



Short communication

Synthesis of doped ceria–zirconia core–shell nanocomposites via sol–gel process

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ABSTRACT

In order to introduce more conductive interfaces, the doped ceria–zirconia core–shell nanocomposites are synthesized via a simple and low-cost sol–gel process. Nitrates, citric acid and polyethylene glycol (PEG) are used as starting materials, and the compositions of the core and the shell are $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ (GDC) and 8 mol% Sc_2O_3 doped ZrO_2 (ScDZ), respectively. The room-temperature ammonia co-precipitation method is used to prepare the core materials. X-ray diffraction (XRD) indicates that the average grain sizes of the core and shell materials are about 6 nm and 8 nm. The core–shell nanostructure with about 60 nm diameter GDC core (approximate) and about 20 nm thick ScDZ shell, is supported by the field-emission scanning electron microscopy (FESEM) and the transmission electron microscopy (TEM) results. The effects of PEG and the mechanisms during the process of forming the core–shell nanocomposites are discussed in detail.

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1. Introduction

The solid oxide fuel cell (SOFC) is one of the most important applications for solid oxide electrolytes. Decreasing the operation temperature of SOFCs and SOFC stacks is one of the most significant objectives being addressed in relation to increasing reliability, operation life, and reducing the fuel cell fabrication and balance of plant costs. Generally, zirconia based electrolytes have been extensively applied in SOFC due to the property of pure oxide ion conductivity under reducing conditions. Among these electrolytes the scandia doped zirconia is known to have exhibited the highest conductivity, which has been attributed to the low association enthalpy of the defect reactions and the similarity between the ionic radii of Sc^{3+} and Zr^{4+} [1–3]. Moreover, ceria doped with Sm^{3+} or Gd^{3+} also exhibits higher conductivity, which determines their potential applications in SOFCs [1–3]. In order to reduce the operating temperature further, alternative electrolytes with higher oxygen ion conductivity should be designed and investigated.

Recently, creating highly conductive paths along the interfaces is known to be an effective method of dramatically increasing the ion conductance of electrolytic crystalline materials [4–9]. Zhu groups [4,5] and Mao groups [6,7] both found that the electrical conductivity of the composites of doped ceria–carbonate was enhanced by introducing the two-phase interfaces. Sata et al. found that an increase in the interface density in a two-phase multilayered calcium and barium fluoride structure (CaF_2 – BaF_2)

drastically enhances the fluoride ion conductance of the material along the interfacial directions, compared with either bulk CaF_2 or BaF_2 [8]. Based on the phenomena above, layer-by-layer structures of Gd-doped ceria (GDC) and zirconia (GDZ) have been synthesized on Al_2O_3 (0 0 1) using oxygen plasma-assisted molecular beam epitaxy by Azad et al. [9]. Oxygen ion conductivity greatly increases with an increasing number of layers compared to bulk polycrystalline Gd-doped ceria and Y-doped zirconia. Two conductivity enhancement mechanisms have been proposed. The first mechanism is associated with carrier density enhancement due to the redistribution of ions in the space charge regions near the interfaces [10] and the second is associated with the carrier mobility increase due to a slight atomic displacement near the interfaces [11]. In both mechanisms, the interfaces play an important role in enhancing the ionic conductivity in the nanostructured materials.

However, the highly conductive layer-by-layer structure thin films can only have a special impact on single-chamber fuel cells where both electrodes are located on the same side of a thin electrolyte film deposited onto a substrate, because the ionic current flows in a lateral direction parallel to the substrate. So it is necessary to realize a bulk material with more highly conducting interfaces as found in the multilayered GDC/GDZ film. And ceria-based nanocrystals overcoated with zirconia-based nanocrystals can be suitable as raw materials. As reported by Omata et al. [12], the synthesis of $\text{CeO}_2/\text{ZrO}_2$ core–shell nanocomposites without doping, which are pure CeO_2 nanocrystals overcoated with a thin pure ZrO_2 layer, has been studied using a hot surfactant colloidal route. However, too many expensive starting materials, such as zirconium isopropoxide propanol complex and oleylamine, are needed. Also, it will be very complicated to synthesize doped $\text{CeO}_2/\text{ZrO}_2$ core–shell

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nanocrystals with the above method. As a result this method is not suitable to be applied in fabricating bulk materials.

Therefore, in the present work, the doped $\text{CeO}_2\text{-ZrO}_2$ core-shell nanocomposites were synthesized by a simple sol-gel method. Cheap nitrates were used as starting materials, and the compositions of the core and the shell are $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ (GDC) and 8 mol% Sc_2O_3 doped ZrO_2 (ScDZ), respectively.

