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Sintering characteristics of nano-sized yttria-stabilized zirconia powders prepared by spray pyrolysis

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Nano-sized Y_2O_3-stabilized ZrO_2 (YSZ) powders were prepared by the spray pyrolysis of solutions containing citric acid and ethylenediaminetetraacetic acid. The resulting hollow particles were heated at between 600 and 900 °C and planetary milled to nano-sized powders that showed mixed crystal structures of monoclinic, cubic, and tetragonal phases. Pellets formed from the YSZ powders had fine grains of below 1 μm after sintering at 1300 or 1400 °C. Sintering at 1500 °C led to large grains of 2.3 μm.

Key words : Nano powders, Spray pyrolysis, Zirconica, Electrolyte material.

Introduction

Solid oxide fuel cells (SOFCs) can efficiently convert chemical fuels into electricity, although a significant disadvantage is their high operating temperatures of up to 1000 °C, which can cause electrode sintering and interfacial diffusion. This also restricts the range of materials from which cells can be fabricated, increasing costs [1-5]. If the operating temperature can be reduced below 800 °C, the costs of materials and fabrication will be greatly reduced and operating lifetimes of cells will be extended [5-8]. However, lower operating temperatures increase resistive losses across solid electrolytes. Reducing the electrolyte thickness can increase the performance of cells at lower temperatures through reducing the ohmic losses in the electrolyte [9-14]. Therefore, fine electrolyte powders are required to produce thin and dense electrolyte layers at low sintering temperatures.

Y_2O_3-stabilized ZrO_2 (YSZ) is a widely used electrolyte in SOFCs because of its high ionic conductivity and good chemical stability. Unaggregated YSZ powders with nanometre sized particles are required for thin electrolyte layers with maximized densities at low temperature. Nano-sized YSZ powders are generally prepared by liquid solution methods, although they show aggregated structures [15, 16]. Therefore, gas-phase processes have been developed for the preparation of unaggregated YSZ powders. Heel et al. prepared zirconia- and ceria-based electrolytes by flame spray pyrolysis [17]. The resulting nano-sized electrolytes were phase pure with high crystallinity.

Spray pyrolysis has also been used for the gas-phase preparation of nano-sized ceramic powders [18-20]. Precursor powders prepared from spray solutions with organic additives by spray pyrolysis have hollow structures with thin walls, which, after heating, can be milled to unaggregated, nano-sized powders. This study reports the synthesis of nano-sized Y_2O_3-stabilized ZrO_2 powders by the spray pyrolysis of solutions containing organic additives. The sintering of 3 and 8 mol% Y_2O_3-stabilized ZrO_2 powders was also investigated.

Experimental procedure

Spray pyrolysis was conducted using a droplet generator, quartz reactor, and a Teflon bag filter. The 1.7 MHz ultrasonic spray generator had six vibrators. It generated large amounts of droplets, which were carried into the 1000 °C, high-temperature tubular reactor by a carrier gas at 40 L minute^{-1}. The starting materials were yttrium nitrate and zirconyl nitrate. The total metal content was 0.1 M, with varying yttrium concentrations. 0.2 M citric acid and 0.05 M ethylenediaminetetraacetic acid (EDTA)

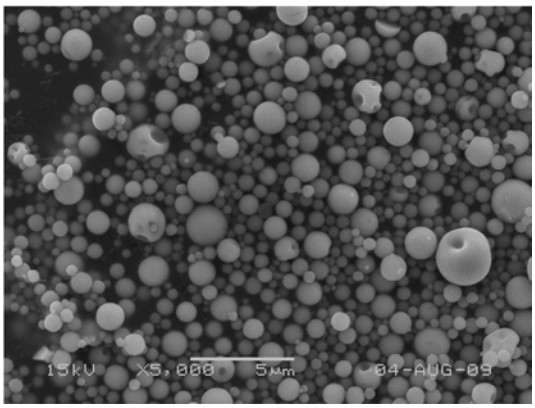

Fig. 1. SEM image of the precursor powders prepared from the spray solution without organic additives.

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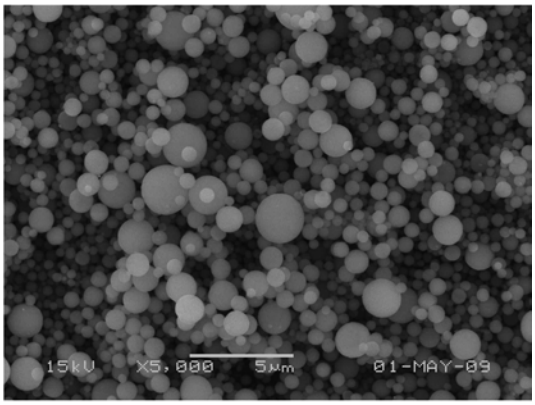
were used as organic additives to improve the hollowness of the precursor particles. The precursor powders were treated at between 600 and 900 °C under air and ball milled to form nano-sized YSZ powders. The powders were pelletized and sintered at temperatures between 1200 and 1500 °C.

