



Superior sinterability of nano-crystalline gadolinium doped ceria powders synthesized by co-precipitation method

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ABSTRACT

Reduced sintering temperature of doped ceria can greatly simplify the fabrication process of solid oxide fuel cells (SOFCs) by utilizing the co-firing of all cell components with a single step. In the present study, nano-crystalline gadolinium doped ceria (GDC) powders of high sinterability at lower sintering temperature has been synthesized by co-precipitation at room temperature. The successful synthesis of nano-crystalline GDC was confirmed by XRD, TEM and Raman spectroscopy analysis. Dilatometry studies showed that GDC prepared by this method can be fully densified (97% relative density) at a sintering temperature of 950 °C which is fairly lower than ever before. It has also been found that the sintered samples have a higher ionic conductivity of $1.64 \times 10^{-2} \text{ S cm}^{-1}$ at 600 °C which is suitable for the intermediate temperature SOFC application.

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1. Introduction

Application of doped ceria materials are of special interest as the electrolyte for solid oxide fuel cells (SOFCs) operated at intermediate and low temperatures because of their high ionic conductivity compared to that of the state-of-the art materials such as yttria stabilized zirconia (YSZ) [1–10]. The electrolyte membrane is usually fabricated by screen printing and tape casting with doped ceria as the starting materials. It is generally known that the powder characteristics of starting materials will have a great effect on the densification process during the sintering [7,11]. Thus, the synthesis route for the powder preparation would eventually determine the densification kinetics of powder as well as its overall sinterability. When doped ceria is used as the electrolyte material, lower densification temperatures would greatly facilitate the fabrication technique since the electrolyte can be co-fired with the anode or the cathode at a relatively lower temperature to form the electrode supported electrolyte membrane. Hence, lot of efforts have been done to lower the sintering temperature of doped ceria for SOFC applications [11–16].

Ceria-based ceramics have been prepared by different synthesis methods such as hydrothermal [17], precipitation [18–23], combustion [24–27], two-emulsion [28], decomposition [29], and mechanochemical methods [30]. It has been shown that doped ceria powders synthesized by some soft chemical routes may have

high sinterability [13,14], and the effect of particle size is shown to have an important role in the densification behavior of ceramics [15,16].

In our previous studies [25,26], we were successful to lower the sintering temperature of GDC powder down to 1200 °C by controlling the powder characteristics via a combustion synthesis and a post-milling process, which is significantly a lower sintering temperature compared to that of conventional one. The main objective of this work is to develop a noble synthesis route to obtain high quality GDC powder of which characteristics are fairly adaptable to reduce the sintering temperature below 1000 °C.

2. Experimental

Nano-crystalline powders of GDC were prepared by a co-precipitation method. Individual solutions of 0.1 M of cerium nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, Kanto chemicals) and gadolinium (III) nitrate hexahydrate ($\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, Aldrich) were made by dissolving the nitrates in distilled water. Ammonium hydroxide was added drop-wise to this mixture which was stirred continuously to complete precipitation under controlled pH. Afterwards, the mixture was stirred for 2 h and aged for 6 h. After aging, the precipitate was separated from the supernatant by vacuum filtration. The precursor precipitates were washed several times thoroughly by using distilled water and ethanol to remove the impurities. NH_4^+ ions which were physically adsorbed on the precipitate were removed when the precipitates were washed with distilled water. After the precipitates were washed thoroughly with ethanol and dried in air at room temperature for 48 h for the complete removal of the absorbed water, de-hydrated GDC powders were formed.

Phase identification of these powders was performed by using X-ray diffractometer (PW 3830). The crystallite size was determined by means of Scherrer equation, $D = (0.9\lambda) / (\beta \cos \theta)$, where D is the crystallite size, λ is the wave length of the radiation, β is the corrected peak width at half maximum intensity and θ is the peak position. Raman spectra were measured using a conventional back scattering geometry with a Raman spectrometer (T 64000, Jobin-Yvon) which consists

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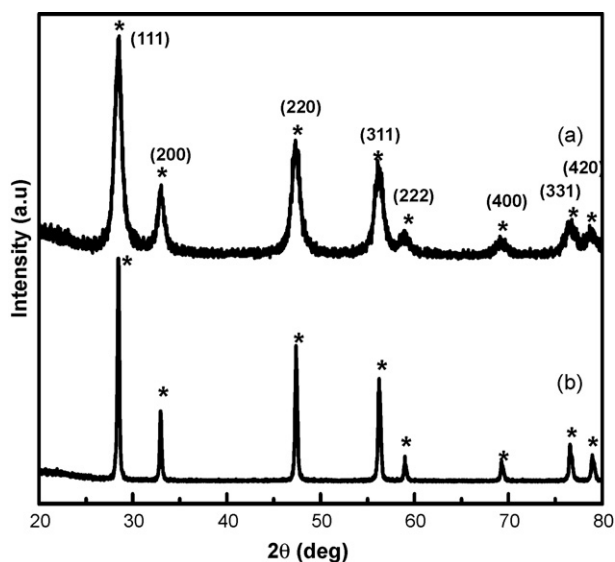


