Synthesis and properties of SDC powders and ceramics for low temperature SOFC by stearic acid process

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Abstract $Ce_{0.8}Sm_{0.2}O_{1.9}$ (SDC) powders were prepared by a novel solution combustion process using molten stearic acid as dispersive medium and reducing agent. The powders prepared with the molar ratio of NO_3^- to stearic acid at 1:1.5 exhibited a narrower distribution in sizes and the average agglomerate size is about 157 nm. The non-agglomerated particles are in the range 10–40 nm. The as-combusted powders prepared by the present method were pure oxides powder with low crystallinity, which exhibited excellent sintering properties, easily achieving high dense SDC ceramics with lager grains (0.85 μm).

Keywords Stearic acid · SDC · Low crystallinity · High dense

1 Introduction

Many studies have been done on solid oxide electrolytes with high oxide ion conductivity at low temperature (400–700 °C) [1–5]. Rare earth oxide doped ceria such as samarium doped ceria($Ce_{0.8}Sm_{0.2}O_{1.9}$, SDC) is a very promising material for the electrolytes of the low temperature solid oxide fuel cell because it exhibits higher oxide ion conductivity at low temperature than YSZ [6].

As solid electrolytes, SDC ceramics should be high dense for practical applications due to gas-tight require-ments [7]. Moreover it should have evenly and larger grain size when the effect of grain size becomes obvious in low temperature because the small grain size in solid electro-lytes results in decreasing the electrical conductivity caused by grain boundary effect [8]. However previous study [9] showed samarium doping retarded both densification and grain growth of SDC ceramics especially doping concen-tration exceeded 10%, grain growth became difficulty. And the average grain size of SDC ceramics sintered at 1400 °C for 4 h was only about 0.75 μm.

It is well known that nanocrystalline powders can provide fast densification kinetics and low sintering temperature [9]. So the objective of this work is to yield desired nanocrystalline oxide powders in order to get SDC ceramics with high dense and large grains. In this work, the nanocrystalline powders were prepared by a novel solution combustion process using molten stearic acid as dispersive medium and reducing agent [10]. The different molar ratios of NO_3^- to stearic acid were used in order to manufacture nanocrystalline SDC powders. The sintering behavior of SDC powders was also discussed.

2 Experimental

2.1 Sample preparation

$Sm(NO_3)_3$ (99.9%) and $Ce(NO_3)_4$ (99.9%) were dissolved in deionized water with high concentration. The stearic acid was melted at 140 °C and the nitrate solutions were dropped into the stearic acid melt with vigorous stirring in order to evaporate the excess free water. After dehydration, the mixture formed a solution. Then the solution was heated to foam and the foams were ignited to flame. The as-

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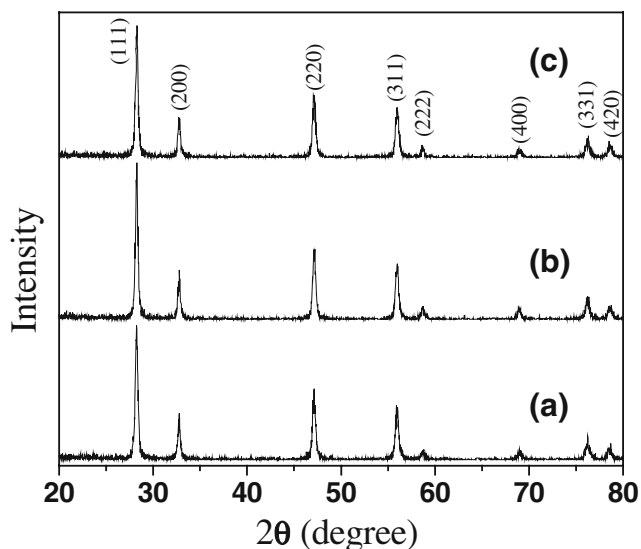e-mail: wengwj@zju.edu.cn

Fig. 1 XRD patterns of SDC powders prepared with different molar ratio of N/s (**a**) 1:1, (**b**) 1:1.5, and (**c**) 1:2

combusted powders were milled in an agate mortar and calcined at different temperature to get oxide powders.

