Abstract

8 mol% yttria stabilized zirconia (8YSZ) nanopowders have been synthesized via a co-precipitation-solvothermal treatment process at 200°C for 2-48 h. The co-precipitated amorphous hydroxide precursors were obtained by adding rare earth nitrate solution in an ammonia solution. Then the hydroxide precursors were solvothermal treated in various reaction media namely water, ammonium solution and ethanol, followed by drying at 80°C over night. The influence of reaction medium on crystallization and agglomeration state of 8YSZ nanopowders were investigated using XRD, SEM, and BET. Correlation between dielectric constant, boiling point and surface tension of reaction medium with crystallization and morphology of as-synthesized powders were discussed. The crystallization rate could be accelerated with the use of a low boiling point reaction medium. Crystallite size was increased with increasing dielectric constant and reaction time. The agglomeration state during drying process strongly depended on surface tension of the reaction medium. Improvement of agglomeration of primary particles was also proposed. The average crystallite sizes from all conditions were lower than 10 nm.

1. Introduction

8 mol% yttria stabilized zirconia ceramics (8YSZ) are the most common electrolyte in Solid Oxide Fuel Cells (SOFCs) owing to its high oxygen ions conductivity and chemical stability over a wide range of temperatures and oxygen partial pressure [1]. For the production of 8YSZ ceramics, yttria has to be distributed in the zirconia matrix. Several processing methods have been employed to improve the
properties and reliability of YSZ based ceramics. It is essential to have powders of high purity, nanometer-sized primary particles, narrow particle distribution and weakly bonded primary particles. The most commonly used method for powders preparation in order to achieve these properties is co-precipitation technique. The stabilizing amount of yttrium as an yttrium salt or alkoxide is introduced to a solution of purified zirconium salt or alkoxide. After coprecipitation and calcining, the stabilizing yttria is homogeneously distributed within the zirconia grains [2].

In the co-precipitation process, precipitates are generated simultaneously and uniformly dispersed throughout the solution. In spite of the high purity and the homogeneous distribution of amorphous precipitate precursors, the formation of undesirable hard aggregates during calcination step was found. Consequently, a milling step must be adopted to favour their successive densification, which in turn might introduce contamination from the grinding media and inhomogeneous grain size distribution of the powder. To avoid such step, a solvothermal treatment of the amorphous precursor, which allows to obtain powders with weakly agglomerated primary particles, monomodal particles sizes distribution and, finally, a better control of the crystal sizes has been suggested [3].

Solvothermal processing was reported to be a soft chemical route with important advantages due to low crystallization temperatures enabling the direct production of nanocrystalline powders without any firing step [4]. Such processing can take place in a wide variety of solvent systems. It was reported that the shape of nanoparticles could be controlled by the solvent in a hydrothermal process [5]. The particle agglomeration states are related to the properties of solvents such as surface tension, dielectric constant and steric effect [6].

In the present study, 8YSZ nanopowders were synthesized via co-precipitation and then solvothermal treatment. In order to understand the influence of reaction medium properties on microstructure of nanocrystalline YSZ prepared by solvothermal synthesis process. Three types of reaction media with different properties were selected, water, ammonia solution, and ethanol. Phase change, microstructure and the relationship with the reaction medium of as-synthesized powder were investigated.

2. Experimental

ZrO(NO₃)₂·xH₂O (99.5%, Cerac Incorporated) and Y(NO₃)₃·6H₂O (99.9%, Sigma-Aldrich Co.) were used as the starting materials and 30% ammonia solution was used as the precipitation agent. The ZrO(NO₃)₂·xH₂O and Y(NO₃)₃·6H₂O were first mixed to form a starting solution of the total cation concentration of 0.1 M, together with 1 wt% surfactant PEG4000 (polyethylene glycol, Fluka). The starting solution was slowly poured to ammonia solution under continuous stirring until pH 9 was obtained. The precipitate was kept at pH = 9 for 12 h in the ammonia solution. The solution then filtered and washed with distilled water many times to remove remaining nitrates. Finally the precipitate was washed with absolute ethanol in order to remove adsorbed water in the gel. The washed precipitate was re-dispersed in various reaction media under the solvothermal treatment at 200°C for 2-48 h. After solvothermal treatment, a slurry containing 8YSZ nanoparticle was obtained. As-synthesized powders were collected by centrifuge and drying at 110°C over night. The phase structure and morphology of powder were examined using XRD technique (Philips, X’pertPro MPD, Netherlands), Scanning Electron Microscope (SEM) (JEOL, model JMS-5410LV) and Transmission Electron microscope (TEM) (JOEL, model JEM-2010). The line broadening method was used to determine the crystallite size of the powders, using the Scherrer equation as follows:

\[
D_{\text{XRD}} = \frac{0.9\lambda}{\beta \cos \theta},
\]
where $D_{\text{XRD}}$ is the crystallite size, $\beta$ is the calibrated width of the diffraction peak measured at half maximum intensity, $\lambda$ is the wavelength of the X-ray radiation and $\theta$ is the Bragg angle.

The Brunauer-Emmet-Teller (BET) (TriStar 3000 SHIMADZU) specific surface area was obtained via $N_2$ adsorption and the measured result was calculated into the equivalent particle size, using the following equation:

$$D_{\text{BET}} = \frac{6 \times 10^3}{(\rho_{th} S_{\text{BET}})}.$$  \hspace{1cm} (2)

where $D_{\text{BET}}$ (nm) is the average particle size, $S_{\text{BET}}$ is the specific surface area expressed in $\text{m}^2/\text{g}$ and $\rho_{th}$ is the theoretical density of the solid solution oxide ($\text{g}/\text{cm}^3$).

3. Results and discussion

The XRD patterns of the as-synthesized powders after the solvothermal treatment in ammonia solution, water and ethanol at 200°C with different reaction times are shown in Figs 1-3. From Fig 1, crystallinity with broad peaks was observed when ammonia solution was used as the reaction medium after 2 h of reaction time. Broad reflection peaks can be indexed to be the fluorite-type cubic structure. However, no crystallinity was observed when water and ethanol were used at this condition. As-synthesized powders from ethanol and water became crystalline after 12 h and grew to larger size with increasing reaction time as shown in Fig, 2 and 3 respectively. Moreover, the peak width of powder from ethanol is much broader than that of using water and ammonia solution. This indicates smaller crystalline size of synthesized powders from ethanol. The crystalline size of synthesized powders at various conditions are plotted in Fig 4. It showed increasing of crystalline size when reaction time was increased. Table 1 compared crystalline size from BET specific surface area of as-synthesized powder from ethanol for different reaction times. The result showed the same trend of crystallite size from XRD peak. This results confirmed that primary particles of as-synthesized powder were in nano scale.

![XRD patterns](image1.png)

Fig. 1. XRD patterns for as-synthesized powder after hydrothermal treatment at 200°C in ammonium solution for (a) 2, (b) 12, (c) 24, and (d) 48 h.
Fig. 2. XRD patterns for as-synthesized powder after hydrothermal treatment at 200°C in water for (a) 2, (b) 12, (c) 24, and (d) 48 h.

Table 1. Average crystalline size of powders solvothermally synthesized in ethanol for 12–48 h.

| Reaction time (h) | D_{XRD} (nm) | S_{BET} (m^2/g) | D_{BET} (nm) |
|------------------|--------------|-----------------|--------------|
| 12               | 1.75         | 350.06          | 2.91         |
| 24               | 2.35         | 245.97          | 4.13         |
| 48               | 4.11         | 211.52          | 4.81         |
Morphology of as-synthesized powder after solvothermal treatment with different reaction mediums were compared in Fig. 5. It can be seen that when ammonia solution and water were used as the reaction medium, the obtained oxide powders were strongly agglomerated with irregular shape. While powder synthesized in ethanol showed lower agglomeration state.

