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Fabrication of yttria stabilized zirconia nanoparticles by the reverse microemulsion method for SOFC applications

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Yttria stabilized zirconia powders were synthesized by the reverse microemulsion method. Powders were calcined from 600 °C to 1000 °C and sintered at 1450 °C. Crystalline properties and microstructure of samples were characterized by X-ray diffraction and scanning electron microscopy, respectively. Oxygen ionic conductivity was measured by electrochemical impedance spectroscopy. Sizes of yttria stabilized zirconia particles calcined at 1000 °C are lower than 100 nm, and approximately, 1 μm grain was obtained after sintering at 1450 °C.

Keywords: *yttria stabilized zirconia; chemical synthesis; electron microscopy; ionic conductivity*

1. Introduction

High performance ceramic material, yttria stabilized zirkonia (YSZ) is the most commonly used as an electrolyte. YSZ is an important material for oxygen sensors, oxygen pumps, catalysts and fuel cells. When doped with 8 mol % of yttria, the structure is stabilized and this modified electrolyte shows high ionic conductivity as well as high thermal stability, and has excellent mechanical properties. In recent decades, there has been great interest in the conductivity of YSZ based electrolytes [1–4].

Many different methods exist for the preparation of nanosized YSZ such as sol -gel technique, precipitation, spark-plasma sintering and hydrothermal synthesis leading to final products differing in properties. Therefore, the choice of preparation route and particular heat treatment strongly influence the synthesis, sintering and properties of the YSZ powders, and are very important for optimizing the properties of the YSZ electrolytes.

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In recent years, a relatively new microemulsion method has been used for preparation of ultrafine powders [5, 6]. It was invented in the 1980s as an effective process of fabrication of nanoparticles. Microdroplets containing solved reactants act as nanoreactors in the microemulsion system. When the droplets collide with each other, the precipitation occurs. A powder of spherical particles, with a uniform size distribution and good dispersibility can be obtained. The size and shape of reverse micelles would change with the molar ratio of the water to surfactant value (w_0), the type of ions and electrolyte concentration in the aqueous phase, and the type of co-surfactant used. Droplets with spherical, ellipsoidal, rod-like, cylindrical, or planar shapes would appear, depending on the w_0 value or the electrolyte concentration in the aqueous phase. By further addition of the aqueous solution or by increasing the ionic strength in aqueous phase, a bicontinuous structure or normal micelles might even be formed [5–11]. Fang et al. [6] obtained ultrafine YSZ using 1-hexanol–water–CTAB microemulsion system. Ultrafine powders of tetragonal crystalline zirconia having particle diameters of 40–70 nm were obtained. Ma et al. [7] employed cyclohexane–water–TritonX-100 –hexyl alcohol system to fabricate ultrafine spherical particles of 30–40 nm tetragonal zirconia powders. Tai et al. [8] obtained yttria stabilized zirconia by the reverse microemulsion technique using a system of water–CTAB–hexanol.

The aim of this study was to investigate the fabricate nanoscale uniform YSZ powder by the reverse microemulsion method. The microstructure and ionic conductivity of YSZ material were studied in detail.

2. Experimental

Reverse micelles were fabricated by using Triton X-100 (Merck, 99%) as a surfactant, hexanol (Merck, 98%) as co-surfactant, isooctane (Sigma, 99.5%) as an oil phase. $ZrOCl_2 \cdot 8H_2O$ (Merck, 99.9%), $Y(NO_3)_3 \cdot 6H_2O$ (Sigma, 99.9%) were used as inorganic precursors. Two organic phases containing equal amounts of Triton X-100, hexanol and isooctane were prepared separately. The mixture of inorganic salts containing 8 moles of Y_2O_3–92% mol ZrO_2 was dissolved in an appropriate amount of water and added dropwise into one of organic phases. NH_4OH was added dropwise into the other organic phase. Finally, these two transparent microemulsions were mixed together and refluxed. The mixture was magnetically stirred at 80 °C for 3 h. The stability of the mixture was broken by adding ethanol and then centrifuging. The residue was washed with ethanol repeatedly until no Cl^- ions could be detected with $AgNO_3$ solution, and sample was then dried in an oven at 180 °C for 12 h. The dried product was calcined at 1000 °C for 6 h. After calcination, the powders were ground using a ball milling system (Retsch-S100).