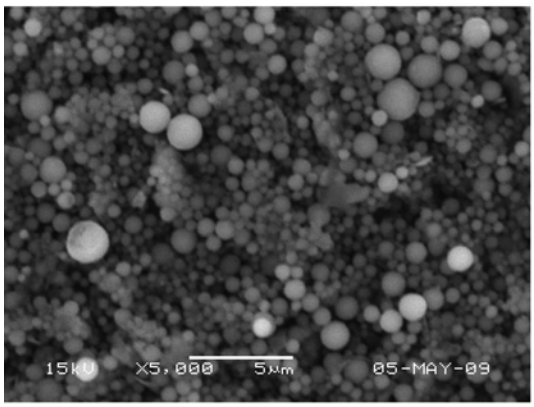
The crystal structures of the powders and the sintered pellets were investigated by X-ray diffraction (XRD) using Cu Kα radiation (λ=1.5418Å). Their morphologies were investigated by scanning electron microscopy (SEM).

Results and discussion

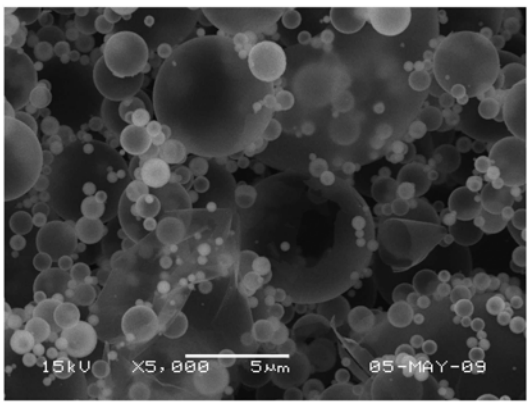
SEM showed that the morphologies of the powders were affected by the type and concentration of the organic additives (Figs. 1 and 2). The additives influenced the powders' drying and decomposition. Precursor powders prepared with 3 mol% yttrium and without organic additives had dense, spherical particles, even at the high carrier gas flow rate of 40 L minute^{-1}. Precursor particles prepared with citric acid (Fig. 2(a)) and EDTA (Fig. 2(b)) were micrometre sized, with dense structures, similar to those prepared without organic additives. Powder prepared using both 0.2 M citric acid and 0.05 M EDTA comprised spherical, hollow particles with thin-walled structures due to the evolution of gas during the decomposition of the additives (Fig. 2(c)). Differences of gas penetration in



(a) CA

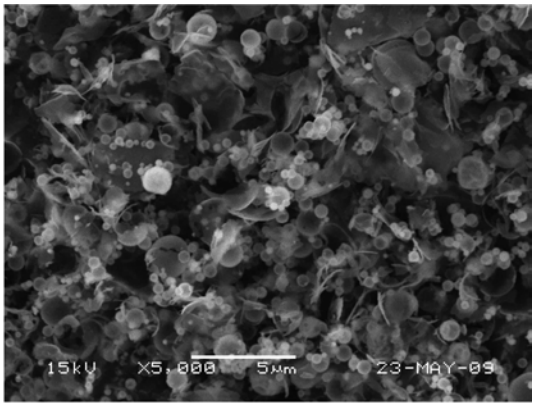


(b) EDTA

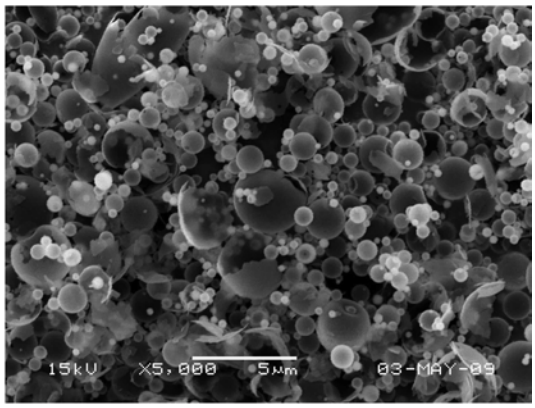


(c) CA and EDTA

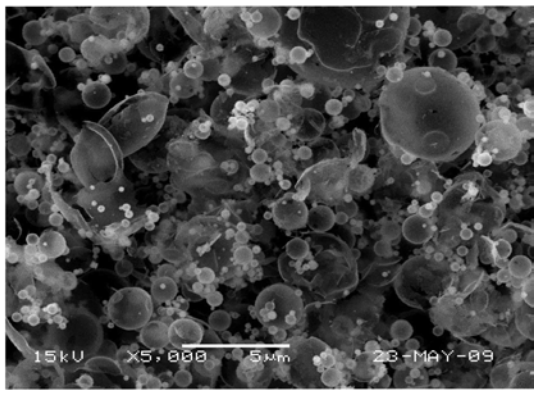
Fig. 2. SEM images of the precursor powders prepared from a spray solution with organic additives.