Powders for sintering were dry-pressed at 100 MPa into cylindrical pellets (15 mm diameter and 1 mm thick) using a uniaxial die-press. The green SDC pellets were then sintered at 1200 °C for 4 h with a heating rate of 1 °C/min.

2.2 Characterization

The thermal weight loss of as-combusted powders was examined by means of thermogravimetry (Model WRT-3P) from room temperature to 800 °C at a heating rate of 10 °C/min in air. The crystalline structure of the oxide powders was determined by X-ray diffraction (XRD, Model D/MAX-RA, RIGAKU) analysis using Cu Kα radiation. Also the crystallite size of the powders was calculated from XRD data using the Scherrer equation. The particle size distribution was measured by Malvern Zeta-Sizer (Nano-S90, Malvern). Particle morphology, agglomeration state and size of powders were observed via both field emission scanning electron microscopy (FESEM, Model SIRION-100, FEI) and transmission electron microscopy (TEM, Model JEM-00CX, JEOL Co.).The sintering body was also characterized by FESEM.

3 Results and discussion

3.1 The influence of the amount of stearic acid

In this method, The Ce and Sm ions were dispersed in the stearic acid by replacing some of the hydrogen atoms of carboxyl groups to get a molecular level distribution when the solution formed [10]. Shown in Fig. 1 are the XRD patterns of SDC powders prepared with different molar ratio of NO_3^- to stearic acid (N/s). The data indicate that all the characteristic diffraction peaks corresponding to the fluorite structure of CeO_2 have appeared. The crystallite size was calculated from XRD data with Scherrer equation. The crystallite size of the SDC is 29, 25 and 32 nm, respectively. It means that the crystallite size is influenced by the initial molar ratio of NO_3^- to stearic acid obviously. When the amount of stearic acid is small, the ions can not be evenly dispersed in the stearic acid, and if it is too large, lots of excess heat is generated and lead to growth of crystallite and agglomerate.

Shown in Fig. 2 is the size distribution of powders. It can be seen that, comparing with other samples, the powders prepared at the molar ratio of N/s at 1:1.5 exhibit a narrower distribution in sizes and the average agglomerate

Fig. 2 Particle distribution of powders prepared with different molar ratio of N/s (**a**) 1:1, (**b**) 1:1.5, (**c**) 1:2 and (**d**) is the as-combusted powders prepared with the molar ratio of N/s at 1:1.5
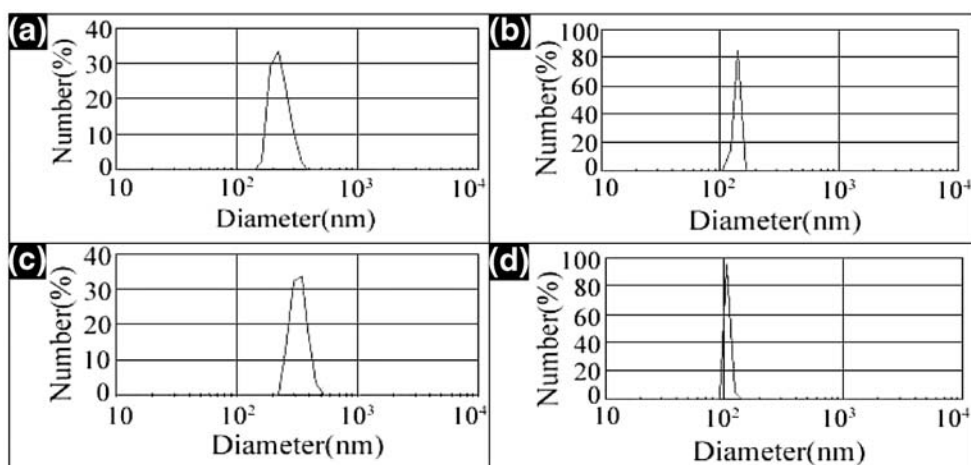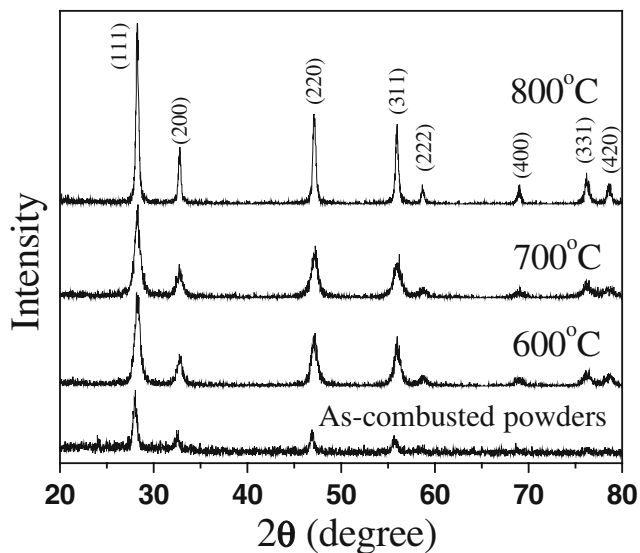
Fig. 3 XRD patterns of SDC powders calcined at different temperature for 4 h

