Preparation of dense yttria stabilized zirconia ceramic by low-temperature sintering zirconium oxalate sol

Tingting LIU, Jianjun FANG, Sufang LI, Congcong WANG and Cunlu JI

College of Chemistry and Chemical Engineering, Hunan University, Changsha 410000, People’s Republic of China

This article reports a novel method of sintering zirconium oxalate (ZrOC₂O₄) sol to prepare dense yttria stabilized zirconia (YSZ) ceramic at a low sintering temperature below 1300°C. A YSZ ceramic as control group was also prepared by sintering its nano-powder. The thermal decomposition process and sinter programme of the YSZ green bodies were investigated by thermogravimetry and differential thermal analysis. The sintered ceramics showed a crystallization structure in cubic phase and the crystal size increased with the increasing sintering temperature in the range of 550 to 1200°C. For preparing dense YSZ ceramic, a zirconium oxalate sol was prepared by sol–gel method and then sintered with a temperature of 1000, 1100, 1200 and 1300°C. Compared with the ceramic obtained from YSZ ceramic nano-powder, the ceramic prepared by zirconium oxalate sol exhibited an enhancement of densification with higher relative density of 98.5% and higher electrical conductivity at all test temperatures.

Key-words : Zirconium oxalate sol, Yttria stabilized zirconia ceramic, Low-temperature sintering, Densification, Electrical conductivity

1. Introduction

Dense yttria stabilized zirconia (YSZ) ceramic is an important engineering material substance and has attracted considerable attention for a variety of applications in batteries, thermal barrier coatings (TBCS) and tissue engineering.1-6 due to its high ionic conductivity, high fracture toughness, low thermal conductivity, high coefficient of thermal expansion and high hardness.7-9 To date, the most popular principle for preparing YSZ ceramic is sintering its powders at a high temperature (ca. >1400°C).3,10,11 However, the high sintering temperature would result in a series of disadvantage, such as high cost, coarse particles and poor mechanical properties.12,13 In addition, YSZ is often co-sintered with other materials, such as platinum paste in the oxygen sensor,14 which can’t be treated at such a high temperature.

To overcome these problems, several strategies have tested to achieve YSZ ceramic by low-temperature sintering. The straightforward method involves sintering YSZ nano-powder to lower the sintering temperature.10,15-17 Some assisting method, such as introducing low-temperature assisted sintering additive,11,18,19 could also achieve YSZ ceramic by low-temperature sintering. However, the shortcomings of the above two methods such as poor densification were not overcome. For the method of sintering YSZ ceramic nano-powders, since nanoparticles tend to spontaneously agglomerate together to reduce the interfacial energy and the total surface area of the system,20,21 the final YSZ ceramic is inevitable to produce agglomerated particles, which results in the formation of large pores in the region of ceramic.22 Introducing low-temperature assisted sintering additive can result in a decreased properties of the YSZ ceramic, such as low ionic conductivity, poor mechanical properties and low coefficient of thermal expansion due to the introduction of sintering aids.11,19 In addition, the above two methods require complex multiple steps, including the preparation of ceramic powder and sintering ceramic powder to form ceramic. Thus, the preparation of dense YSZ ceramic by low-temperature sintering with a simple process will still constitute an important research direction.

Sol–gel method is a common wet chemical technique to synthesize nanoparticle sol based on the reactions of the hydrolysis and condensation from molecular precursors.23,24 Due to its important advantages, including excellent chemical purity and homogeneity,25-27 low temperature synthesis,24-27 predictable composition25-27 and simple preparation process,24,28,29 sol–gel method has become a particularly attractive route to prepare zirconyl oxalate (ZrOC₂O₄) sol. Recently, porous ceramic membranes with ZrOC₂O₄ sol have been prepared based on sol–gel method30 under a firing temperature lower than 1000°C. These works provide important academic support for possibility of preparing dense YSZ ceramic by low-temperature sintering with a simple process based on sol–gel method. However, to the best of our knowledge, few papers on the preparation of dense YSZ ceramic with ZrOC₂O₄ sol have been published.

