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Preparation and electrical characterization of ultra-fine powder scandia-stabilized zirconia

ZHOU Jing (周 静), ZHANG He (张 赫), XU Hong (徐 宏), XUE Qiannan (薛倩楠), HUANG Xiaowei (黄小卫), FENG Zongyu (冯宗玉)*, LONG Zhiqi (龙志奇)

(National Engineering Research Center for Rare Earth Materials, General Research Institute for Non-ferrous Metals, and Grirem Advanced Materials Co., Ltd., Beijing 100088, China)

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Abstract: Ultrafine powders of scandia-stabilized zirconia (ScSZ) were prepared by the co-precipitation method, using $ZrOCl_2$ and ScO_2 as raw materials and $NH_3{\cdot}H_2O$ as a precipitant. In this paper, the optimum process parameters were investigated. The pH of the reaction solution directly impacted the precursor structure, which further affected the obtained crystal forming. Many experiment methods of thermogravimetric analysis and differential thermal analysis (TG-DTA), X-ray diffraction (XRD), transmission electron microscopy (TEM), Raman spectroscopy (Raman), and nitrogen adsorption were employed to characterize the ScSZ powder. The structure transition mechanism from cubic to rhombohedral was discussed. In addition, the electrical conductivity of the powders was also studied after dry-pressing and calcining. The results showed that the structure of ScSZ with complete crystal surface belonged to the cubic phase. The crystallite sizes of the powders prepared are about 60–80 nm, meet the conditions of $(D_{90}–D_{10})/2D_{50}\leq1$, and exhibited the good flow properties. The electrical conductivity was more than 190 mS/cm in air measured at 850 ºC.

Keywords: scandia-stabilized zirconia; ScSZ; precursor; pH; electrical conductivity; rare earths

Solid oxide fuel cell (SOFC) is known as one of the most promising energy for its characteristics of high efficiency, good adaptability, low cost and less pollution. With the unique solid-state structure, it meets the needs of the regional power supply and heating[1–5]. The Fluorite type oxide crystal has the cubic phase structure which can easily generate the oxygen vacancies with low steric hindrance. As the conducting carrier of oxygen ions, the more the oxygen vacancies, the higher the conductivity is. As the electrolyte material, the fluorite-type structure oxide is becoming popular. Currently, the fluorite-type electrolyte includes three categories of zirconium oxide (ZrO_2) group, bismuth oxide (Bi_2O_3) group, and cerium oxide (CeO_2) group[6–10]. The scandia-stabilized zirconia (ScSZ) with the *c*-phase, is a solid oxygen ion conductor[11–13]. The dopant cations are believed to substitute for Zr^{4+} ions in the thereby created cation sublattice. Because of charge compensation, one oxygen vacancy is produced by every two trivalent Sc^{3+}. Meanwhile, the partial pressure of oxygen ion conductivity range has also been expanded. The ScSZ structure belongs to the cubic phase from room temperature to the high temperature. So, a large number of oxygen vacancies exist in zirconia lattice, making it an excellent oxygen ion conductors.

Currently, yttria-stabilized zirconia (YSZ) as a solid electrolyte is used for commercial SOFC. But it still has some disadvantages, including high operating temperature, prone to produce the bad interface reaction, low conductivity, sealing difficulties and so on. The problem how to increase the conductivity has become an inevitable trend in the development of commercial SOFC[14–17]. ScSZ co-doped with CeO_2 have been widely investigated. The *c*-phase 10 mol.% Sc_2O_3 and 1 mol.% CeO_2 (ScSZ) show high oxide ion conductivity[18,19]. The ScSZ co-development by Toho Gas Company and Daiichi Kigenso Kagaku Kogyo Co., Ltd. has doubled the oxygen ions through capacity. So far there are few studies related to the high property ScSZ powder preparation.

In recent years, the preparation method of ScSZ powder include liquid phase, gas phase and solid phase method, in which the liquid phase method has more categories, including precipitation, hydrothermal and sol-gel methods[20–28]. The liquid precipitation method, which is concerned characterize of its simple equipment, easy operation and low cost, becomes more and more prominent. In this paper, the co-precipitation method was chosen and studied to prepare the ScSZ powder. Also the phase structure, particle size, morphology and conductivity of the obtained power were tested to support the

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* **Corresponding author:** FENG Zongyu (**E-mail:** fengzongyu1120@163.com; **Tel.:** +86-10-82241189)

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analysis. The result exhibited that the electrical conductivity was higher than that of commonly used YSZ electrolytes.

1 Experimental

1.1 Materials and sample preparation

$ZrOCl_2$ (analytical-reagent grade, Tianyao Chemical Plant, Qingdao, PRC), ScO_2 (99.5%, Hunan General Research Institute of Nonferrous Metals) and $NH_3{\cdot}H_2O$ (analytical-reagent grade, Beijing Chemical Works) were used to prepare the stock solutions.