size is 157 nm. In this method, 1:1.5 is an optimal ratio to prepare desired SDC powders.

3.2 Characterization of the SDC powders

Figure 3 shows the XRD patterns of as-combusted and SDC powders prepared with the molar ratio of N/s at 1:1.5 and calcined at different temperature. XRD results show that the fluorite structure of CeO_2 has appeared in the as-combusted powders and increasing intensities are observed as the calcination temperature was increased, indicating increasing crystallite growth. The crystallite size of the
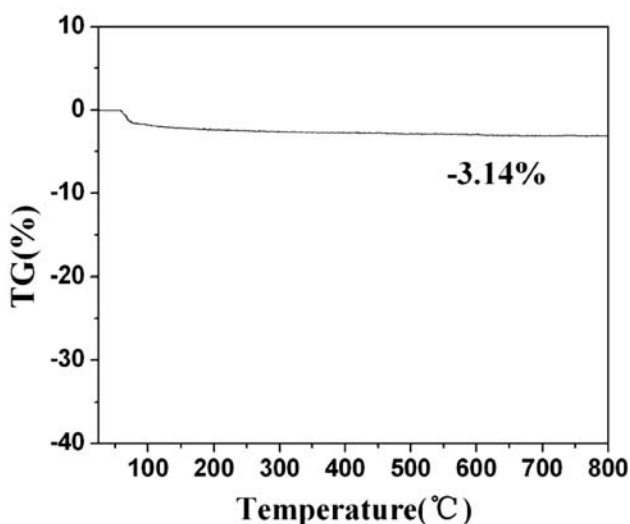
SDC is 16, 18, 23 and 30 nm respectively according to the XRD data.

Figure 4 shows the TGA curve of the as-combusted powders. The cure exhibiting almost no weight loss after 100 °C indicates there is no carbon exiting in the as-combusted powders. It shows that the as-combusted powders are pure SDC with low crystallinity. And Fig. 2(d) shows that the as-combusted powders have a narrow distribution in sizes and their average agglomerate size is 105 nm.

Typical particle morphology of the SDC powders is shown in the Fig. 5, from which it can be seen that the nanocrystalline particles are nearly spherical and only loosely agglomerated in FESEM micrograph and the agglomerates are composed of spherical particles packed closed together. The particle size observed from TEM micrograph shows that the non-agglomerated spherical particles are in the range 10–40 nm.
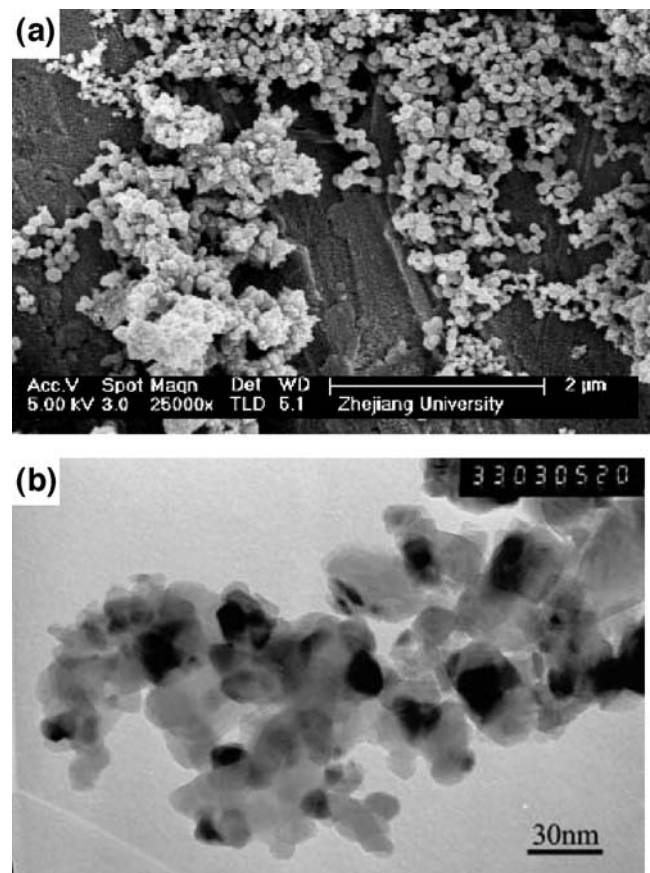