In the present study, to obtain low-temperature sintering with a simple process for preparing dense YSZ ceramic, we attempted to develop a novel method of direct sintering ZrOC₂O₄ sol. The thermal behavior and sinter programme of the ceramic green bodies, the effects of sintering temperature on the crystallization behaviors and structures, microstructures and densification and the electrical conductivity of the sintered YSZ ceramic have been investigated. The differences of the properties between the YSZ ceramic prepared by zirconyl oxalate sol and that prepared by sintering nano-powder were also studied.

2. Experimental procedures

2.1 Preparation of zirconyl oxalate sol

Zirconyl chloride hydrate (ZrOCl₂·8H₂O) (AR), yttrium nitrate hydrate [Y(NO)₃·6H₂O] (AR) and oxide acid dihydrate (H₂C₂O₄·2H₂O) (AR) were used as starting materials in the experiment.
Ethyl alcohol (CH₂CH₂OH) (AR) was used as solvent. All reagents were used directly without any further purification. Zirconyl oxalate sol was prepared from ZrOCl₂ and H₂C₂O₄ in alcohol solution. 1 mol/dm³ ZrOCl₂ alcohol solution was obtained by dissolving ZrOCl₂·8H₂O in ethyl alcohol. Then Y(NO)₃·6H₂O was added to the ZrOCl₂ solution as the precursor of Y₂O₃ stabilizer. The molar ratio of Zr and 2Y was 92/8. Then 20 vol% deionized water was added into the solution to promote dissolution of the organic salts. H₂C₂O₄·2H₂O was dissolved in ethyl alcohol to prepare 0.5 mol/dm³ H₂C₂O₄ solution. The molar ratio of ZrOCl₂ and H₂C₂O₄ was 2:1. H₂C₂O₄ solution was dropwise added to ZrOCl₂ solution at room temperature with continuous gentle stirring to form homogeneous ZrOC₂O₄ sol. The mixture would be continuously ground until paste-like solid was formed, which was made into strip-like membrane to experimentize. So ceramic green body was achieved in this way. For comparison, the YSZ ceramic was also prepared by the YSZ nano-powder, and the nano-powder was prepared by calcining ZrOC₂O₄ sol at 600°C in a muffle furnace and then were ball-milled for 24 h. The YSZ powder was shaped to ceramic green body in the same method. The ceramic directly prepared from the sol was labeled as YSZ1, and the ceramic prepared from the powder was labeled as YSZ2. The dimensions of the green bodies were 100 × 10 × 5 mm³ for both YSZ1 and YSZ2.

The green bodies were sintered in a high temperature furnace in air atmosphere under different final temperatures of 1000, 1100, 1200 and 1300°C, to study the change of the microstructure with the increase of sintering temperature. YSZ ceramic was obtained after natural cooling of the furnace. The sinter programme will be discussed latter in section 3.1.

2.3 Characterization of the ceramic

Thermogravimetry (TG) and differential thermal analysis (DTA) of YSZ1 and YSZ2 green bodies were performed by a STA 449 C thermal analysis system. The tests were carried out in flowing air with a flow rate of 70 mL/min from room temperature to 800°C at a heating rate of 1°C/min. Al₂O₃ was used as the reference for the DTA measurement.

The ceramic green bodies and the ceramics heat treated at 550, 800, 900, 1000, 1200 and 1300°C for 2 h were characterized by X-ray diffraction (XRD, Rigaku D/max-2500). The measurements were operated by using Cu-Kα as X-ray source in the 2θ range of 5°-80° with a step size of 0.02°, voltage at 40 kV and current at 250 mA.

The microstructure of YSZ1 and YSZ2 ceramic sintered at different final temperatures of 1000, 1100, 1200 and 1300°C were observed by field emission scanning electron microscopy (FESEM, Hitachi S-4800) at an accelerating voltage of 5.0 kV.

