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Preparation and conductivity of Sc_2O_3–CeO_2–ZrO_2

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ABSTRACT

The cubic 10Sc1CeSZ (10 mol% Sc_2O_3–1 mol% CeO_2–89 mol% ZrO_2) was prepared by controlling the concentration of the urea varied from 0.4 to 0.6 mol/L in the hydrothermal process. XRD results depict that the 10Sc1CeSZ blocks have a stable cubic phase structure at room temperature after sintering at 1150–1450 °C. SEM characterization of the fracture surface of the 10Sc1CeSZ blocks shows that the grain size increases from 0.3 to 8 μm during heat treatment up to 1150–1450 °C, correspondingly, the relative densities increase from 98.3% to 99.7%. The impedance spectra measured at 300 °C reveal that the grain boundary resistance reduces with the increase of sintering temperature. Impedance analysis results show that the 10Sc1CeSZ block sintered at 1450 °C for 4 h has the highest total ionic conductivity of 0.137 S cm^{-1} at 800 °C.

1. Introduction

Solid oxide fuel cells (SOFCs) have attracted particular interest due to their high energy conversion efficiency, low pollution emission, and ability to work with various fuels [1]. Yttria stabilized zirconia is most widely used material for electrolyte in SOFCs at high temperatures (800–1000), because of its high ionic conductivity and good chemical and mechanical stabilities [2]. However, SOFCs worked at high temperature, which could lead to a rapid degradation of the stack, and interconnect materials are generally expensive [1,3]. In addition, scandia stabilized zirconia (ScSZ) was a promising material to be used as a solid electrolyte in SOFCs at medium temperatures (600–800 °C). 10 mol% Sc_2O_3–1 mol% CeO_2–89 mol% ZrO_2 (cubic 10Sc1CeSZ) was used as the electrolyte in SOFCs due to superior electrical properties, good coefficient of thermal expansion, and excellent high temperature long-term operating characteristics [4].

10Sc1CeSZ materials were usually prepared by co-precipitation and azeotropic distillation technique, such as the commercial DKKK powders manufactured by Daiichi Kigenso Kagaku Kogyo (Japan). In this method, the water absorbed on the surface of zirconia was removed, to avoid the formation of hard agglomeration, the results, good dispersed and narrow distribution nanocrystalline were obtained. However, the reversible cubic to rhombohedral and rhombohedral to cubic phase transitions at 300–500 °C has been reported during heating of 10Sc1CeSZ ceramics [5–7]. 10Sc1CeSZ powders were also obtained by sol–gel method, but the subsequent sintering process was completed at higher temperature due to the low activity of the powders [8]. The hydrothermal homogeneous urea precipitation method has been reported to synthetize ultrafine YSZ powders and SSZ materials [9–14], but the electrical properties of the materials were not very desirable. The hydrothermal synthesis of 10Sc1CeSZ was less reported, and their sintering and electrical properties were also rarely studied.

In this paper, we synthesized cubic 10Sc1CeSZ powders by controlling the concentration of the urea in the hydrothermal process. The obtained 10Sc1CeSZ powders and blocks were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscope (TEM), energy dispersive spectroscopy (EDS), impedance spectroscopy. The effects of sintering temperatures on densification and electrical properties of 10Sc1CeSZ blocks were studied.