Fig. 4 TGA curve of the as-combusted powders

Fig. 5 FESEM (a) and TEM (b) micrograph of SDC powders calcined at 750 °C for 4 h
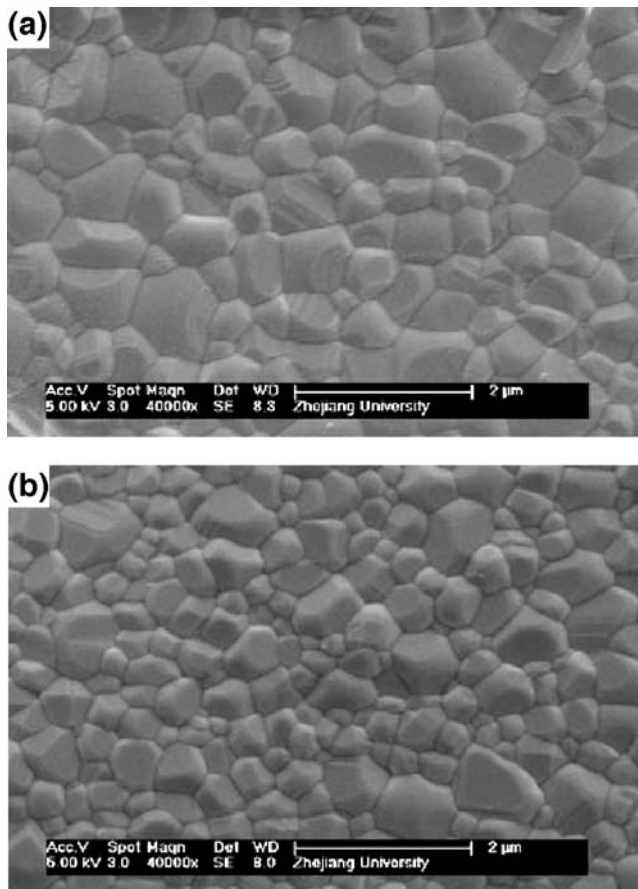
Fig. 6 FESEM micrographs of pellets prepared by (**a**) as-combusted powders and (**b**) SDC powders calcined at 750 °C

3.3 Sintering behavior of SDC

Figure 6 shows the FESEM micrographs of pellets prepared by (a) as-combusted powders and (b) SDC powders calcined at 750 °C. It can be observed that both pellets have high dense. And the grains in Fig. 6(a) are larger and more evenly than Fig. 6(b). Average grain size was calculated by the linear intercept method. The result shows that the average grain size in Fig. 6(a) is 0.85 μm, however,

the average grain size in Fig. 6(b) is only 0.51 μm. It indicates that lowly crystallized SDC powders make for growth up of grain and the uniform distribution of grain profits from narrow distribution, and the nanosized powders are also propitious to get high dense pellet [8].

4 Conclusions

A novel solution combustion process using molten stearic acid as dispersive medium and reducing agent was used to prepared SDC powders. The result showed that the molar ratio of NO_3^- to stearic acid at 1:1.5 was an optimal ratio to prepare nanocrystalline SDC with a narrower distribution in sizes and the average agglomerate size was about 157 nm. The as-combusted powders prepared by this method were nearly pure SDC powder with low crystallinity, which exhibited excellent sinterability, achieving high dense SDC ceramics with large grains (0.85 μm) at a low sintering temperature of 1200 °C for 4 h.

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