Low temperature fabrication of dense gadolinia-doped ceria electrolyte with enhanced electrical conductivity

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By combination of supercritical drying route and coprecipitation synthesis method, ultrafine $Ce_{0.8}Gd_{0.2}O_{1.9}$ (GDC20) nano-powders are successfully prepared using $(NH_4)_2CO_3$ as the precipitant. The as-synthesized powder has a specific surface area of $113.4\,m^2\,g^{-1}$ and an average crystalline size of $\sim 6\,nm$ after calcination at $400\,°C$, together with other favorable properties like high dispersibility, weak agglomeration and remarkable flowability. The powder shows high sintering activity, where the relative density reaches $\sim 99.9\%$ with an average grain size of $\sim 100\,nm$ after sintered at $900\,°C$ for 4 h. Low temperature sintering not only suppresses grain growth but also improves electrical performance of the electrolyte. The sample sintered at $900\,°C$ exhibits high electrical conductivity of $5.39\,S\,m^{-1}$ at $700\,°C$, which is superior to most of the reported ceria-based electrolyte.

1. Introduction

Solid oxide fuel cell (SOFC) attracts extensive attention in recent years due to its high energy-transfer efficiency and low pollution [1]. Nowadays, there are rapidly growing concerns about developing intermediate-temperature (500∼700 °C) solid oxide fuel cells (IT-SOFCs) for the reason that high temperature operation induces application obstacles like strict material limitation [2], obvious interface reactions [3], fast electrode performance degradation [4], sealing difficulty [5] and, consequently, poor long-term stability. Ceria solid solution is widely recognized as a promising electrolyte for IT-SOFCs due to higher oxygen ionic conductivity and better chemical compatibility to electrode materials than conventional yttria stabilized zirconia (YSZ) [6–13]. However, one of the main difficulties encountered in application about ceria-based materials is to obtain densified electrolytes at low temperatures, which usually need to expose to high temperatures over 1600 °C when solid-state reactions are applied, leading to electrochemical performance degradation [14]. Fortunately, nanometric powder preparation has shown to be effective for low-temperature densification of ceria solid solution, which is of significance for cost-effective fabrication of IT-SOFCs [15–17].

As mentioned above, synthesizing ultrafine nanopowders is an original strategy for reducing sintering temperature of compacted ceramics compared to other strategies like adding sintering aids.

Among typical wet-chemical synthesis methods, coprecipitation is the most overwhelming route due to its simplicity, short reaction time, and feasibility for scaling up. The powders prepared by coprecipitation always show good homogeneity with high specific surface areas, which endues them with huge surface free energy and correspondingly remarkable sintering activity [18,19]. Based on the advantages of this route, powders with superior quality could be obtained by further optimizing synthesis process, especially the vital part. Ammonium carbonate is widely considered to be one of the most valuable precipitants for practical application, and plenty of literatures have obtained high-grade ceria solid solution powders with fine dispersibility and weak agglomeration [16,20]. In addition, in order to maintain powders' high sintering activity, drying process indeed is meaningful but mostly overlooked. In fact, nanocrystalline electrolyte powders with high sintering activity were successfully synthesized through a special coprecipitation route whose highlight is the supercritical fluid drying process [21,22]. Hence, there is no doubt that, by introducing supercritical fluid drying process, the dispersing state of the resultant powder is well developed without obvious hard-agglomeration and the powder still possesses significant driving force for densification.

Low-temperature sintering not only reduces fabrication cost and improves operation stability of IT-SOFCs, but also provides an opportunity to prepare dense nanocrystalline ceramic electrolytes. Nanocrystalline doped cerias attract increasing attentions because they are considered to have higher ionic conductivities and superior mechanical performances compared with the others [23,24].

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$Ce_{0.8}Gd_{0.2}O_{1.9}$ (GDC20) is one of the most promising electrolytes for IT-SOFCs due to its superior electrical behavior to other rare and/or alkaline earth doped ceria and has been extensively investigated to further improve electrical conductivity. This paper synthesized ultrafine nanocrystalline GDC20 powders by coprecipitation combined with supercritical ethanol drying [25,26] process using ammonium carbonate as the precipitant. The properties of the powder and the low-temperature densification behaviors of the compacted pellets were investigated in detail, and the electrical conductivities of the dense ceramics were also measured. Moreover, general analysis and discussion were made based on the experimental results.

2. Experimental

The nano-sized GDC20 powder was synthesized by $(NH_4)_2CO_3$-coprecipitation jointed with supercritical ethanol drying [25,26] technique. All of the reagents were analytically pure. Firstly, a mixed aqueous solution of $0.1\,mol\,L^{-1}$ ($Ce(NO_3)_3$ and $Gd(NO_3)_3$) was prepared according to the stoichiometric ratio of $Ce_{0.8}Gd_{0.2}O_{1.9}$, using polyethylene glycol (PEG) as surfactant. $(NH_4)_2CO_3$ was chosen to be the precipitant and the solution concentration was prepared to be $0.25\,mol\,L^{-1}$. Both of the above-mentioned solutions were continuously stirred at $70\,°C$ for 2 hours and then volume-equally mixed together. To make sure the reaction proceed completely, mild stirring was lasted for at least 2 hours. Next, the obtained precipitate was collected by vacuum filtering, and the hydrogel was washed with deionized water for about 5 times to remove the salt anions and then with absolute ethanol for at least 5 times to remove the water in the filter cake. Then the alcogel was dispersed into absolute ethanol through ultrasonic processing, and subsequently transferred into an autoclave. The supercritical ethanol drying process was operated at $260\,°C$ for $1\sim2\,h$ and the pressure was controlled at about 8 MPa.