2. Experimental procedure

2.1. Materials synthesis

10Sc1CeSZ powders were synthesized using raw materials of $ZrOCl_2 \cdot 8H_2O$ (Aladdin Chemistry Co., Ltd.), and Sc_2O_3 (Sc_2O_3, Ronghua Technology Co., Ltd. ≥99.99%), and $Ce(NO_3)_3 \cdot 6H_2O$ (Shanghai Shanpu Chemistry Co., Ltd. ≥99%). $Sc(NO_3)_3$ aqueous solution was obtained by Sc_2O_3 dissolved in boiling concentrated nitric acid. A given quantity of $ZrOCl_2 \cdot 8H_2O$, $Sc(NO_3)_3$, $Ce(NO_3)_3 \cdot 6H_2O$ and $CO(NH_2)_2$ (Xilong Chemical Co., Ltd. ≥99%) were dissolved in deionized water to form a starting solution with the total cation concentration of 0.2 mol/L. The concentrations of the urea were tuned between 0.2 and 1.6 mol/L. The obtained mixture solution was stirred, and then poured into a 80 mL Teflon lined autoclave (DuPont, Wilmington, DE). The autoclave was sealed and put in an electrical oven at 130 °C for 4 h and subsequently heated at 200 °C for another 24 h. The precipitates were filtered, washed with deionized water and ethanol for several times, dried in a vacuum oven at 60 °C. The powders obtained from the hydrothermal method were

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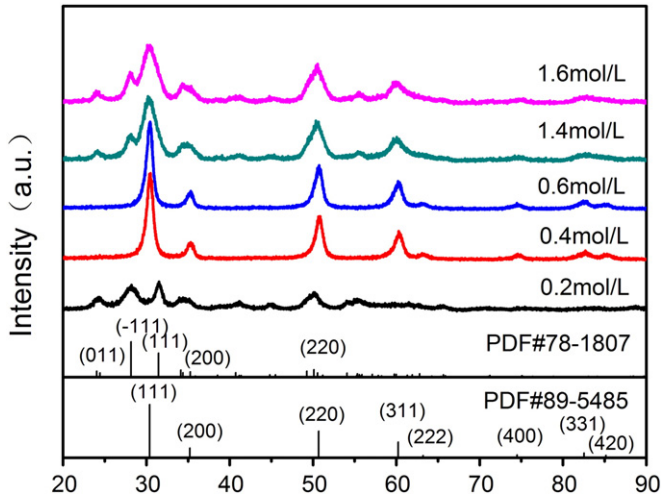

Fig. 1. XRD patterns of 10Sc1CeSZ powders prepared by adding the different concentrations of urea.

calcined at 800 °C for 2 h. The obtained powders were uniaxially pressed into discs with a diameter of 12 mm and a thickness of 2–3 mm under 12 MPa. Then, the pressed blocks were sintered at 1150 °C for 4 h, 1250 °C for 4 h, 1450 °C for 4 h, respectively.

2.2. Structural characterizations

The crystalline phase of the powders was characterized by X-ray diffraction (XRD) at room temperature, using a Rigaku D/Max 2500 powder diffractometer with Cu Kα radiation (λ = 1.5406 Å) at a scanning rate of 8 °C/min in the 2θ range of 20–90°. The 10Sc1CeSZ powders and the impact fracture surface of sintered blocks were observed by scanning electron microscopy (SEM, FEI SIRION 200). DSC/TG were performed on simultaneous thermal analyzer (STA449C) at a heating rate of 10 °C/min from room temperature to 1200 °C under air atmosphere. FTIR spectra were recorded by Nicolet-6700 (USA) spectrophotometer with 4 cm^{-1} resolution in range of 4000–400 wave numbers (cm^{-1}). The relative density of the sintered blocks was determined via Archimedes' method. The oxide ionic conductivity of the blocks was measured using a frequency response analyzer (Wayne Kerr, WK-6500; HDMS-1000 high temperature dielectric measurement system developed by Wuhan Partulab Company) over a frequency range from 100 Hz to 1 MHz at temperature range of 300–800 °C in air with Pt electrodes. The ionic conductivity, σ, was calculated from the impedance data and the activation energy (E_a) of the conductivity was determined by the Arrhenius law:

$$\sigma T = \sigma_o \exp(-E_a/kT),$$

where σ_o was the pre-exponential factor and k was the Boltzmann constant.