Fig. 1. XRD patterns of (a) GDC powder prepared by co-precipitation method and (b) commercial GDC powder.

of a triple polychromator and a CCD detector. The excitation source was an Ar⁺ ion laser ($\lambda = 514.23$ nm) and the laser power was 10 mW at the sample point. The morphology of the powders was observed by using a transmission electron microscope (TEM, Technai G2F20). A scanning electron microscope (EDS/SEM, XL-30 FEG ESEM) is used for the compositional and microstructural analyses. A particle size analyzer (PSA) (Microtrac UPA 150) was used to determine the average value of the apparent particle size.

For observing the sintering behavior, uni-axially formed pellets were pressed at 200 MPa by using cold isostatic pressing (CIP). Shrinkage of the green bodies was measured with a dilatometer (Netsch Dil 402C/3/G) up to 1500 °C in air with a heating rate of 3 °C/min. The relative density of the prepared samples was estimated by using the relation: relative density (%) = $(d_m/d_{th}) \times 100$, where d_m is the density of the samples measured using Archimedes method and d_{th} is the theoretical density of the GDC sample. The conductivity of the sintered pellet specimen was measured in the temperature range of 400–800 °C in air by using Potentiostat/Galvanostat (IVIUMSTAT, Netherlands) with four-point DC method. Before the measurement, Pt paste was painted onto either side of the sintered pellets and fired at 850 °C for 1 h to act as porous gas electrodes.

3. Results and discussion

The XRD pattern obtained from the as-prepared powder is shown in Fig. 1(a). For comparison, an XRD pattern of commercial GDC (Nextech, U.S.A.) is shown in Fig. 1(b). As shown in Fig. 1, as-prepared powder clearly shows the single crystalline phase without any secondary phase. This indicates that the GDC single phase can be formed at room temperature without any further treatment. It is a common knowledge that the synthesis of complex oxides by a co-precipitation method involves two steps: (1) the formation of hydroxide or hydrate oxides and (2) the heat treatment at an elevated temperature to dehydrate and form oxides with the right phase. The above result, however, demonstrates that GDC phase can be directly formed at room temperature without any heat treatment. Similar results were also obtained by Gu and Meng

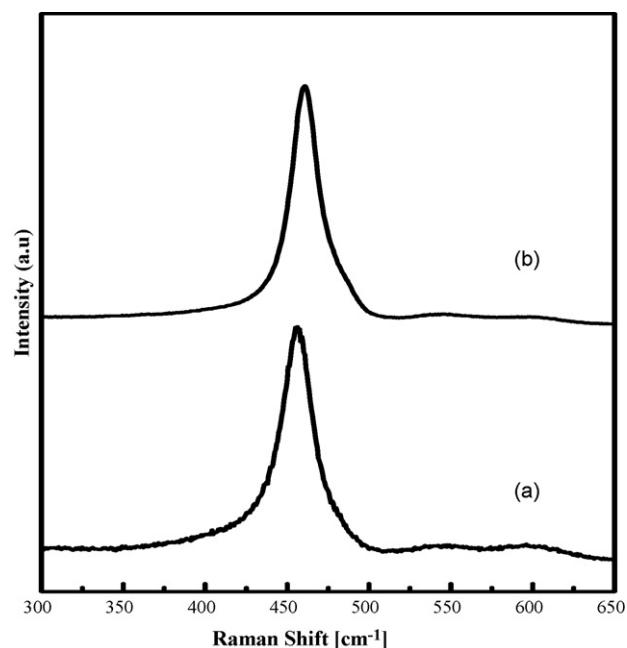


Fig. 2. Raman spectra of (a) GDC powder prepared by co-precipitation method and (b) commercial GDC powder.

[31] and Godinho et al. [32] for the synthesis of doped ceria at room temperature.

The XRD peaks of the as-prepared GDC are relatively broad, which indicates that the formed crystallites were small in size. The average crystallite size, determined by the Scherrer equation, was 8.7 nm. This was in good agreement with TEM results. Table 1 shows the crystallite and particles sizes of GDC obtained by XRD, PSA and BET analyses. When compared with our previous studies [25,26], GDC powder prepared by this method showed smaller crystallite and particle sizes.