Differential and thermogravimetric analyses (DTA/TGA) of the dried product were carried out using a thermal analyzer (Linseis) at thea heating rate of 10 °C/min in air. The phase identification was performed by X-ray diffraction (XRD) using a Rigaku D/max-2200 diffractometer with CuK_α radiation (λ = 0.15418 nm) and, operat-

ing at 30 kV, 20 mA. The crystallite size of the calcined powders was calculated by the X-ray line broadening technique, performed on the (220) diffraction pattern of YSZ, using the Scherer equation: $D_{XRD} = (0.9\lambda)/(\beta\cos\theta)$, where D_{XRD} is the crystallite size (nm), λ is the radiation wavelength (0.15418 nm), θ is the diffraction peak angle and β is the corrected half-width at a half-maximum (FWHM).

In order to further investigate high temperature behaviour of this 8YSZ powder, a disk-shaped sample of 15 mm diameter and 1 mm thickness was obtained by cold isostatic pressing (CIP) at 95 MPa. Subsequently, the sample was sintered at 1450 °C for 6 h. The morphology of powders calcined at 1000 °C and of discs sintered at 1450 °C were examined using a scanning electron microscope (SEM, JEOL 6335F). The oxygen conductivity measurements were performed on a sintered sample using a two-probe ac impedance analyzer (Solartron 1260 FRA and 1296 interface) at 300 °C. Pt wire and Pt paste (Alfa Aesar) were used as electrode materials. The data were analysed in the impedance mode using a computer software (Z view, Scribner Associates).

3. Results and discussion

TGA and DTA curves of the analysed samples are shown in Fig. 1. The exothermal peak at 325 °C in DTA, and the rapid weight loss between 260 °C and 380 °C in TGA can be attributed to the decomposition of organic compounds [7]. The endothermal peak at 468 °C should be due to the dehydration process of $Zr(OH)_x$. The crystallization of zirconia began with a slight exothermal peak at around 550 °C.

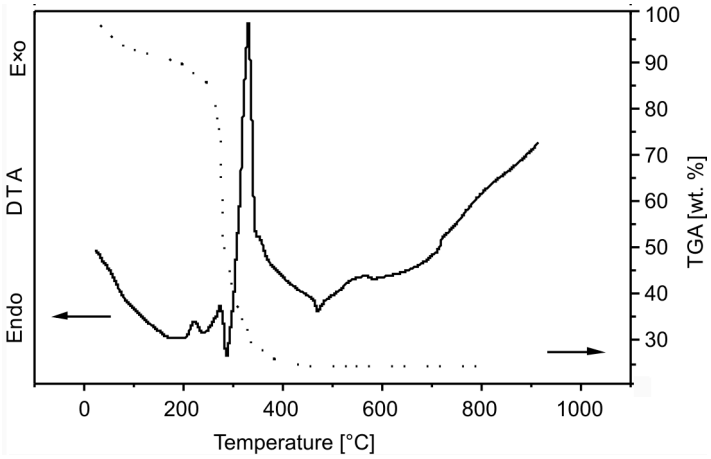

Fig. 1. The TGA/DTA curves of as prepared YSZ samples

The XRD patterns of samples calcined between 600 and 1000 °C are shown in Fig. 2, and those sintered at 1450 °C are in Fig. 3. The peak intensities increase and

get sharper as the calcination temperature increases. The YSZ sample shows the cubic phase of ZrO_2 Tetragonal and cubic phases can be distinguished with the characteristic (212) peak of tetragonal phase. This peak, as reported previously, has not been observed for any cubic samples [1, 2, 5, 12, 13]. The peaks observed in this study are attributed to the cubic phase, and it can therefore be concluded that the Y_2O_3 was completely dissolved in the zirconia structure.