For solvothermal processing, the nucleation and crystal-growth processes for the formation of primary particles started when a critical supersaturation level was reached. The reaction rate and the reaction equilibrium point depend on properties of the reaction medium [6]. Physical and chemical data of the reaction media are shown in Tab. 2.

The use of a low boiling point reaction medium has the advantage on increased pressure generated during the reaction [7]. It provides advantage in increasing rate of nucleation of nanoparticles. As can be seen from Tab. 2, ammonia solution showed the lowest boiling point. It exhibited highest pressure and nucleation rate. Thus, as-synthesized powders in this system were already become crystalline within 2 h of reaction time. as-synthesized powders.

Dielectric constant corresponds to the specific solubility of the inorganic solute and consequently the specific supersaturation degree in the reaction system [6]. A higher dielectric constant of reaction medium corresponds to a higher solubility of the inorganic solute and a lower supersaturation degree in the system, which processing exhibits less nucleation numbers and slower crystal-growth rates. Different reaction media will show different supersaturation degree that influence the nucleation numbers and the crystal-growth rates.

From Tab. 1, both dielectric constant and surface tension of water are significantly higher than those of ammonia solution and ethanol. Therefore, as shown in Fig. 2, after solvothermal in water for 2 h, the as-synthesized powders were still in an amorphous form. Dielectric constant of ethanol \((\varepsilon = 24.3)\) is higher than that of ammonia solution, thus crystals grow faster in ethanol should be slower than ammonia solution. From Fig. 3, as-synthesized powders from ethanol became crystalline after 12 h reaction time.

Surface tension of the reaction medium has strongly influence agglomeration during drying process. Agglomeration of particles is a natural phenomenon. In the case of nanoparticles, agglomeration occurs very easily because of the high surface forces such as Van der Waals forces, capillary forces and electrostatic forces. When water and ammonia were used as reaction medium, surface tensions of reaction media...
medium were about three times higher than ethanol system. Therefore, capillary forces of ethanol system was lower and the agglomeration of powder was also reduced.

Fig. 5. SEM micrographs of as-synthesized powder after hydrothermal treatment at 200°C for 24 h in (a) ammonium solution (b) water and (c) ethanol.

Table 2. Physical and chemical data of reaction media.

| Reaction medium | Boiling point (°C) | Surface tension (mN/m) | Dielectric constant (ε) |
|-----------------|--------------------|------------------------|-------------------------|
| Water           | 100.00             | 72.80                  | 80.40                   |
| 30% NH₃         | 28.33              | 62.15                  | 16.50                   |
| Ethanol         | 78.30              | 22.10                  | 24.30                   |

Although using ethanol as a reaction medium showed lower agglomeration but a significant level of agglomeration was still observed. Thus, agglomeration state should be improved by controlled co-precipitation step. Recently, it was reported that using spraying co-precipitate could prepare smaller nanoparticles with more uniform particle sized than those prepared by conventional means [8]. It was also proposed that using the spraying process the reactants can be broken up into much smaller droplets, resulting in a more homogeneous mixture [8].
Thus, the next experiment was conducted by changing the co-precipitation step from pouring to spraying using airbrush spray gun of the starting solution into ammonium solution. Then the precipitate gel was washed and solvothermal treatment with the same procedure. SEM micrograph of as-synthesized powders from spray co-precipitate and solvothermal treatment in ethanol for 12 h is shown in Fig 6. It is obvious that the agglomeration of as-synthesized powders was reduced. It is thus suggested that agglomeration of primary particles can be reduced by spray-co-precipitation step.

Fig. 6. SEM micrographs of powders from (a) conventional and (b) spraying co-precipitate process.

4. Conclusion

From solvothermal processing was found that properties of solvent affect the formation of oxide powders. The dielectric constant of the solvent has an important influence on the growth rate of oxide powder during solvothermal synthesis. A solvent with a low dielectric constant exhibits reaction rate faster than a solvent with a high dielectric constant, while the surface tension of the solvent has influence agglomeration during drying process. In addition, the agglomeration of as-synthesized powders could be reduced by using spray-coprecipitation-solvothermal treatment process.

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