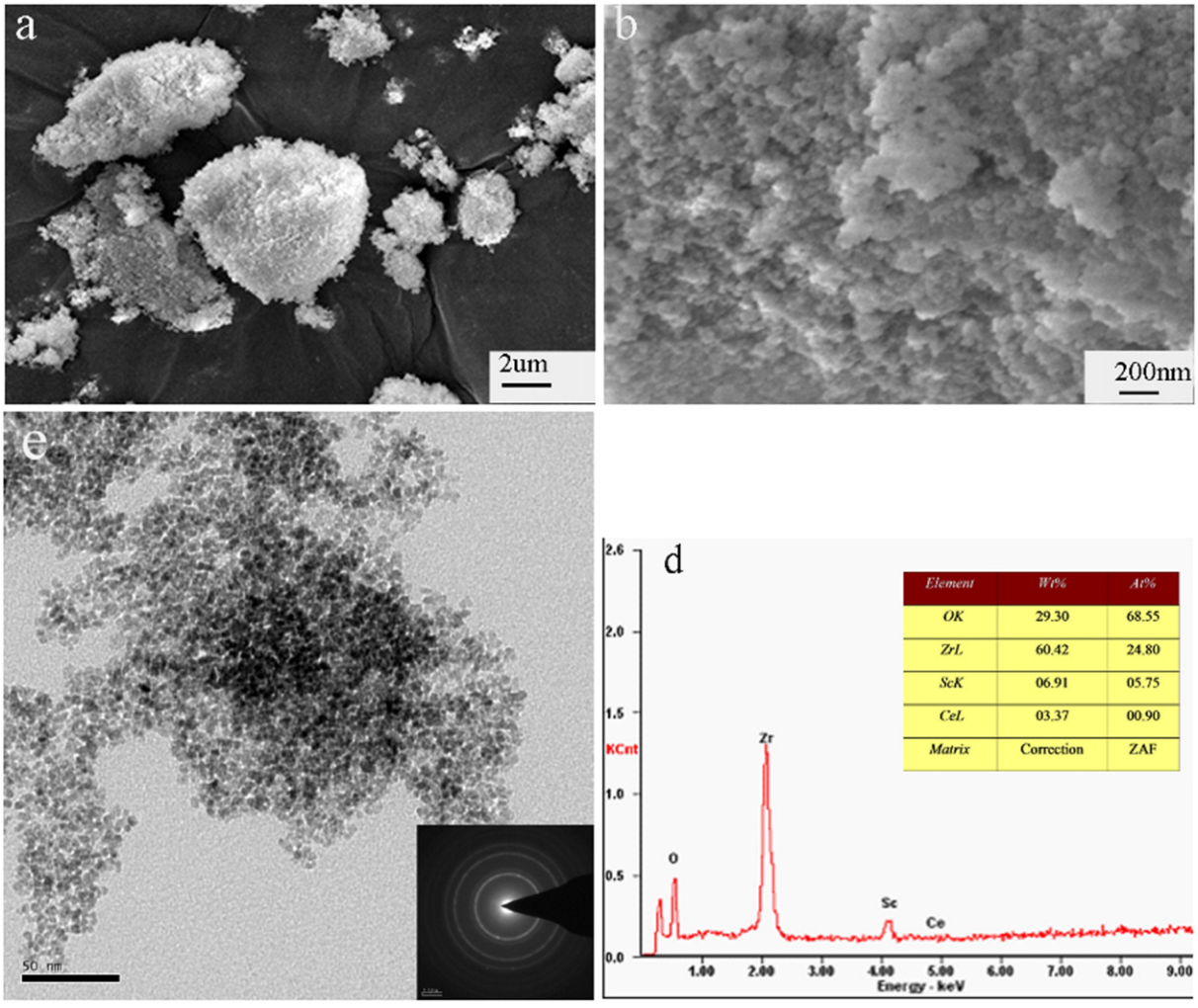

Fig. 2. (a) SEM images of the as-synthesized 10Sc1CeSZ powder. (b) The high magnification SEM images. (c) TEM images of 10Sc1CeSZ powder (inset: SAED pattern of the 10Sc1CeSZ nanocrystals). (d) The EDS result of 10Sc1CeSZ powder.