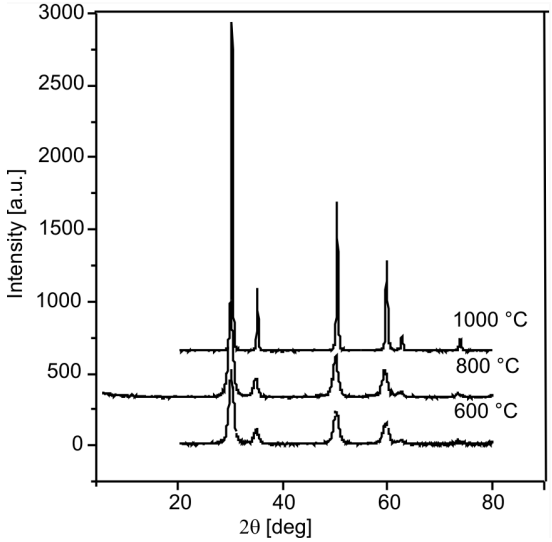

Fig. 2. XRD results in YSZ samples calcined at 600, 800 and 1000 °C

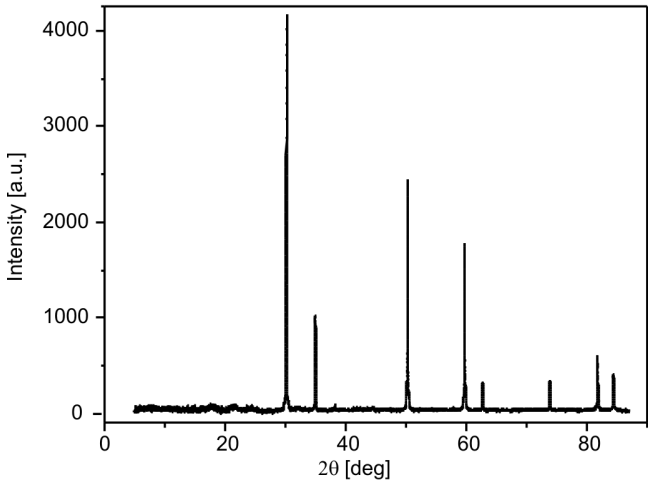

Fig. 3. XRD results for an YSZ sample sintered at 1450 °C for 6 h

The lattice constants of YSZ were found to be 5.135 Å and 5.133 Å, for samples calcined at 1000 °C and sintered at 1450 °C, respectively. It is generally known that

the lattice parameter of ZrO_2 increases with Y_2O_3 doping because ionic radii of Y^{3+} are higher than those of Zr^{4+}. When the coordination number is equal to 8, the ionic radii are 0.84 Å in Zr^{4+} and 1.02 Å in Y^{3+} [14].

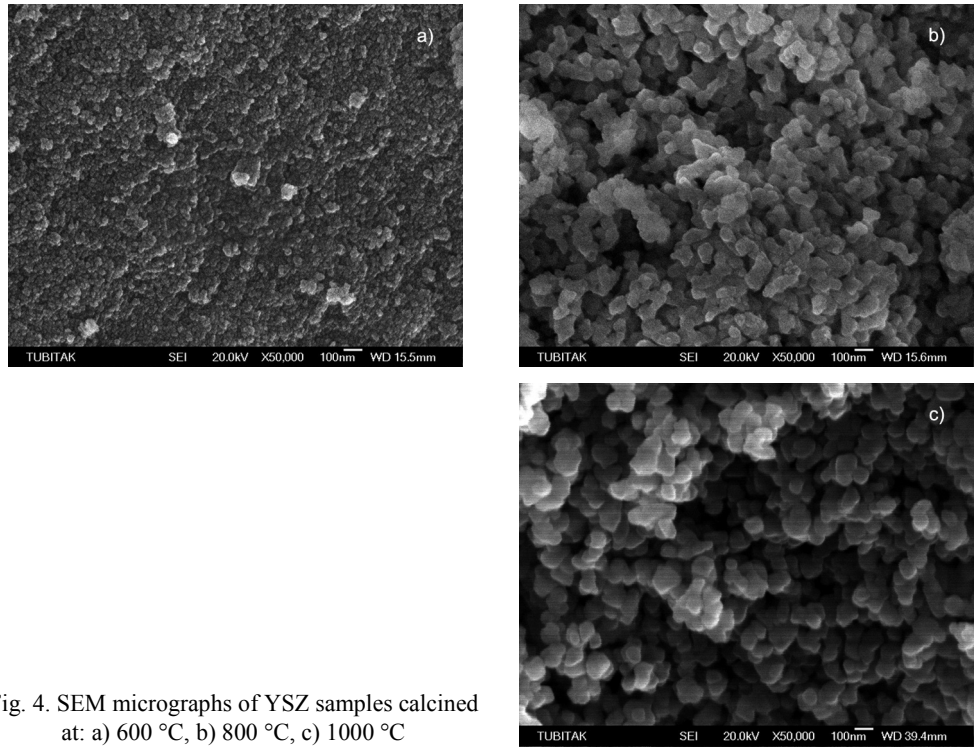

Fig. 4. SEM micrographs of YSZ samples calcined at: a) 600 °C, b) 800 °C, c) 1000 °C