$ZrOCl_2{\cdot}8H_2O$ was dissolved in distilled water to prepare the aqueous solution of 1.3 mol/L. Under the condition of stirring, the mixed solution was neutralized with 1.0 mol/L $NH_3{\cdot}H_2O$ under different pH environment. Then the precursor of un-doped ZrO_2 was obtained. Sc_2O_3 and Ce_2O_3 were dissolved in hydrochloric acid respectively to prepare the solution containing Sc^{3+} and Ce^{4+}. Then the above three solutions were mixed at the molar ratio of ZrO_2, Sc_2O_3 and CeO_2 89:10:1. Under the condition of stirring, the mixed solution was neutralized with 1.0 mol/L $NH_3{\cdot}H_2O$ under different pH environment. The precursor of ScSZ was obtained by filtering and washing with distilled water and absolute ethanol. After drying for 24 h in the dry box at 150 ºC, it was sintered at high temperature for about 2 h. Then the ultrafine powder of SCSZ was obtained.

1.2 Characterization methods

To characterize the ScSZ powder, many experiment methods such like TG-DTA, XRD, TEM and nitrogen adsorption were employed. The DSC-TG patterns were obtained by a Simultaneous Thermal Analysis STA 449 F5 (NETZSCH Co., Ltd., Germany). The XRD patterns for powders were recorded by an X' Pert PRO MPD X-ray diffractometer (PANalytical Co., Ltd., Netherlands) using Cu-Kα radiation. Transmission electron microscopy (TEM) observation was performed with a JEM-2000FX (JEOL Co., Ltd., Japan). The Raman spectra were recorded on a Jobin-Yvon HR800. The excitation source was an Ar^+ ion laser of 514 nm with a power level of 800 mW, with the spectrum resolution of 1 cm^{-1}. The specific surface area was measured using ST-8 automated surface area (Qipu Analysis Instrument Institute, PRC). The electricity conductivity was measured using 4PT Conductivity Testing Manual (Bloom Energy Co., Ltd., USA) after powder being pressed and sintered. The structure models were finished using Diamond 5.0. Further analysis was performed with FindIt 5.0 to gain accurate lattice parameters and possible space groups.

2 Results and discussion

2.1 Preparation of un-doped ZrO_2 precursor

When $ZrOCl_2{\cdot}8H_2O$ is dissolved in water, the hydrolysis and polycondensation reactions occur in aqueous solution. The components are mainly in the form of tetramers. Tetramers are of a square formed by four zirconium atoms; each zirconium atom is connected by four OH bridges and four water molecules[29,30]. The equation of tetramer with bound water loses H^+ and a proton is described as follows:

$$[Zr(OH)_2{\cdot}4H_2O]_4^{8+} \rightleftharpoons [Zr(OH)_{2+x}{\cdot}(4-x)H_2O]_4^{(8+4x)}+4xH^x \quad (1)$$

With further polycondensation reactions, polymers containing 16 zirconium atoms are formed by OH bridges. Normally the obtained precursors include three allotropes such as α ($Zr_4(0H)_8(OH)_8{\cdot}nH_2O$), β ($Zr_4O_2(OH)_4(OH)_8{\cdot}H_2O$) and γ ($Zr_4O_4(OH)_8{\cdot}H_2O$). Because the polymers before sintering are amorphous, it is difficult to distinguish the allotropes by XRD patterns with broad and disperse diffraction peaks.

Fig. 1 exhibits the XRD spectra of the un-doped ZrO_2, which was prepared from the polymers by calcination at 1000 ºC. It was obvious that the ZrO_2 obtained in the experiments was mainly in monoclinic phase under the conditions from the basicity value pH 3–4 to 12–13. In Fig. 1, the diffraction peaks marked by the black diamond are the characteristic peaks of tetragonal ZrO_2 structure. The changes of the peak intensity stand for the content of tetragonal structure ZrO_2 changing with the pH values. Clearly, the tetragonal phase powders can be easily obtained at pH 12–13. While under other cases, the contents of the tetragonal phase powders are respectively low. Since the tetragonal structure ZrO_2 affects the property of the final doped sample, lower content is preferred.

The pH of the aqueous precursor solution and the rate of the monomers polymerization significantly affect the structure of ZrO_2 precursor, and then determine the final crystalline structure of ZrO_2 powder. It is reported in the literature[30] that, by calculations of the density functional theory, there are four electron models of ZrO_2 precursor structure, which are $[Zr(OH)_2(H_2O)_4]^{2+}$ (pH<7),

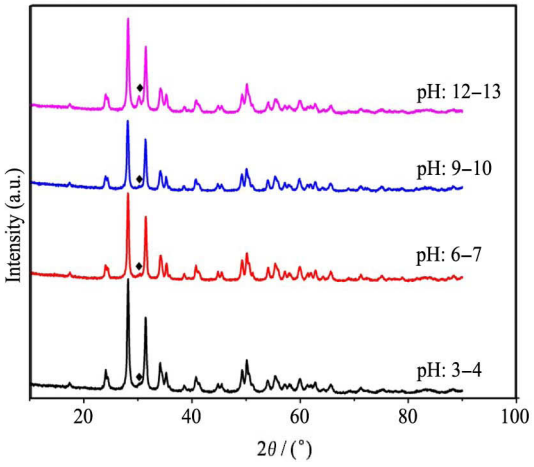

Fig. 1 XRD spectra of un-doped ZrO_2