2. Experimental

2.1. Synthesis of $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ (GDC) cores

$\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ as core materials was synthesized by applying the room-temperature ammonia co-precipitation method. Analytical reagents $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (≥ 99.9 wt%, Yutai Qingda, China), $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (≥ 99.9 wt%, Yutai Qingda, China), $\text{NH}_3 \cdot \text{H}_2\text{O}$ and polyethylene glycol (PEG, molecular weight = 6000) were used as the starting materials. In a typical experiment, stoichiometric amounts of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were dissolved in deionized water to form a 0.1 mol l^{-1} solution. PEG (PEG/ $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ = 1.5 wt%) as surfactants were also dissolved in the solution. Then the solution was dropped into dilute ammonia (pH 9) solution under vigorous stirring and ultrasonic oscillation to form a white gel at room temperature. The gels were then collected through vacuum filtration, washed three times with water and three times with alcohol until it became a yellow color, and then dried at room temperature for 48 h. In addition, for comparison, the powders were also prepared via a similar process with the exception of not adding PEG into the solution.

2.2. Coating of $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ cores with 8 mol% Sc_2O_3 doped ZrO_2 (ScDZ)

GDC-ScDZ core-shell nanocomposites were prepared by the sol-gel process. Stoichiometric amounts of $\text{Sc}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (≥ 99.9 wt%, Yutai Qingda, China) and $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (≥ 99.9 wt%, Yutai Qingda, China) were dissolved in deionized water to form a 0.1 mol l^{-1} solution, containing citric acid as a chelating agent for the metal ions. The molar ratio of metal ions to citric acid was 1:2. As a cross-linking agent, PEG was added with the final concentration of 0.08 g ml^{-1} . The solution was magnetically stirred for 2 h to form a precursor sol, and then $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ particles, which had been dispersed in alcohol under ultrasonic oscillation, were added under stirring for 5 h. Then the $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ particles were separated by centrifugation. The obtained samples were immediately dried at 100°C for 1 h. The dried samples were then calcined at 600°C for 1 h in air. The core-shell structured $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ -ScDZ materials have been prepared in this manner. For the purpose of comparison, the coating sol was evaporated to form gels, which were calcined via a similar process to produce the ScDZ powders.

2.3. Characterization

Thermo-chemical properties of the dried core-shell materials (before calcinations) were investigated by thermogravimetry (TG)/differential calorimetry (DSC) (STA409PC, Netzsch, Selb, Germany) in the temperature range of $25\text{--}820^\circ\text{C}$ with a heating rate of $10^\circ\text{C min}^{-1}$ in air. X-ray diffraction (XRD, Rigaku, D/max-RB, Japan) was used to analyze the crystalline structure, the grain size of the core (GDC) and the shell (ScDZ) materials. The dispersion of GDC materials (with and without PEG) was characterized by scanning electron microscopy (SEM, Jeol-6301F, Tokyo, Japan). A very small amount of the resulting core-shell structure was ultrasonically dispersed in ethanol. A drop of this solution was dripped onto a carbon-covered copper net and then placed in a sample holder. The