In order to further confirm the formation of complete GDC solid solution, Raman spectroscopy was used to analyze the powder. Raman spectra were obtained for commercial (Nextech, U.S.A.) GDC and GDC produced by this method. Fig. 2 depicts the Raman spectra of the GDC powders. Fig. 2(a) shows that GDC obtained by the co-precipitation method exhibited the same spectrum with commercial GDC (Fig. 2(b)). If a mixture of CeO₂ and Gd₂O₃ is formed during the synthesis, the Raman spectra will show a characteristic vibrational mode at 360 cm⁻¹ attributed to the main strongest band of the Gd₂O₃ cubic phase [33]. However, this vibrational mode is not present in our sample. As can be seen in the figure, there is only one clear vibrational mode at 465 cm⁻¹ which corresponds to F_{2g} symmetry of the CeO₂ cubic phase [34]. Thereby, we can assume that the gadolinium oxide is completely dissolved into the ceria fluorite structure by partially replacing the Ce⁴⁺ ions of the lattice with the Gd³⁺ ions, resulting in the formation of a single cubic GDC phase.

Table 1
Comparison of properties of GDC nano-powders prepared by various synthesis methods.

Synthesis method	Crystallite size (nm) ^a	Apparent particle size (nm) ^b	Surface area equivalent particle size (nm) ^c	Sintered density (%)
Co-precipitation method	8.7	184	12.2	97 (950 °C) ^d
Glycine-nitrate process [26]	17	250	18.4	97 (1200 °C) ^d
Sol-gel thermolysis [25]	10	1138	13.1	96 (1500 °C) ^d

^a Calculated from XRD.

^b Measured by PSA.

^c Calculated from BET.

^d Values in the parenthesis indicate the sintered temperature.

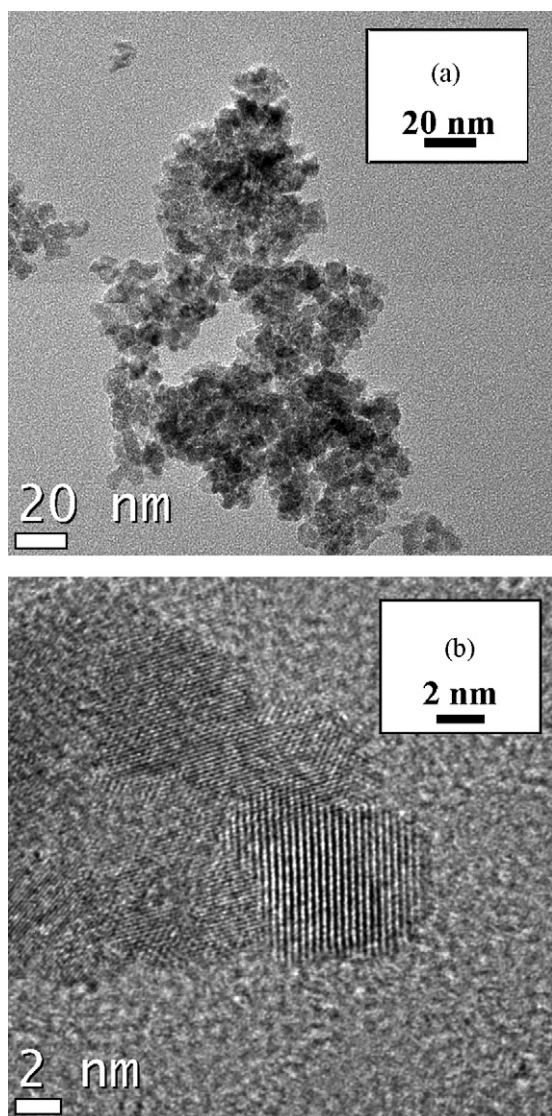


Fig. 3. (a) TEM and (b) HR-TEM images of as-prepared GDC powder.

TEM images of GDC powder are shown in Fig. 3. From Fig. 3(a) it can be observed that the particle size of the GDC powder is very small and the obtained particle size is around 10–12 nm. The presence of crystalline nano-particles is further confirmed by the HR-TEM image displayed in Fig. 3(b). The nano-crystalline size estimated by TEM images is similar to the calculated nano-crystalline size obtained by XRD patterns, which further shows the nanometric nature of the GDC powder. GDC composition of the prepared powder was confirmed from EDS analysis which is shown in Table 2.

Fig. 4 shows the linear shrinkage spectra and the shrinkage rate of the green compact. The linear shrinkage starts at a lower temperature of 400 °C where the sintering of nano-sized particles is started and showed one shrinkage rate maxima at around ~775 °C where the densification rate becomes the highest. Existence of only one maxima of shrinkage rate indicates the homogeneity of GDC powder compact mainly due to the good powder characteristics with

Table 2
Composition of the GDC powder analyzed by EDS.