The as-prepared powder was calcined in a muffle furnace at the standard temperature (depending on the characterization results) for 2 h with a heating rate of $5\,°C\,min^{-1}$. After the residual ethanol was totally removed and the carbonate was completely decomposed, faint yellow GDC20 powders were obtained.

Thermogravimetry/differential scanning calorimetry (TG/DSC, Netzsch STA 449, Germany) was used to characterize the thermal decomposition behavior of the as-prepared powder to determine the proper calcination temperature. The investigation was executed in flowing air with a heating rate of $10\,°C\,min^{-1}$. The crystal structures of the as-prepared and the calcined powders were analyzed using X-ray diffraction (XRD, X'Pert MPD Pro, PANalytical, the Netherlands) with Cu Kα radiation in the scanning range of $2\theta = 10\sim90°$. The crystallite size was estimated by line broadening analysis based on the reflection from the (111) plane. The specific surface area of the calcined powder, S_{BET}, was measured by Brunauer–Emmett–Teller isothermal adsorption analysis (Autosorb-1, QUANTACHROM, USA) and the equivalent particle size was calculated according to the following equation:

$$d_B = \frac{6 \times 10^3}{\rho_{th} \cdot S_{BET}} \tag{1}$$

where d_B (nm) is the average diameter of the spherical particle, S_{BET} is the surface area of the powder ($m^2\,g^{-1}$), and ρ_{th} is the theoretical density of $Ce_{0.8}Gd_{0.2}O_{1.9}$ solid solution ($g\,cm^{-3}$), which could be calculated to be $7.2327\,g\,cm^{-3}$.

The morphology and the crystalline size of the calcined powder were characterized using high-resolution transmission electron microscope (HR-TEM, JEM-2100, JEOL, Japan). Field-emission scanning electron microscope (FESEM, JSM-6700F, JEOL, Japan) was also used to observe the morphology and the agglomeration

state of the calcined powder. Uniaxial pushrod dilatometry (L75/1550, LINSEIS, Germany) was used to investigate the non-isothermal sintering behavior of the calcined powder. The compacted cylinders were prepared by uniaxially pressing under a pressure of about 500 MPa with geometric size of about $\Phi10 \times 2$ mm. The non-isothermal sintering tests were conducted from room temperature to $1300\,°C$ with a heating rate of $10\,°C\,min^{-1}$. The instantaneous relative density of the measured compact, ρ, was calculated via the following equation:

$$\rho = \frac{\rho_0}{\left(1 + \Delta L/L_0\right)^3} \tag{2}$$

where ρ_o is the relative density of an as-prepared compact determined by its weight, geometric dimensions and ρ_{th}, L_0 is the initial sample length (2.08 mm), and, $\Delta L = L - L_0$, where L is the present sample length as a function of temperature. Isothermal sintering was performed in a muffle furnace at $800\sim1150\,°C$ for 4 h with a heating rate of $2\,°C\,min^{-1}$. The densities of the as-sintered bodies were determined by the Archimedes method in deionized water. Microstructures of the sintered ceramics were observed via FESEM, and average grain sizes of the sintered samples were calculated by the linear intercept method in which at least 200 grains were randomly selected.

For sintered samples, silver paste was painted onto both sides and then solidified at an intermediate temperature. Silver wires were fixed onto the silver electrodes to transfer current. Ionic conductivity measurements were carried out from 300 to $700\,°C$ with an interval of $50\,°C$ in air atmosphere, using a two-probe impedance spectroscopy (IM6ex, Zahner, Germany) over 0.1 to 3×10^6 Hz. Results of electrical measurements were simulated by Z-view software package to separate bulk and grain boundary contributions to the total conductivity.

3. Results and discussion

3.1. Powder synthesis and characterization

The thermal decomposition behavior of the as-dried powder is shown in Fig. 1. The results indicate that continuous weight loss of the powder lasts until $\sim410\,°C$, which can be divided into two stages with a rough transition at $\sim250\,°C$. According to the TG/DSC curves, an obvious exothermic peak occurs at $\sim210\,°C$, and the first stage has a total weight loss of $\sim9\%$, which might be attributed to the desorption and burn-off of the residual adsorbed ethanol. In the second stage, rapid weight loss appears and the thermal decomposition reaction is revealed to be endothermal. It is inferred
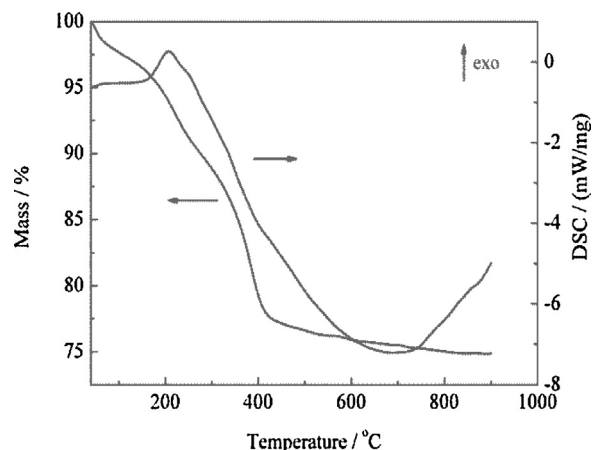

Fig. 1. TG/DSC curves of the as-prepared GDC20 powders in flowing air at a heating rate of $10\,°C\,min^{-1}$.