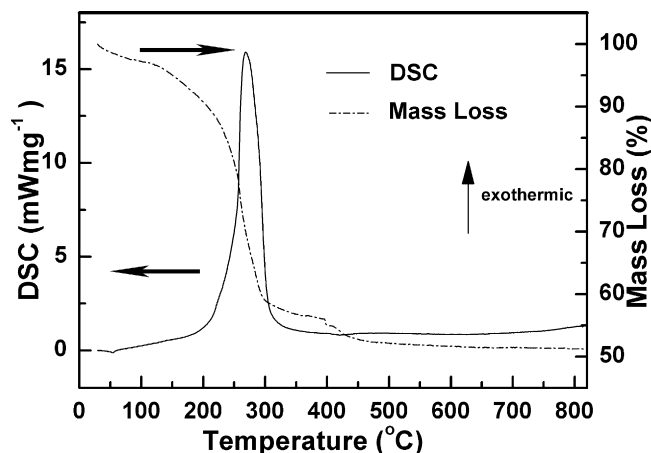


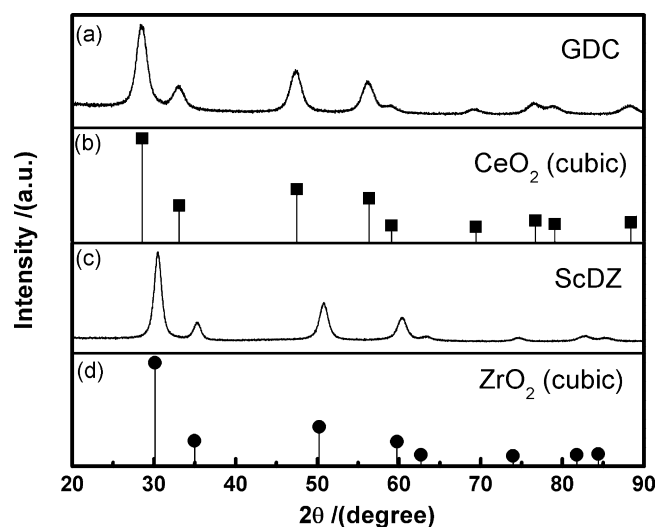
Fig. 1. TG/DSC curves of the dried core-shell samples (before calcinations) from 25 to 820°C with the heating rate of $10^\circ\text{C min}^{-1}$ in air.

morphology and composition were inspected by transmission electron microscopy (TEM, Jeol JEM-200CX, Tokyo, Japan) with energy dispersive X-ray analysis (EDX).

3. Results and discussion

The simultaneous TG/DSC curves of the dried core-shell samples (before calcinations) are shown in Fig. 1. A strong exothermic peak can be clearly seen at about 268°C , at which the maximum weight loss occurs, so the exothermic behavior at about 268°C should correspond to the cleavage of the organic components composed of PEG, free citric acid and the polymeric complexes. Moreover, the TG curve turns flat above about 600°C , showing that the impurities (carbons) are all removed above 600°C . Consequently, the calcined temperature was determined to be 600°C .

Fig. 2 shows the XRD patterns of $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ obtained at room temperature (a) and ScDZ (c) calcined at 600°C for 1 h. Compared with JCPDS 81-0792 for CeO_2 (b) and JCPDS 49-1642 for ZrO_2 (d), all the diffractions are indexed as those for the cubic phase, while the diffractions are broadened due to their small crystal size. According to the Scherrer equation, the average crystallite sizes of $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ and ScDZ are estimated to be about 6 nm and 8 nm, respectively. The particle size can be investigated below. As investi-



5

Fig. 2. XRD patterns of $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ (core) powders obtained at room temperature (a) and ScDZ (shell) powders (c) calcined at 600°C for 1 h (cubic ceria (b); cubic zirconia (d)).

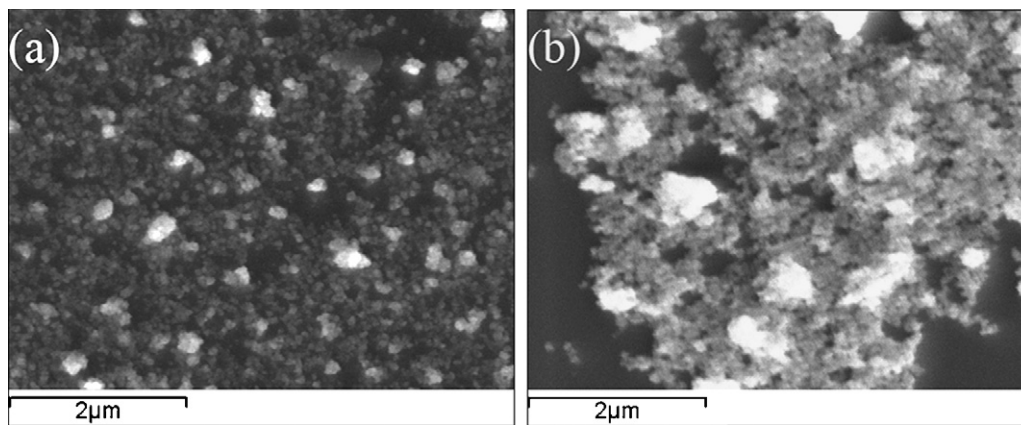
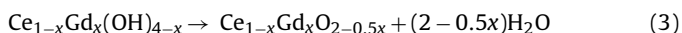
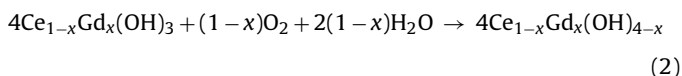
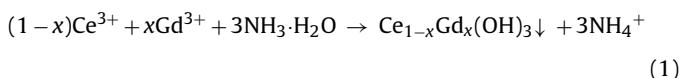