GDC powder	Element	wt%	mol%
As-prepared	Ce	88.66	89.76
	Gd	11.34	10.23

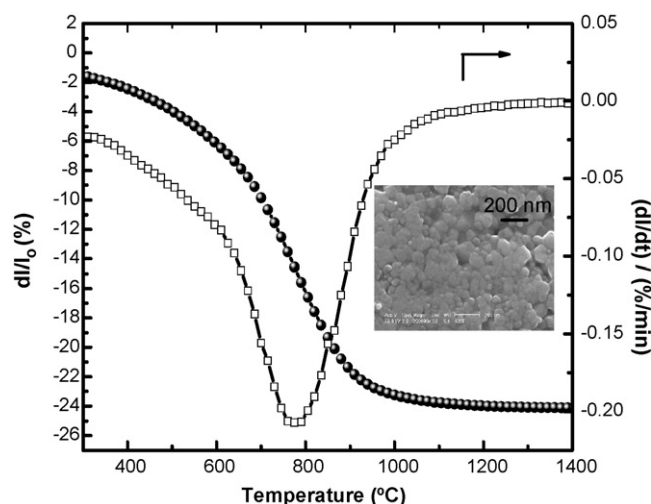


Fig. 4. Linear shrinkage and shrinkage rate of GDC pellet and inserted figure shows the SEM image of GDC sample sintered at 950 °C.

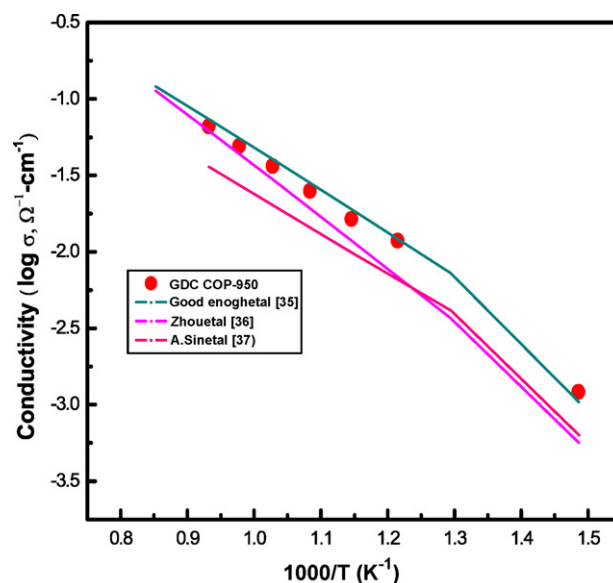


Fig. 5. Arrhenius plot of the ionic conductivity of GDC prepared by co-precipitation method.

uniform particle size and distribution. As shown in Fig. 4, a linear shrinkage of 24% (with a sintered density of 97%) is observed for the GDC sample below 1000 °C, indicating the full densification of as-synthesized powders below 1000 °C. Such a superior sinterability can be explained by the synthesis of crystalline GDC powder at room temperature by this method. Since any thermal treatment has not been involved during the synthesis, nano-crystalline GDC with a high surface area and smaller particle size can be successfully formed. Inserted figure in Fig. 4 shows the SEM image of 950 °C sintered GDC sample with a sintered density of 97%. We can observe that the grain size is less than 200 nm.

Arrhenius plot for the GDC sample sintered at 950 °C is depicted in Fig. 5. As shown in Fig. 5, the GDC sample sintered at lower sintering temperature of 950 °C showed the conductivities similar to those reported in the literature [35–37] where the GDC samples were sintered at relatively higher temperatures above 1200 °C. The GDC samples exhibit a conductivity of $1.64 \times 10^{-2} \text{ S cm}^{-1}$ at 600 °C and the activation energy was around 0.62 eV. All these results show that the GDC powder prepared by this method can be co-fired effectively with other cell components by achieving sufficiently

high sintered density at relatively lower sintering temperatures. Performance evaluation of the cell made with this GDC powder would be the topic of forthcoming paper.

4. Conclusions

Single-phase nano-crystalline GDC powders have been prepared successfully by co-precipitation method at room temperature. Formation of single-phase nano-crystalline powder has been confirmed by XRD and Raman spectroscopy analyses. The calculated crystallite size and particle size obtained from XRD, BET and TEM were around 8–12 nm. From the density measurements, a relative density of 97% is achieved at comparatively lower sintering temperature of 950 °C. The nano-crystalline GDC obtained by this method showed low temperature sinterability with good electrical conductivity and low activation energy, which in fact could assist co-firing with other cell components of SOFC at lower temperature.

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