Relative density of the ceramics was measured through drainage according to Archimedes principle, using distilled water. Used in the calculations, the theoretical density was 5.96 g/cm³.

Electrical conductivity of the YSZ1 and YSZ2 ceramics sintered at 1300°C was measured in temperature range 400-900°C with intervals of 100°C, using impedance spectroscopy method. The sintered specimens of dimensions 45.7 × 4.6 × 2.5 mm³ for YSZ1 and 67.2 × 6.8 × 3.7 mm³ for YSZ2 were printed with platinum paste on both surfaces as electrodes, and then heated to 1000°C at 2°C/min and kept constant for 1 h. The measurements were carried out by an impedance analyzer (Solartron SI 1260) in the frequency range varying from 1 Hz to 10⁵ Hz.

3. Results and discussion

3.1 Thermal analysis of YSZ1 and YSZ2 green bodies

We investigated the TG–DTA curves of YSZ1 green body in order to understand its thermal behavior and then determine its suitable sinter programme. Following by the previous discussion, sintering nano-powders is a well-know route to achieve low-temperature sintering of YSZ ceramic. In order to evaluate the performance difference of YSZ ceramic prepared by sintering between the zirconyl oxalate sol and nano-powders, YSZ ceramic prepared by the YSZ nano-powder (YSZ2) was set as control group. As shown in Fig. 1(a), in the TG–DTA curves of YSZ1 green body, during the first step from a temperature of 30 to 200°C, a broad endothermic peak in the range of 101 to 126°C with a weight loss of 29% is attributed to the decomposition of nitrates. During the second step between the temperature of 200 to 526°C, only one sharp exothermic peak appeared at 360°C with a weight loss of

Fig. 1. TG–DTA curves of the ceramic green bodies (a: YSZ1, b: YSZ2).
17% due to the burning of organic auxiliary agents and no exothermic peak around 515°C is observed. This is because the crystallization of YSZ ceramic powder has completed before 515°C, since it was prepared by calcining ZrO\textsubscript{2}C\textsubscript{2}O\textsubscript{4} sol under a temperature of 600°C. Based on the above results, a suitable sinter programme was established that the heating rate was 1°C/min before 550°C, and then increased to 2°C/min. Specially, the temperature points of 110, 138, 360 and 515°C for YSZ1 and those of 110 and 360°C for YSZ2 were kept constant for 1 h.

3.2 XRD characterization of YSZ

To understand the crystallization behavior of YSZ1 and YSZ2 green bodies, and their sintering ceramics, XRD were performed. As shown in Fig. 2(a), it can be observed from the XRD results, YSZ1 green body showed the amorphous character. However, when the YSZ1 after heat treatment at 550 and 1300°C, obviously, characteristic diffraction peaks with crystallization in pure cubic phase (ICDD card number 30-1468) appeared in the XRD pattern. This result, associating with the result displaying in the TG-DTA analysis [Fig. 1(a)] that no significant weight loss was observed after the heat treatment temperature of 526°C, indicates that YSZ1 could be well transited from green body to YSZ at the treat treatment temperature of 550°C. For the XRD pattern of YSZ2 green body and its sintering ceramic [Fig. 2(b)], it can be seen that all samples showed a similar crystallization structure of cubic phase.

To further estimate crystallite grain growth with the heat treatment temperature, YSZ1 was subject a sintering temperature of 550, 800, 900, 1000, 1100, 1200 and 1300°C, and the highest XRD diffraction peaks were presented in Fig. 2(c). It can be observed that the width of the peaks decreased with the increase of sintering temperature. This finding indicates that the crystallite integrity of YSZ ceramic increases along with sintering temperature. The mean crystallite size of YSZ ceramic heated treatment under the above temperatures was also evaluated from the highest intensity XRD diffraction peak using Scherrer formula\textsuperscript{35,36} As shown in Fig. 2(d), the average crystallite sizes of YSZ heated treatment at 550, 800, 900, 1000, 1100, 1200 and 1300°C were calculated to be about 14.3, 15.7, 18.7, 25.9, 31.8, 40.0 and 40.1 nm, respectively. The crystallite size increased with the increase of heat treatment temperature, but remained stable over the sintering temperature of 1200°C. Between 900 and 1200°C, the crystallite behaved in a nearly liner growth. According to the reports of Z. R. Hesabi and K. Rajeswari et al.,\textsuperscript{37,38} the small crystallite size of about 40 nm is beneficial to the improvement of mechanical properties and the ionic conductivity of the YSZ ceramic.