Fig. 3. SEM micrographs of the $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ powders (cores) prepared by adding (a) or not adding PEG (b).

gated by Djuricic and Pickering [13], pure ceria can be synthesized through precipitation of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ with ammonium hydroxide. Oxidation of $\text{Ce}(\text{OH})_3$ occurs readily in air at room temperature, forming yellow $\text{Ce}(\text{OH})_4$, which is not stable and can easily be transformed into CeO_2 in air. Therefore, the following reactions can be proposed for Gd-doped ceria:



Pure Gd-doped ceria was obtained at room temperature, avoiding the growth and agglomeration of the grains at higher temperature. Additionally, the ScDZ precursors (obtained by evaporating the residual sols) and the core-shell precursors were both calcined

by a similar process, so the average grain size of the ScDZ powders (Fig. 2(c)) should consist with that of the shells of the core-shell structures.

In order to synthesize the core-shell structure, the first step is to make the core materials disperse well. Fig. 3 displays the SEM micrographs of the $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ powders with the same amount prepared by adding or not adding PEG. From Fig. 3, it can be observed that the powders without PEG are severely agglomerate. However, with the addition of PEG, a thin layer of PEG as surfactants perhaps adheres to the surface of the particles obtained by co-precipitation, which can effect the dispersion. And the effect will not vanish because the core powders were synthesized at room temperature and do not need to be calcined at higher temperature. The average particle size is about 60 nm, as shown in Fig. 3(a). Besides the effect of dispersion, PEG can also be considered as a cross-linking agent in the process of forming the core-shell structure, which will be discussed below.

Fig. 4(a) shows the TEM-image of the core-shell structure, amongst the core is prepared by adding PEG. Observing the results from the EDX (Fig. 4(c)), the compositions of the structure include Zr, Ce, Sc and Gd elements. The peaks corresponding to Cu and C

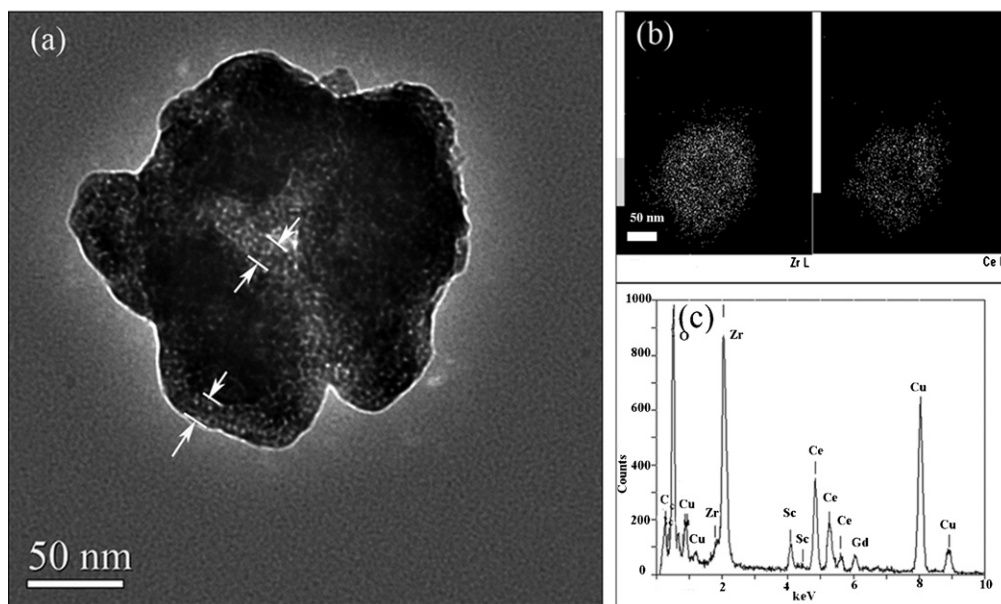


Fig. 4. TEM-image of the core-shell structure, whose core is prepared by adding PEG (a); the corresponding maps scanning results of Zr and Ce elements (b); the corresponding EDX results (c).

