, and it was found that particle morphology of the precipitate is dependent on the ionic radius of the element. It was demonstrated clearly

![Fig. 3. DTA/TG traces of the precursors synthesized with AHC and urea, with (a) DTA and (b) TG. The data were taken at a heating rate of 10 °C/min.](image)

![Fig. 4. Crystallite sizes of the 20SDC oxides, as a function of the calcination temperature.](image)
that going from larger La\(^{3+}\)(0.116 nm for eightfold coordination [23]) to smaller Yb\(^{3+}\)(0.0985 nm [23]) the particles steadily get smaller and change from irregularly shaped to spherical shaped under identical precipitation conditions [24]. Such a phenomena is a manifestation of the lanthanide contraction law, which predicts continuous property changes of the lanthanides along with a variation in the ionic size. Our work suggests that such a size effect also operate in the rare-earth-doped CeO\(_2\) systems. Prior to us, the only work on mixed rare-earth oxide via urea-based precipitation was conducted by Matijevic et al. [25] on Y-doped CeO\(_2\). Due to the smaller size of Y\(^{3+}\)(0.1019 nm [23]), the resultant particles are spherical in shape. Obviously, the particles become irregularly shaped with
a larger dopant of Sm$^{3+}$(0.1079 nm [23]), as can be seen in Fig. 6a.

The different particle morphologies between the powders from the two methods are expected to affect the sintering behavior, as was shown below.

3.2. Densification behavior of the 20SDC oxides

Fig. 7 shows densification behaviors of the 20SDC oxides processed via the two methods. For the powders from the AHC method and calcined below 700 °C, difficulties are encountered during compaction due to the extremely fine crystallite sizes and the compacts tend to crack upon sintering. It can be seen from Fig. 7 that the AHC-method derived powders show a higher onset temperature of rapid densification at a higher calcination temperature, because of the crystallite growth and reactivity loss. The powders calcined at 700 °C was densified to >99% of the theoretical up to ~1300 °C at a constant heating rate of 10 °C/min, exhibiting excellent sinterability. The excellent sinterability mainly comes from the ultrafine size and good dispersion of the primary crystallites (Fig. 5b). Calcining to 900 °C caused considerable reactivity loss, and the powder requires ~1500 °C to reach ~99% of the theoretical due to the crystallite coarsening during high temperature calcination.

The powders synthesized with urea exhibit very sluggish densification upon sintering. At the same calcination temperature of 700 °C, the powders from the urea and the AHC methods have almost the same crystallite sizes (~15 nm, Fig. 4), but the former shows much slower sintering kinetics. This is due to the large particle size and irregular particle shape of the powder. Irrespective of the calcination temperature, the powders show similar green densities, similar densification behaviors, and sinter to similar final densities (~63–64%), which are understandable from their similar particle size and particle shape.

Fig. 8 compares microstructures of the 20SDC ceramics sintered at 1200 °C for 4 h, using the powders calcined at 700 °C. The powder prepared by the AHC method sintered to >99% of the theoretical, as determined by the Archimedes method using distilled water as an intrusion medium. The high sintered density was also evidenced by the dense microstructure shown in Fig. 8a, where the average grain size was determined by the linear intercept method to be ~0.23 μm. The densification temperature achieved in this work is significantly lower than the previously reported ones, typically ≥1700 °C for powders obtained via solid-state reaction and 1400–1600 °C for the powders processed via other wet chemical routes (such as oxalate coprecipitation and hydrothermal treatment). The preferred particle morphologies for low-temperature densification include ultrafine particle/crystallite size, less aggregation, and nearly spherical particle shape, as were shown in Fig. 5b and c. The powders made via solid-state reaction lack all of these powder characteristics. The wet-chemical routes mentioned above yield primary crystallites of nanodimension, but the crystallites are hard aggregated to form secondary particles of large size (up to tens of microns) and irregular shape [5–7]. Therefore, these powders, though show better reactivity than those via solid-state reaction, still require high sintering temperatures. The low sintering temperature achieved in this work makes it possible to fabricate dense electrolytes with almost any type of sintering furnace, which is very advantageous from the view point of energy saving and the ease of the fabrication process. On the other hand, the powder synthesized via the urea method can only be sintered to ~67.2% dense, and interpenetrating network of pores are seen clearly in the microstructure. The low sintered density is mainly due to the large and irregular particles of the powder (Fig. 6b and c).
3.3. Electrical conductivity of the densified 20SDC ceramic

