Synthesis and characteristics of nanocrystalline YSZ powder by polyethylene glycol assisted coprecipitation combined with azeotropic-distillation process and its electrical conductivity

Hong-Chang Yao, Xian-Wei Wang, Hao Dong, Rui-Rui Pei, Jian-She Wang, Zhong-Jun Li [*]

Department of Chemistry, Zhengzhou University, Zhengzhou 450001, PR China

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Abstract

Nanoscale 8 mol% yttria stabilized zirconia (YSZ) powders were prepared by polyethylene glycol (PEG-1540) assisted coprecipitation coupling with azeotropic distillation drying process. The role of PEG and azeotropic-distillation on the morphology and particle size of YSZ was studied. Thermogravimetry and X-ray diffraction results showed that azeotropic-distillation could reduce the formation temperature of YSZ phase. X-ray patterns of the YSZ powders revealed that the crystallite size of the powders increases with increasing calcination temperature, which is consistent with transmission electron microscopy observations. The sintering behavior and the ionic conductivity of the pellets prepared from YSZ powders calcined at 800 °C were also studied. At sintering temperatures ≥ 1400 °C, more than 99% of the relative density was obtained. The alternating-current impedance spectroscopy results showed that the YSZ pellet sintered at 1450 °C has ionic conductivity of 0.0726 S cm^{-1} at 800 °C in air. The present work results have indicated that the PEG assisted coprecipitation combined with azeotropic-distillation drying process is an alternative method to synthesize yttria stabilized zirconia powders with a high sinterability and a good ionic conductivity.
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1. Introduction

Yttria stabilized zirconia (YSZ) is the most widely used electrolyte for solid oxide fuel cells (SOFCs) because of its high ionic conductivity, good mechanical strength and excellent chemical stability in both oxidizing and reducing environments [1–3]. However, YSZ, as a commonly used electrolyte material, has relatively high ionic conductivity only when operating at a temperature of about 1000 °C. Operation at such a high temperature limits the choice of stable materials for SOFC components and leads to degradation and sealing problems in devices. Hence, enormous efforts for the improvement of YSZ ionic conductivity at lower temperatures could be found in the literature. For example, Hui et al. [4] have recently reviewed various approaches to enhancing the ionic conductivity of polycrystalline zirconia-based oxide electrolytes in the light of composition, microstructure, and processing. According to Hui's opinion, the ionic conductivities of the YSZ electrolyte are not only influenced by the composition, but also influenced by the microstructure, and even processing conditions. The microstructures of YSZ electrolyte, i.e. the properties of grain and grain boundary, are primarily correlated to the quality of the starting powder such as particle size, surface morphology and homogenate. Therefore, many researches have focused on the preparation of homogeneous fine YSZ ceramic powders to maximize the electrolyte ionic conductivity.

Wet chemical approach is the most common methods to produce the nano-structured zirconia based ceramic powders due to its advantages such as atomic level doping and excellent control of stoichiometric homogeneity. Up to now, a number of wet chemical approaches for synthesizing nanocrystalline YSZ powders have been reported, such as spray drying [5], plasma spray [6], organic precursor route [7], homogeneous precipitation [8], sol–gel route [9], Pechini method [10],

* Corresponding author. Tel.: +86 371 6778 3123; fax: +86 371 6778 3123.
  E-mail addresses: yaohongchang@zzu.edu.cn (H.-C. Yao),
  lizhongjun@zzu.edu.cn (Z.-J. Li).

hydrothermal [11] and solvothermal synthesis [12]. Investigations indicated that the key to produce nanocrystalline YSZ powder was to prevent particle agglomeration in the process of formation of the precursors as well as the following drying step. Thus, various measures were introduced to deagglomerate, such as polymerized complex method [13] and balling milling method [5,7]. However, only a few researches paid attention to the effectiveness of deagglomeration treatment to the wet precursor particles for improving the property of the final product [9].

In the present study, we introduce a PEG assisted coprecipitation combining with an azeotropic-distillation process for the facile synthesis of nanocrystalline YSZ powder. Coprecipitation method is one of the widely adopted techniques for synthesis of nanocrystalline powder, but suffering from broad particle size distribution because of agglomeration. In order to alleviate agglomeration, polyethylene glycol (PEG-1540) as dispersant was employed to refine the grain size of the precursor and azeotropic distillation as drying technique was applied to reduce the formation of hard agglomeration in this work. It was found that the deagglomeration treatments were effective and weakly agglomerated and homogeneous YSZ nanoparticles could be obtained. The sinterability experiment and the ionic conductivity measurement of YSZ nanoparticles demonstrated that this method is an effective route to produce highly sinterable YSZ ceramic powders.