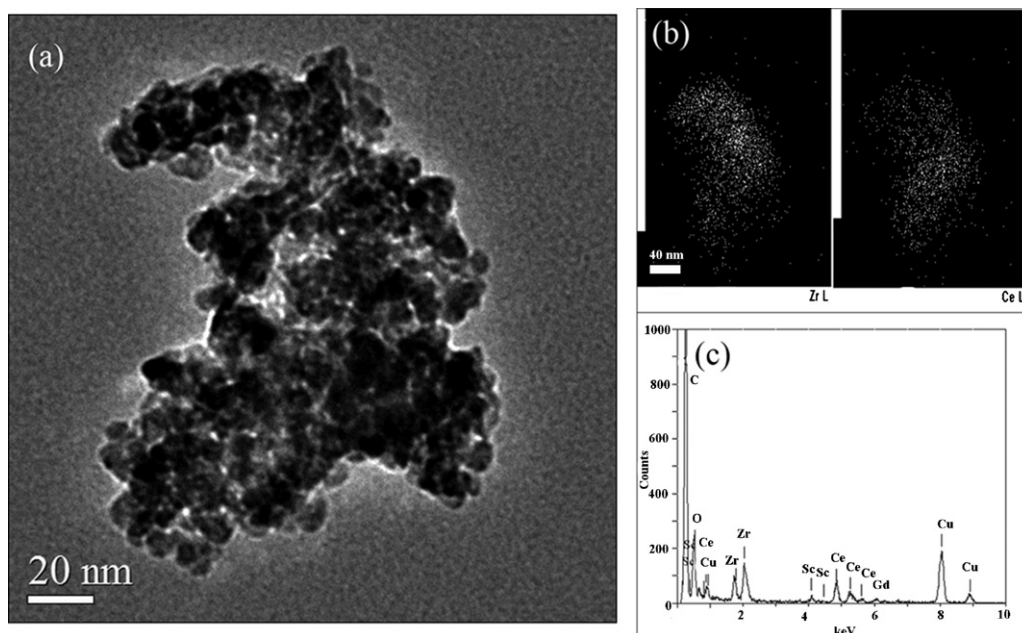


Fig. 5. TEM-image of the core-shell structure, whose core is prepared by not adding PEG (a); the corresponding maps scanning results of Zr and Ce elements (b); the corresponding EDX results (c).

originate from carbon-covered copper net. As shown in Fig. 4(b), the dispersion area of Zr element is larger than that of Ce element, demonstrating that the overcoated core-shell structure is successfully formed. It can be seen from Fig. 4(a) that there are three core-shell particles, and every particle consists of a 60 nm diameter $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ core and a 20 nm thick ScDZ shell. The size of the cores agrees well with the results displayed in Fig. 3(a). However, seen from the maps scanning graphs of Fig. 5(b), the particle is only a simple mixture of GDC and ScDZ powders. The upside of the particle (shown in Fig. 5(b)) shows a larger amount of ScDZ than GDC, corresponding to higher intensity for Zr; while the downside displays the contrary case. Moreover, the dispersion region of Ce is not covered with that of Zr, suggesting that the core-shell structures were not formed. Combined with the results of Figs. 4 and 5, a thin layer of PEG coating on the surfaces of the cores perhaps plays an important role in forming the core-shell structures. Therefore, the formation mechanism is put forward as follows: In the precursor solution, the citric acid can form chelates with the metal ions (Zr^{4+} , Sc^{3+}). These chelates can be bonded together to form a polymer when PEG is added (the two $-\text{OH}$ groups in PEG can connect with the $-\text{COOH}$ groups in citric acid via hydrogen bonding, making them more homogeneously distributed in the solution). PEG can be considered as a cross-linking agent. When the cores (GDC) are added into the precursor solution, the PEG layer on the surfaces of the cores can also react with citric acid. After the precursor structures are heated to remove the organic compositions, the core-shell structures are obtained. In this process, the thickness of the shells can be adjusted by controlling the PEG concentration. The PEG concentration will affect the viscosity of the polymer sol solution. Low viscosity of the sol will result in easy deposition of a thin layer of ScDZ on the GDC particles, but the cores will not be coated fully when the viscosity of the sol solution is too low. In order to introduce more interfaces of zirconia-ceria, the shell should be as thin as possible. Therefore the optimum PEG concentration is being studied.

4. Conclusions

The core-shell nanocomposites, which consist of a 60-nm diameter GDC core and a 20 nm thick ScDZ shell observed by FESEM and TEM, are synthesized by the sol-gel method. The X-ray diffraction (XRD) indicates that the average grain sizes of core and shell materials are approximately 6 nm and 8 nm. The technique used here is simple and cost effective. The core-shell nanocomposites with a high density of highly ionic conducting interfaces can be used for the fabrication of the bulk solid electrolytes. In order to avoid the ceria-zirconia solid solution, the low-temperature sintering will be needed, such as spark-plasma sintering, microwave sintering and hot-pressing sintering.

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