3.3 FESEM analysis of the YSZ ceramic

To be intuitionistic determine the advantages of YSZ ceramic prepared by directly sintering zirconium oxalate sol, YSZ1 and YSZ2 ceramics under a final sintering temperature of 1000, 1100, 1200 and 1300°C were prepared, and their microstructure were
observed by FESEM. Since the decomposition of ZrOCl₂, YSZ1 ceramic may have larger propriety than YSZ2 ceramic at low sintering temperature. However, as shown in Fig. 3, YSZ1 ceramic had greater enhancement of densification with increasing the sintering temperature, although, agree with the results of XRD, the crystallite integrity and size of both YSZ1 and YSZ2 ceramic increased. The samples of YSZ1 ceramic exhibited a porous structure at a sintering temperature below 1200°C, while a dense morphology was observed at the sintering temperature of 1300°C. The particles piled up together loosely as the sample sintered at 1000°C, sintering together to form net structure when the temperature increased, and the microstructure became compact with a few pores of about 100 nm as the temperature reached to 1200°C. Further increases the temperature to 1300°C, the surface was almost flat and the microstructure was dense without pores, which indicated that the ceramic was sintered. In addition, the microstructure was homogeneous with fine particles, which was beneficial for facilitating the densification. However, all groups of YSZ2 showed a less homogeneous structure than YSZ1, which induced by agglomerated nano-particles. And then the sintering behavior was adversely affected. The specimen sintered at 1200°C maintained porous and possessed a less uniform pore size distribution than YSZ1, from 100 nm to 1 μm. When the temperature increased to 1300°C, small pores disappeared, but some large pores still presented although the ceramic was locally sintered. This result is consistent with the previous finding that YSZ ceramic prepared by sintering its nano-powder is inevitable to produce large pores in the region of ceramic.²²)

The average grain size of dense YSZ1 ceramic sintered at 1300°C were displayed in Table 1, comparing with other average grain sizes of dense YSZ ceramic prepared by conventional method in pervious literatures ³⁷) and ³⁹). Especially, all the YSZs were 8 mol% Y₂O₃-stabilized ZrO₂, and all the average grain sizes were estimated using the linear intercept method. The average grain size of dense YSZ1 ceramic was 0.27 μm, much smaller than the values in literatures ³⁷) and ³⁹). Usually, YSZ ceramic with fine grains possesses high conductivity, which will be ascertained in section 3.4.

![Fig. 3. The FESEM micrographs of YSZ sintered between 1000 and 1300°C.](image-url)
3.4 Relative density and electrical conductivity of YSZ ceramic

High relative density and high electrical conductivity are necessary for excellent YSZ ceramic used as solid electrodes. In order to confirm that YSZ ceramic prepared by sintering zirconyl oxalate sol was suitable for solid electrodes, we tested the relative density and electrical conductivity of both YSZ1 and YSZ2 ceramic. As shown in Fig. 4(a), the relative density for both YSZ1 and YSZ2 ceramic increased as the sintering temperature increased. At a low sintering temperature of 1000 and 1100°C, the relative density of YSZ1 ceramic was 60.9 and 70%, respectively, with no significant differences compared with that of YSZ2 ceramic. However, when the sintering temperature increased to 1300°C, YSZ1 ceramic exhibited higher relative density of 98.5% than YSZ2 ceramic of 92.3%. The low relative density of YSZ2 ceramic could be explained by the porous structure formed in the ceramic, which has been observed by FESEM images (Fig. 3).