(a) 600 °C



(b) 700 °C



(c) 900 °C

Fig. 3. SEM images of the post-treated 3YSZ powders obtained from the spray solution with CA and EDTA before milling.

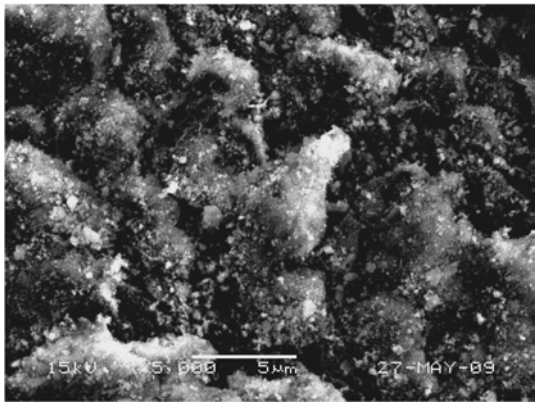


Fig. 4. SEM image of the post-treated 3YSZ powder obtained from the spray solution with CA and EDTA after milling.

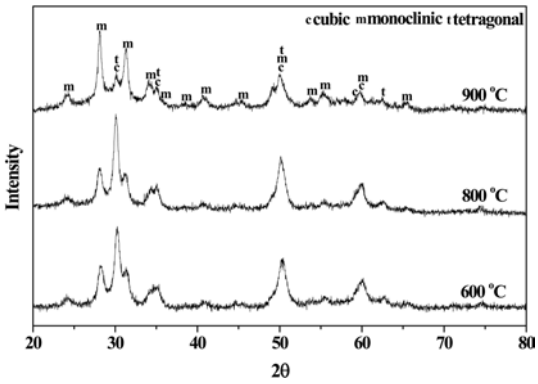


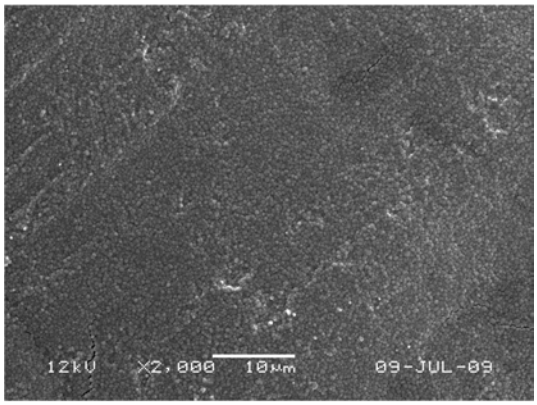
Fig. 5. XRD patterns of the 3YSZ powders post-treated at various temperatures.

the intermediate powders depended on the type of the organic additive, it affected the resulting morphologies of the precursor powders.

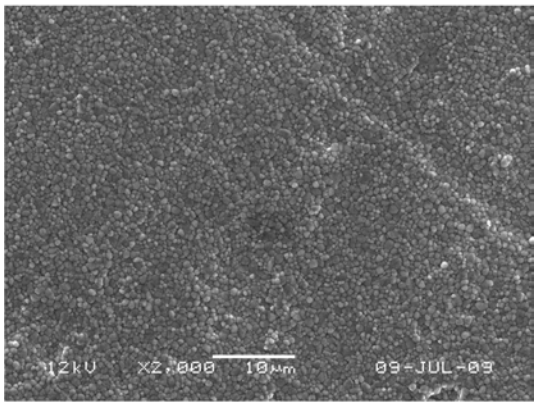
Precursor powder prepared with 0.2 M citric acid and 0.05 M EDTA was heated at temperatures between 600 and 900 °C in air. The heated powders retained their hollow, spherical morphologies irrespective of the treatment temperature (Fig. 3). Figure 4 shows a SEM image of the subsequently milled YSZ powder. The hollow particles treated at 900 °C were milled into nano-sized particles.

XRD patterns of the 3 mol% Y_2O_3-stabilized ZrO_2 (3YSZ) powders post-treated at various temperatures show that the powders contained mixed crystal phases, with monoclinic, cubic, and tetragonal ZrO_2 phases occurring irrespective of post-treatment temperature (Fig. 5). As the treatment temperature was increased from 600 to 900 °C, the peak intensity of the monoclinic ZrO_2 phase became stronger and those of cubic and tetragonal ZrO_2 phases became weaker.

