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Ionic conductivity and mechanical properties of Y_2O_3-doped CeO_2 ceramics synthesis by microwave-induced combustion

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Abstract

We developed a new method, i.e. microwave-induced combustion synthesis to produce highly sinterable Y_2O_3-doped CeO_2 nanopowders. The process took only 15 min to yield Y_2O_3-doped CeO_2 powders. We also investigated the conductivity of Y_2O_3-doped CeO_2 ceramics. It was found Y_2O_3 concentration to have a large effect on the morphology, activation energy, ionic conductivity, and mechanical properties of Y_2O_3-doped CeO_2 ceramics. The results revealed that the bulk densities of Y_2O_3-doped CeO_2 ceramics sintered at 1420 °C for 5 h were all higher than 92% of the theoretical densities, and the maximum ionic conductivity, $\sigma_{800\ ^\circ C} = 0.023$ S/cm at 800 °C, the minimum activation energy, $E_a = 0.954$ eV determined in the temperature of 300–800 °C and the maximum fracture toughness, $K_{IC} = 1.825 \pm 0.188$ MPa $m^{1/2}$ were found for 9 mol.% Y_2O_3-doped CeO_2 specimen. The grain size of CeO_2 decreases with increasing Y_2O_3 concentration. The fracture toughness was found to increase at increased Y_2O_3 concentration, because of the decrease of CeO_2 grain size.

Keywords: A. Microwave processing; C. Hardness; C. Ionic conductivity; D. CeO_2; E. Fuel cells

1. Introduction

Nanopowders have many excellent properties suited for various applications of ceramics such as gas sensors, rechargeable batteries, fuel cells, and so on. In addition, they can significantly enhance sintering rates, decrease sintering temperature, and improve optical, electric, and magnetic properties compared to micrometer size powders [1,2]. As such, solid oxide fuel cells are attracting widespread attention due to their high-energy conversion efficiency and low pollution. The high oxide ionic conducting solid electrolytes based on zirconia have been intensively investigated in the past [3,4]. In order to reduce the operation temperature from 1000 to 800 °C or even lower, doped ceria has been considered as the solid electrolyte for moderate temperature solid oxide fuel cells. Contrary to pure yttria-stabilized zirconia (YSZ), $CeO_{2-\delta}$, has the fluorite structure and oxygen vacancies ($V_O^{\bullet\bullet}$) as the predominant ionic defect [5–7]. The oxygen vacancy concentration and concomitant oxide ion conductivity, in CeO_2 can be increased by the substitution of a lower-valent metal such as Y, Sm, Gd, and Ca. Also, Y_2O_3-doped CeO_2 has been considered as the solid electrolyte for moderate temperature solid oxide fuel cells [8]. However, the ion conductivity of CeO_2 can be significantly improved upon substitution of some trivalent oxides, because the number of oxygen vacancy will be greatly increased for charge compensation. The electrical conductivity in doped ceria is influenced by several factors such as the dopant ion, the dopant concentration, the oxygen vacancy concentration, and the defect association enthalpy. Their relationships are closely and complicatedly related to the electrical conductivity in doped ceria. Such relationship is not simple point to point, but a combined result of several factors. However, besides the global lattice parameter change, localized defect structure and energetics might also have significant influence [9–11].

There are several methods for preparing Y_2O_3-doped CeO_2 nanopowder such as hydrothermal synthesis [12], thermophoresis-assisted vapor phase synthesis [13], and sol–gel techniques [14]. In this research, we have attempted a new method, the microwave-induced combustion synthesis process, to produce Y_2O_3-doped CeO_2 nanopowders and the advantage of this process The advantages of this process are (1) simple process: all the reactions take only a few minutes, not like the other

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methods that require tedious process; (2) simple equipment: this method does not require complicated equipment; (3) cheap sources: chemicals used in this method are cheap, unlike special materials needed in sol–gel process. Moreover, microwave processing of materials is fundamentally different from the conventional processing due to its heating mechanism. In a microwave oven, heat is generated within the sample itself by the interaction of microwaves with the material. In conventional heating, the heat is generated by heating elements, which is then transferred to the sample surfaces. The microwave-induced combustion synthesis process involves the dissolution of nitrates and urea in water, followed by heating the solution in a microwave oven. The urea and metal nitrate decompose and give flammable gases. After the solution reaches the point of spontaneous combustion, it begins burning and results in burning at high temperature. Combustion is not complete until all the flammable substances are consumed, and the resulting material is a loose, highly friable substance exhibiting voids and pores formed by the escaping gases during the combustion reaction [15,16]. The whole process takes only a few minutes to yield Y_2O_3-doped CeO_2 nanopowder. These nanoscale Y_2O_3-doped CeO_2 powders can reduce sintering temperature compared to those powders prepared by solid-state reaction.