Fig. 9 shows electrical conductivity of the 20SDC ceramic densified at 1200 °C (from the AHC method). An almost linear relationship was found in the measured temperature range of 400–700 °C. The apparent activation energy for oxygen ion immigration was calculated to be $60.5 \text{ kJ/mol}$ or $0.627 \text{ eV}$ (pure CeO$_2$: 1.03 eV [26]) from the equation:

$$\sigma T = \sigma_0 \exp\left(-\frac{E_a}{RT}\right).$$

Direct comparison of the electrical property of 20SDC is somewhat difficult, as some researchers only focus on the synthesis and sintering of 20SDC powders while most of the others either study other compositions or measure electrical properties in temperature ranges different from this work. Available data indicate that at the same measurement temperature of 600 °C, the 20SDC ceramics prepared via other techniques show conductivities of ~2.0–5.0 mS/cm [26,27], which are lower than the value obtained in this work (~5.7 mS/cm). The electrical conductivity obtained in this work can be regarded as pure ionic conductivity (owing to the migration of oxygen ions), since Sm-doped CeO$_2$ is the least reducible among the rare-earth-doped CeO$_2$ materials [3] and the low measurement temperature used in this work is also not favorable for reduction (causing electron conduction). The activation energy derived in this work is also lower than the previously reported data: 0.824 eV (~79.5 kJ/mol) for solid-state reaction method [28] and 0.87 eV (~83.9 kJ/mol) for the hydrothermal method [26]. The lower activation energy and the higher conductivity obtained in this work are possibly derived from the high cation homogeneity of the ceramic, and detailed analysis on the atomic level is now being considered to resolve the microstructural features of this 20SDC ceramic.

4. Conclusions

Two carbonate coprecipitation routes have been used to synthesize the precursors for 10 mol% Sm$_2$O$_3$-doped CeO$_2$ solid solutions (20SDC), with ammonium bicarbonate (AHC) and urea as the precipitants, respectively. The precursor processed with AHC is an amorphous hydroxyl carbonate (Ce,Sm)(OH)CO$_3$·2H$_2$O having nanosized (~10 nm) spherical particles, while that from urea is a mixture of crystalline (Ce,Sm)$_2$(CO$_3$)$_2$(OH)$_2$·H$_2$O and (Ce,Sm)$_2$O(CO$_3$)$_2$·H$_2$O phases showing irregular particle morphologies. Both the precursors convert to oxide solid solutions without any phase detected corresponding to Sm$_2$O$_3$ during calcination. The oxide powder processed via the AHC method can be sintered to >99% of the theoretical at a low temperature of 1200 °C, due to the good dispersion and ultrafine size (~15 nm) of the particles, while that from the urea method can only reach ~67.2% dense at the same temperature. Electrical conductivity of the densified ceramic was measured in air in the range 400–700 °C by the DC three-point method, and the apparent activation energy for oxygen migration was found to be ~60.5 kJ/mol.
References