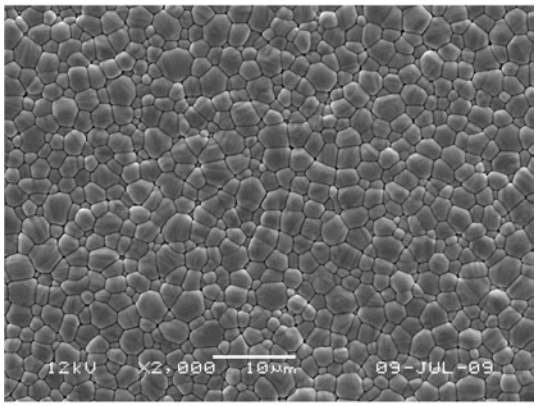
The milled 3YSZ powders (Fig. 4) were pelletized into disks. The pellets were sintered at temperatures between 1300 and 1500 °C. Their SEM images show dense structures and regular grain sizes irrespective of the sintering temperature (Fig. 6). The pellets sintered at 1300 and 1400 °C had fine grain sizes below 1 μm.



(a) 1300 °C



(b) 1400 °C



(c) 1500 °C

Fig. 6. SEM images of the sintered pellets formed from the 3YSZ powder post-treated at 900 °C.

Those sintered at 1500 °C showed large grains of 2.3 μm. The grain size generally increased with an increase in the sintering temperature.

The XRD patterns of the variously sintered 3YSZ pellets show crystal structures composed of monoclinic, cubic, and tetragonal phases (Fig. 7), with the monoclinic phase prevailing and the cubic and monoclinic phases showing very weak signals irrespective of the sintering temperature.

XRD patterns of sintered pellets formed from 8 mol% Y_2O_3-stabilized ZrO_2 (8YSZ) powders post-treated at 900 °C show mainly cubic and monoclinic phases (Fig. 8). The content of Y_2O_3 affects the properties of the YSZ electrolytes, for example crystal

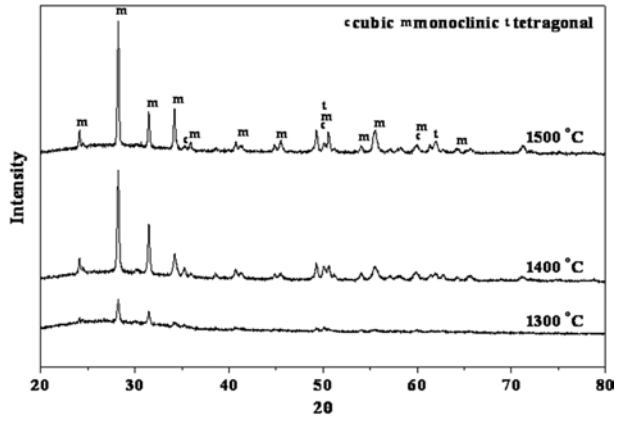


Fig. 7. XRD patterns of the sintered pellets formed from the 3YSZ powder post-treated at 900 °C.

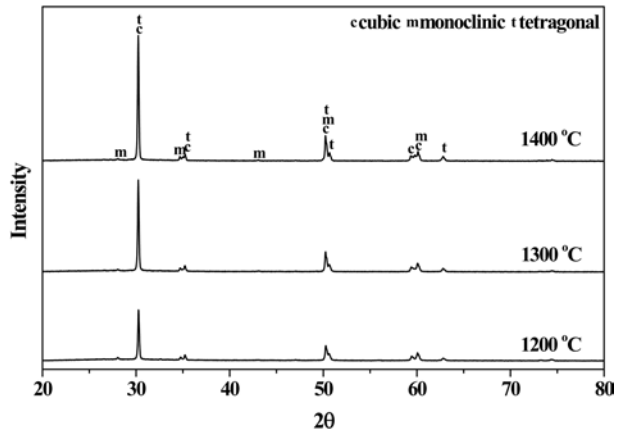


Fig. 8. XRD patterns of the sintered pellets formed from the 8YSZ powder post-treated at 900 °C.

structure, ionic conductivity, and chemical stability.

Conclusions

Hollow precursor powders with thin walls were produced by the spray pyrolysis of solutions containing both citric acid and EDTA. They were milled into nano-sized Y_2O_3-stabilized ZrO_2 powders after heating. Powders prepared from spray solutions containing only citric acid or EDTA had dense structures. The optimum concentrations of citric acid and EDTA were 0.2 and 0.05 M, respectively. The resulting powders had good sintering characteristics and formed Y_2O_3-stabilized ZrO_2 pellets after low-temperature sintering.

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