Materials used in SOFC system may be susceptible to fracture due to thermal stress and mechanical stress during cell fabrication and operation. Unfortunately, ceria-based materials possess weak mechanical strength. It may conduct ceria-based ceramics their application for electrolyte [17]. The addition of rare earth oxide to CeO_2 can slightly improve its mechanical properties. In current research, we present the results of a systematic study of the structure, mechanical and electrical properties of Y_2O_3-doped CeO_2 ceramics which powders were from microwave-induced combustion process.

2. Experimental procedures

2.1. Sample synthesis

The synthesis process involved the combustion of redox mixtures, in which a metal nitrate acted as an oxidizing reactant and urea as a reducing one. The initial composition of the solution containing cerium nitrate, yttrium nitrate hexahydrate, and urea was based on the total oxidizing and reducing valences of the oxidizer and the fuel using the concepts of the propellant chemistry [18].

Stoichiometric amounts of cerium nitrate ($Ce(NO_3)_3{\cdot}6H_2O$), yttrium nitrate hexahydrate ($Y(NO_3)_3{\cdot}6H_2O$), and urea ($CO(NH_2)_2$) dissolved in a minimum quantity of water, were placed in a crucible. The crucible containing the solution was then introduced into a microwave oven (CEM, MDS 81D, 650 W). Initially, the solution boils and undergoes dehydration followed by decomposition with the evolution of large amount of gases. After the solution reaches the point of spontaneous combustion, it begins burning and releases lots of heat, vaporizes all the solution instantly and becomes a solid burning at high temperature. The powder samples prepared by microwave-induced combustion process were pelletized and sintered at 1420 °C for 5 h. The sintered samples were over 92% of the theoretical density for all specimens.

2.2. Characterization techniques

A computer-interface X-ray powder diffractometer (XRD) with Cu Kα radiation (Rigaku D/Max-II) was used to identify the crystalline phase and determine the crystallite size. The crystallite size D_{XRD} was calculated according to the Scherer equation [19]: $D_{XRD} = 0.9\lambda/B\cos\theta$, where λ is the wavelength of the radiation, θ is the diffraction angle, and B is the corrected half-width of the diffraction peak, give by $B^2 = B_m^2 - B_s^2$, where B_m is the measured half-width of the diffraction peak and B_s is the half-width of standard CeO_2 with a crystal size greater than 100 nm. The reflection from the (1 1 1) plane, occurring at 28.620⊖, was used to calculate the crystallite size. The crystallite size determined from the broadening curve is in the range of 14–17 nm. When using the Scherer equation, we assume that the particle size is the only source of peak broadening; however, if compositional non-uniformity occurs in the particles, the particle size will be underestimated. Differential thermal analysis and thermogravimetry (TG/DTA, Rigaku Thermalplus TG 8120) were used to study the exo-endo temperature of as-received CeO_2 powders. A heating rate of 10 °C/min was used in both the DTA and TG measurements up to 1000 °C in air. BET surface area measurements where made by nitrogen adsorption Micromeritics ASAP 2020 and calculated using the five point Brunauer–Emmit–Teller (BET) theory. Mean particle size (D_{BET}) was calculated from the BET data according to $D_{BET} = 6/(\rho_{th}S_{BET})$, where S_{BET} is the measured surface area and ρ_{th} is the theoretical density of the compound [20]. The morphological features of the particle were examined by transmission electron microscope (TEM, JEOL JEM-200CX) with an accelerating voltage of 200 kV. For sintered specimens, the ionic conductivity was measured by a two-point dc method on a sintered Y_2O_3-doped CeO_2 pellet. Electrodes were formed by applying platinum paste to the two ends of the pellet and firing at 800 °C for 1 h. The ionic conductivity measurements were made at various temperatures in the range of 300–800 °C in air. Arrhenius plots (plots of $\log\sigma$ vs. $10^3/T$) were then constructed and activation energies for conduction were computed. Finally, the densities and porosities of sintered ceramics were measured by the Archimedes method.

Vickers hardness was measured using a microhardness tester (Akashi MVK-H110, Tokyo, Japan) with the load 1000 g, and held for 10 s. At least 10 indentations were used for obtained mean and standard deviation value of hardness and fracture toughness. All specimens were polished with a series of emery paper of 800, 1000, 1200, and 1500 grit. Contamination on the surface was ultrasonically cleaned with ethanol. The Vickers indenter hardness was determined by the average value of both diagonals with a Vickers indenter apex of 136° and calculated with follow equation: $H_V = 1.8544\ P/d^2$ where P is the load, and d is the mean value of both diagonals.