Grain interior conductivity and grain boundary conductivity, which can be evaluated from impedance (Cole-Cole) plots, are both contributed to the conductivity of YSZ ceramic. Figure 4(b) gives a representative impedance (Cole-Cole) plots of dense YSZ1 ceramic (sintered at 1300°C) tested at 400°C. The higher frequencies (left semicircle) and lower frequencies (right semicircle) correspond to grain resistivity ($R_g$) and grain boundary resistivity ($R_{gb}$), respectively. The evaluated values of grain, grain boundary and total conductivities of YSZ1 and YSZ2 ceramics (sintered at 1300°C) from 400 to 900°C are shown in Figs. 4(c) and 4(d). The activation energies ($E_A$) of the total conductivity can be calculated by the equation: $\sigma = (\sigma_0/T) \exp[-E_A/(k_B T)]$. YSZ1 ceramic revealed lower activation energy (107 kJ/mol) than YSZ2 ceramic (111 kJ/mol). From the figures it is clear that YSZ1 ceramic with lower $E_A$ exhibited an elevated total conductivity compared with YSZ2 ceramic in all test temperatures. However, the electrical conductivity for both YSZ1 and YSZ2 ceramics increased with an increase of test temperature.
When the test temperature was 900°C, the electrical conductivity reached a value of 127 mS/cm for YSZ1 ceramic, but only 63 mS/cm for YSZ2 ceramic. This result is consistent with the report of Q. Li et al.\(^4\) The ceramic which possesses higher relative density has higher electrical conductivity. Many previous literatures have reported the total conductivity and the corresponding activation energy of YSZ ceramic prepared by conventional method. Table 1 shows a part of the results along with the data of YSZ1 ceramic in the present work. For the activation energy, calculated value in this study was centered, somewhat higher than the value reported in literature 39), but lower than the value reported in literature 37). Compared with the data, conductivity of YSZ1 ceramic prepared by sintering ZrOC\(_2\)O\(_4\) sol in the present work increased more or less.

For traditional YSZ ceramic, the total conductivity is mainly determined by grain boundary conductivity, because the resistivity of grain boundary is much higher than that of grain interior.\(^3\) The high grain boundary resistivity is caused by two main factors, the segregation of a blocking layer with space charges near the grain boundary and the impurity phases at the grain boundary obstructing the oxygen transport.\(^4\) Thus, the influence of grain boundary conductivity for the total conductivity will reduce and that can be evaluated by blocking factor \(R_b\).\(^4\) In other words, the fraction of the electric carriers being blocked in the ceramic is shown from this factor. Based on the equation, the blocking factor (tested at 900°C) of dense YSZ1 ceramic was only 0.19. As a consequence, the YSZ1 ceramic sintered by sintering ZrOC\(_2\)O\(_4\) sol possessed enhanced total conductivity than the values prepared by conventional method reported in previous literatures due to the lower contribution of grain boundary resistivity. However, for YSZ2 ceramic with almost the same average grain size with YSZ1 ceramic, the blocking factor \(R_b\) was up to 0.56 (tested at 900°C) and the total conductivity was poor. This result is caused by the stable pores in YSZ2 ceramic, which hinder the free movement of the oxide ions\(^6\) and decrease the conductivity consequently.

4. Conclusions

In the present study, dense YSZ ceramic has been successfully prepared under a low sintering temperature by a new route of sintering zirconium oxalate sol. The suitable sinter programme of the YSZ ceramic were verified. The resultant YSZ ceramic exhibited an enhanced densification compared with the ceramic that fabricated by conventional method of sintering YSZ nanopowder. Additionally, the dense YSZ ceramic possesses a high relative density of 98.5% and an electrical conductivity of 127 mS/cm at the test temperature of 900°C, and subsequently holds potential for applications as solid electrolytes.

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