2. Experimental procedure

2.1. Material synthesis

Yttria stabilized zirconia nanoparticles were prepared *via* the coprecipitating route. $ZrOCl_2 \cdot 8H_2O$ and $YCl_3 \cdot 6H_2O$ were used as starting materials and dissolved in distilled water to form a solution ($c_{total} = 0.4$ mol L^{-1}), in which Zr^{4+} and Y^{3+} concentration met the formula of $(ZrO_2)_{0.92}(Y_2O_3)_{0.08}$. A given quantity of polyethylene glycol (PEG-1540) was added into the solution under vigorous stirring. Aqueous solutions of NH_4HCO_3 (0.4 mol L^{-1}) containing the appropriate amounts of PEG-1540 were also prepared. Simultaneously, two kinds of solutions were added dropwise into a four-neck angled round-bottom flask with two dropping funnels under stirring. The pH was controlled to keep to ~5.5 with ammonia (3.0 mol L^{-1}) during the process. After aging for 1 h, the precipitates were filtered and washed with distilled water till no Cl^- ions detectable ($AgNO_3$ test). Then, a small part of the as-prepared precursor was dried in air (denoted as **S1**) while the rest was transferred to flask, mixed with *n*-butanol and distilled to remove water as azeotrope. The dehydrated powder was further dried in a vacuum oven at 60 °C for more than 12 h (denoted as **S2**). The obtained powders were calcined at different temperatures for 2 h to examine the phase formation of YSZ. To examine the surfactant effects, control experiment with no PEG-1540 addition was conducted (the dehydrated powder was denoted as **S3**). The conversions of Zr^{4+} and Y^{3+} ions were analyzed by chemical titration method to the primary precipitate.

For fabricating an electrolyte, the powders calcined at 800 °C were uniaxially pressed (10 MPa) into compacts, and subsequently isostatically pressed at 180 MPa pressure. The shaped samples were sintered at different temperatures from 1250 °C to 1450 °C for 2 h in air for determining the optimum sintering temperature. The apparent densities of sintered pellets were determined using Archimedes principle.

2.2. Property measurements

X-ray powder diffraction (XRD) patterns of the resultant powders were recorded on an X-ray diffractometer (PANalytical X'Pert PRO, Netherlands) with Cu $K\alpha$ ($\lambda = 0.15418$ nm) at a step width of $0.03°$ and a scanning range of $10–70°$. The mean crystallite size D was determined from diffraction line broadening using the Scherrer's formula ($D = \kappa\lambda/\beta \cos \theta$), where κ, λ, β, and θ are the Scherrer constant ($\kappa = 0.9$), the wavelength of Cu $K\alpha$ radiation, the full width at half maximum (FWHM) of the (1 1 1) reflection of YSZ phase, and the Bragg angle of the (1 1 1) reflection of YSZ phase, respectively.

The Brunauer–Emmett–Teller (BET) specific surface area was obtained *via* N_2 adsorption at 77 K (NOVA 1000e, Quantachrome Instruments, USA) and the measured result was translated into the equivalent particle size according to the equation: $D_{BET} = 6/(\rho S_{BET})$, where D_{BET} (nm) is the average particle size, S_{BET} is the specific surface area expressed in $m^2 g^{-1}$, and ρ is the theoretical density of YSZ [5.9 g cm^{-3}]. The simultaneous Thermogravimetry and Differential Scanning Calorimeter (TG/DSC) were carried out using a thermal analyzer (Netzsch, STA 409 PC/PG) in a temperature range from room temperature to 800 °C at a heating rate of 10 °C min^{-1} in air atmosphere.

The size distribution and morphology of synthesized particles were observed using transmission electron microscopy (TEM, Tecnai G2 20, FEI Company, Netherlands). The microstructures of the sintered pellets were revealed by scanning electron microscopy (SEM, JSM-6700F).

2.3. Electrical measurements

Electrical conductivities of the sintered pellets were measured by using an impedance analyzer (PARSTAT 2273). The measurements were conducted in air in the temperature range from 250 to 1000 °C and in the frequency range from 0.1 Hz to 1 MHz. Curve fitting and resistance calculation were done by ZSimpWin software. The conductivities were calculated using the expression of $\sigma = l/SR$, where l is the sample thickness and S is the electrode area of the sample surface. Activation energies (E_a) were calculated by fitting the conductivity data to the Arrhenius relation for thermally activated conduction, which is given as: $\sigma T = \sigma_0 \exp(-E_a/kT)$, where σ, σ_0, E_a, k, and T are the conductivity, pre-exponential factor, activation energy, Boltzmann constant and absolute temperature, respectively.