[1] N.Q. Minh, Ceramic fuel cells, J. Am. Ceram. Soc. 76(3) (1993) 563–588.
[2] H. Inaba, H. Tagawa, Ceria-based solid electrolytes, Solid State Ionics 83 (1996) 1–16.
[3] H. Yahiro, K. Eguchi, H. Arai, Electrical properties and reducibilities of ceria-rare earth oxide systems and their application to solid-oxide fuel cell, Solid State Ionics 36 (1989) 71–75.
[4] T. Kudo, H. Ohyashi, Oxygen ion conduction of the fluorite-type Ce1−xLnxO2−δ (Ln = Lanthanoid element), J. Electrochem. Soc. 122 (1) (1975) 142–147.
[5] K. Higashi, K. Sonoda, H. Ono, S. Sameshima, Y. Hirata, Synthesis and sintering of rare-earth-doped ceria powder by the oxalate coprecipitation method, J. Mater. Res. 14 (3) (1999) 957–967.
[6] P. Duran, C. Moure, J.R. Jurado, Sintering and microstructural development of ceria–gadolinia dispersed powders, J. Mater. Sci. 29 (1994) 1940–1948.
[7] K. Yamashita, K.V. Ramanujachary, M. Greenblatt, Hydrothermal synthesis and low temperature conduction properties of substituted ceria ceramics, Solid State Ionics 81 (1995) 60–63.
[8] Y. Wang, T. Mori, J.-G. Li, T. Ikegami, Low-temperature synthesis of praseodymium-doped ceria nanopowders, J. Am. Ceram. Soc. 85 (12) (2002) 3105–3107.
[9] J.-G. Li, T. Ikegami, Y. Wang, T. Mori, Reactive ceria nanopowders via carbonate precipitation, J. Mater. Sci. 85 (9) (2002) 2376–2378.
[10] H. Wakisita, S. Kinoshita, A synthetic study of the solid solutions in the systems La2(CO3)3·8H2O–Ce2(CO3)3·8H2O and La(OH)CO3–Ce(OH)CO3, Bull. Chem. Soc. Jpn 52 (2) (1979) 428–432.
[11] K. Hayashi, S. Toyoda, K. Nakashima, K. Morinaga, Optimum synthetic conditions of ammonium aluminum carbonate hydroxide (AACH) as starting materials for α-Al2O3 fine powders, J. Ceram. Soc. Jpn 98 (5) (1990) 444–449.
[12] S. Kato, T. Iga, S. Hatano, Y. Isawa, Synthesis of NH4AlO(OH)HCO3, Yogyo-Kyokai-Shi 84 (5) (1976) 215–220.
[13] K. Hayashi, S. Toyoda, H. Takabe, K. Morinaga, Phase transformation of alumina derived from ammonium aluminum carbonate hydroxide (AACH), J. Ceram. Soc. Jpn 99 (7) (1991) 550–555.
[14] S. Kato, T. Iga, S. Hatano, Y. Isawa, Effects of synthetic conditions on the sinterability of alumina obtained by thermal decomposition, Yogyo-Kyokai-Shi 84 (6) (1976) 255–258.
[15] E. Matijevic, W.P. Hsu, Preparation and properties of monodispersed colloidal particles of lanthanide compounds. I. Gadolinium, europium, terbium, samarium, and cerium (III), J. Colloid Interf. Sci. 118 (2) (1987) 507–523.
[16] M. Akinc, D. Sordelet, Preparation of yttrium, lanthanum, cerium, and neodymium basic carbonate particles by homogeneous precipitation, Adv. Ceram. Mater. 2 (3A) (1987) 232–238.
[17] D. Sordelet, M. Akinc, Preparation of spherical, monosized Y2O3 particles, J. Colloid Interf. Sci. 122 (1) (1988) 47–59.
[18] D.E. Williams, Lattice constant refinement, Technical Report No. IS-1052, Ames Laboratory, USDOE, Iowa State University, Ames, IA, 1964.
[19] W.H.R. Shaw, J.J. Bordeaux, The decomposition of urea in aqueous media, J. Am. Chem. Soc. 77 (1955) 4729–4733.
[20] N.E. Topp, The Chemistry of Rare-Earth Elements, Elsevier, Amsterdam, 1965.
[21] J.-G. Li, T. Ikegami, T. Mori, T. Wada, Reactive Ce0.8RE0.2O1.9 (RE = La, Nd, Sm, Gd, Dy, Y, Ho, Er, and Yb) powders via carbonate coprecipitation. I. Synthesis and characterization, Chem. Mater. 13 (9) (2001) 2913–2920.
[22] E.L. Head, C.E. Holley Jr., The preparation and thermal decomposition of some rare earth carbonates, in: K.S. Vorres (Ed.), Rare Earth Research II, Gorden & Breach, London, 1964, pp. 51–63.
[23] R.D. Shannon, C.T. Prewitt, Effective ionic radii in oxides and fluorides, Acta Crystallogr. B 25 (1969) 925–946.
[24] M. Akinc, Ceramic powder synthesis: homogeneous precipitation of rare earth carbonates, in: K.S. Vorres (Ed.), Fourth Euro Ceramics, Gruppo Editoriale Faenza Editrice, Faenza, Italy, 1995, pp. 3–13.
[25] B. Aiken, W.P. Hsu, E. Matijevic, Preparation and properties of monodispersed colloidal particles of the lanthanide compounds. III. Yttrium (III) and mixed yttrium (III)/cerium(III) systems, J. Am. Ceram. Soc. 71 (10) (1988) 845–853.
[26] W. Huang, P. Shuk, M. Greenblatt, Hydrothermal synthesis and properties of Ce1−xSm2O3−δ solid solutions, Chem. Mater. 9 (1997) 2240–2245.
[27] W. Huang, P. Shuk, M. Greenblatt, Properties of sol–gel prepared Ce1−xSm2O3−δ solid electrolytes, Solid State Ionics 100 (1997) 23–27.
[28] R.T. Dirstine, R.N. Blumenthal, T.F. Kuech, Ionic conductivity of calcia, yttria, and rare earth-doped cerium dioxide, J. Electrochem. Soc. 126 (2) (1979) 264–269.