SEM results of as-prepared samples are shown in Fig. 4. The particle size of powders calcined between 600 °C and 1000 °C increased. In the case of 600 °C calcinations, mean particle size is below 50 nm and it is approximately 80 nm at 1000 °C . The crystal sizes were calculated from the Debye–Scherer equation and they were found to be 10.6, 11.5, 30.9 nm for calcination temperatures of 600, 800 and 1000 °C, respectively. Consistently, both crystallite and particle sizes increased with the temperature of calcinations. It is also observed that all the calcined powders prepared with reverse-micelles have uniform and spherical particles. Powders calcined at 1000 °C were subjected to cold isostatic pressing at 95 MPa and were sintered at 1450 °C. The density of sintered discs was measured by the Archimedes method and calculated as being 92% of the theoretical density. The SEM data of the disc-shape sintered sample can be seen in Fig. 5. Sintering at 1450 °C resulted in sub-micrometer grain size. In addition, grains are uniform in size and shape, and there is no evidence of exaggerated grain growth. The grain uniformity of sintered samples is important for stable conductivity of YSZ exposed to high temperature. As is seen from Fig. 5, most of the particle sizes are approximately 1 μm after sintering.

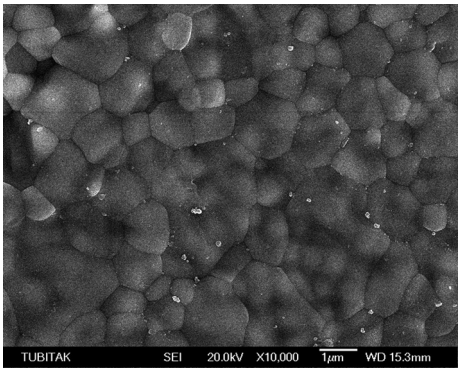

Fig. 5. SEM micrograph of an YSZ sample sintered at 1450 °C

The complex impedance plot of YSZ at 300 °C is shown in Fig. 6. It was observed that grain boundary resistivity is lower than the grain interior resistivity. The ratio of these resistivities is 1.62. It is generally believed that the grain boundary resistivity is higher than the grain interior resistivity of YSZ. In other words, in the case of YSZ, the key factor determining conductivity is the grain boundary resistivity.

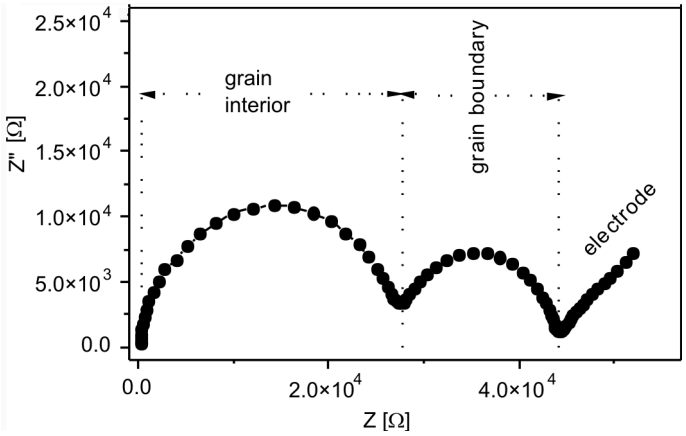

Fig. 6. An impedance plot of a sintered YSZ disc at 300 °C

Higher grain resistivity is attributed to bigger grain size and thicker grain interior. The small grain size, e.g. 1 μ, of YSZ obtained from microemulsions is associated with a thinner grain interior. Therefore it provides higher grain boundary conductivity. It has been reported that the conductivity of YSZ increases when grains are of submicron size. It can be increased by a factor of almost 2 with nanoscale grains [15–17].

4. Conclusions

8YSZ powder was synthesized by the reverse microemulsion method. Uniform, nanosized YSZ particles of the sizes brlow 100 nm were obtained. Most of the

particles were observed to be around 1 μm in grain size when sintered at 1450 °C, which would be suitable for thin film electrolyte applications.

Acknowledgement

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